

Synthesis and Characterization of Polyurethane Foam Matrices for the Support of Granular Adsorbent Materials

Moisés L. Pinto,¹ João Pires,¹ Ana P. Carvalho,¹ João C. M. Bordado,² Manuela B. de Carvalho¹

¹*Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Edifício C8, Campo Grande, 1749-016 Lisboa, Portugal*

²*Departamento de Engenharia Química, Instituto Superior Técnico, Universidade Técnica de Lisboa, Avenida Rovisco Pais 1096 Lisboa, Portugal*

Received 10 July 2003; accepted 24 November 2003

ABSTRACT: Polyurethane foams with different formulations were synthesized and characterized for use as supporting matrices of granular solid adsorbents. The open cell content, specific gravity, thermal stability, and hydrophobicity were determined and related to the formulation composition. The synthesized foams had open cell contents of 88.1–98.5% and specific gravity values of 120–28 kg m⁻³. The thermal stability of the prepared foams was influenced mainly by the water content and the type of isocyanate used. The hydrophobicity was assessed by an analysis of the water adsorption isotherms determined on selected foams, and a

correlation between these results and the formulation of the foams was attempted. Two types of activated carbons were supported in a polyurethane matrix. The adsorption characteristics evaluated before and after the supporting procedure, by nitrogen adsorption, revealed that there was only a moderate surface area reduction of 15–20%. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2045–2053, 2004

Key words: polyurethanes; thermal properties; adsorption; activated carbon; hydrophobicity

INTRODUCTION

The main objective of this study is the development of new polyurethane-based matrices to be used as supports for granular solid adsorbents. The more commonly used adsorbent materials, such as activated carbons and zeolites, are usually obtained as powders or pellets. These are not always the best forms for their uses in, for example, filters for the purification of air streams.

Besides other physical properties, such as the specific gravity, open cell content, and thermal stability, one important property of polymeric matrices used as supports for adsorbents is the hydrophobicity. These adsorbent–matrix compositions may be potentially useful for the gas-phase adsorption of various volatile organic compounds (VOCs) in different systems. However, humidity is also usually present in the medium to be purified, and so it is important to ensure that the adsorption capacity is used in the adsorption of the VOC molecules rather than be saturated by moisture. In this respect, the more hydrophobic matrices are to be preferred in principle. This is of special importance because large amounts of adsorbed water will enhance the possibility

of fungi or bacteria developing, which should be avoided. The method used in this work to obtain information on the hydrophobic–hydrophilic nature of polyurethane foams is based on the analysis of water adsorption isotherms on solid materials.^{1–7} Usually, these analyses are applied to the characterization of adsorbent materials, but the determination and analysis of water adsorption isotherms in polyurethane, to characterize the hydrophilic–hydrophobic nature of polyurethane materials, constitute an innovative approach, as far as we know. Some other methods proposed in the literature for the evaluation of hydrophobicity are based on the measurement of the water loss at different temperatures by thermogravimetry⁸ or on data from thermogravimetry and nitrogen adsorption.⁹ However, for applications in composite adsorbent–polymer materials, the use of thermogravimetric methods present the disadvantage of the possible decomposition of the polymer. Moreover, at high temperatures and in the presence of water, there is also the possibility of hydrolysis of the polymeric matrix. In industrial applications, a method is currently used for the determination of water absorption on rigid cellular plastics^{10,11} that measures the change in the buoyant force resulting from immersion in water for several hours, and other authors have reported measurements of water absorption in the liquid phase by polyurethane foams.^{12–15} These methods are used in cases in which the foams are in direct contact with liquid water; such conditions are quite distinct from those observed in a gas filter.

Correspondence to: J. Pires (jpsilva@fc.ul.pt).

Contract grant sponsor: Fundação para a Ciência e Tecnologia.

Another important question is the regeneration of adsorbents, to recover their original adsorption capacity (which can be achieved in many cases), through heating in a controlled environment, usually in a flux of an inert gas. It would be desirable that the polyurethane foam used to support the adsorbent materials would be stable in such an environment; this would allow the composite adsorbent–matrix filters to be regenerated by similar methods. To investigate this possibility, we used a thermogravimetry/differential scanning calorimetry (TG–DSC) method to evaluate the thermal stability and decomposition temperature (T_d) of the prepared polyurethane matrices.

Many applications of carbon in polyurethane formulations can be found in the literature, and often the small carbon particles or dispersed fibers are used in the polyurethane matrix to modify some properties, including mechanical, thermal, electric, and magnetic properties, to improve the fire resistance, to change the permeability to vapor or liquid solvents, and to enhance the chemical stability of the polymer.^{16–28} However, in most of these applications, the carbon is carbon black, graphite, or fiber, with a surface area lower than $100 \text{ m}^2 \text{ g}^{-1}$. These materials have low adsorption capacities and are not suitable for air-stream purification. Activated carbons normally have surface areas greater than $1000 \text{ m}^2 \text{ g}^{-1}$, mainly because of the high microporosity rather than the external surface area (A_{ext}),²⁹ and they are currently applied to the purification of air streams in pellets or granules. Some filters are made of polyurethane foams with a layer of activated carbon on their surface; they are usually produced by the immersion of a polyurethane foam in a slurry of powdered activated carbon and a polymeric binder.^{30,31} In this work, a different approach is used because the activated carbon is included in the form of pellets in the formulation for the polyurethane synthesis. This allows the production of polyurethane foams with activated carbon in a one-step method, but we can expect some decrease in the adsorption capacity of the adsorbent due to the impregnation and/or reaction of the polyurethane-synthesizing components, namely, diisocyanate, with the surface of the adsorbent. This decrease has to be minimized.

The polyurethane foams produced and characterized in this work were synthesized from toluene diisocyanate (TDI) and polymeric methylene bisphenyl diisocyanate (MDI), these two isocyanates being the most widely used in the polyurethane industry.

EXPERIMENTAL

Polyurethane synthesis

The required quantities of polyol, distilled water, silicone oil, and catalyst were added to a polyethylene

TABLE I
Composite of the Two Series of Formulations

	Formulation series ^a	
	A, TDI	B, MDI
Polyol (g)	20.00	20.00
DBTL (g)	0.23	0.23
Silicone Oil (g)	0.40	0.40
Water content (%)	1–5.5	3–4

^a NCO index = 105%.

flask and mixed vigorously for 1 min with a mechanical stirrer to obtain the formulated polyol. The isocyanate was then added to the same flask, and strong stirring was applied for 15 ± 2 s. The resulting mixture was left undisturbed for 1 min; this allowed the formation and growth of the foam, which was immediately added and kept in an oven at 70 ± 1 °C for 1 h. Several formulation series were tested, but for clarity, only two representative series are discussed. The compositions of these series are given in Table I, except for the water and isocyanate concentrations, which were varied with the compositions of the formulations to maintain the NCO index for each formulation series. To maintain foams with a density of less than 60 kg m^{-3} , water was varied between about 1 and 6% (mass of water/mass of polyol). To maintain the NCO index for each formulation series, we changed the amount of isocyanate accordingly.

1,2,3-Tris(polyoxypropylene ether)propane (Aldrich, Milwaukee, WI; number-average molecular weight ≈ 3600 , $41 \text{ mg of KOH g}^{-1}$) was used as a triol, dibutyltin dilaurate (DBTL; Merck, Darmstadt, Germany; $>97\%$) was used as a catalyst, and silicone oil (193 surfactant, Dow Corning, Midland, MI) was used as a foam stabilizer. The isocyanates used were TDI (Aldrich; 80% 2,4-isomer and 20% 2,6-isomer) and MDI (Lupanat M 50, BASF, Lemförde, Germany).

Specific gravity

Cylindrical samples of the foams were obtained, with special care for the perpendicularity between the base and height of the cylinder. The dimensions of the foam cylinders (the diameter and height) were determined with a vernier caliper with 0.05-mm precision, and the volumes were then calculated. The masses of the samples were determined with a Mettler AE 240 analytical balance with 0.1-mg precision (Greifensee, Switzerland). The specific gravity, determined by the volume of the external geometrical shape and the mass of the sample, is often called the apparent density; it does not measure the specific gravity of the polymeric matrix of the foam.^{32,33}

Open cell content

The volumes of the foam cylinders were determined in an automatic gas pycnometer (AccuPyc 1330, Mi-

chrometrics, Norcross, GA) with helium (Gasin, Matosinhos, Portugal; 99.995%). Ten purges at 68.97 kPa, followed by 10 measurements with expansions at 68.97 kPa, with a $0.0345 \text{ kPa min}^{-1}$ rate of change as the equilibrium criterion, were made for each sample.

The open cell content was calculated from the external geometrical volume of the cylinder (V_e) and from the volume measured with gas (V_g). The fraction of the open volume, called the open cell content, was calculated as a percentage as follows: $(V_e - V_g)/V_e \times 100\%$. The volume of the cells opened by the cylinder cutting operation was small in comparison with the high open volume of these foams, and in this way, a possible correction could be neglected.^{34,35}

TG-DSC

The TG-DSC experiments were performed in a Setaram TG-DSC 111 apparatus (Lyon, France) with 0.001-mg and 0.05-mW precision between 30 and 350°C. Foam samples of 12–22 mg in aluminum crucibles were used at a heating rate of 5°C min^{-1} in a nitrogen atmosphere (Air Liquid, Paris, France; 99.995%) with a flux of $0.5 \text{ cm}^3 \text{ s}^{-1}$ (Brooks Instruments N.V., Hatfield, PA; R-2-15-AA tube size).

Water adsorption

The water adsorption isotherms were determined in a Coulter Omnisorp 100cx automatic apparatus (Hiialeah, FL). Samples of 150–200 mg, determined with an analytical balance with 0.1-mg precision, were placed in a specially handmade glass cell. The degasification of the samples was made, in a vacuum better than 10^{-3} Pa , at 50°C for 2.5 h. The mass loss was corrected by weighing after degasification, and so the results are expressed per gram of the outgassed sample. The adsorption experiments were carried at $30.0 \pm 0.1 \text{ }^\circ\text{C}$ with vapor doses of 3.33 kPa until a maximum of $0.98 p/p^\circ$ was attained (P is the equilibrium pressure and P° is the saturation pressure). A blank experiment, with an empty cell, was performed, and the values were used to correct the values of the adsorbed amounts in the polyurethane foams.

Nitrogen adsorption

The nitrogen adsorption isotherms at -196°C were determined in a Micromeritics ASAP 2010 automatic apparatus. The samples were outgassed, in a vacuum better than 10^{-3} Pa , at 100°C for 2.5 h. The mass loss was corrected by weighing after degasification, and so the results are expressed per gram of the outgassed sample.

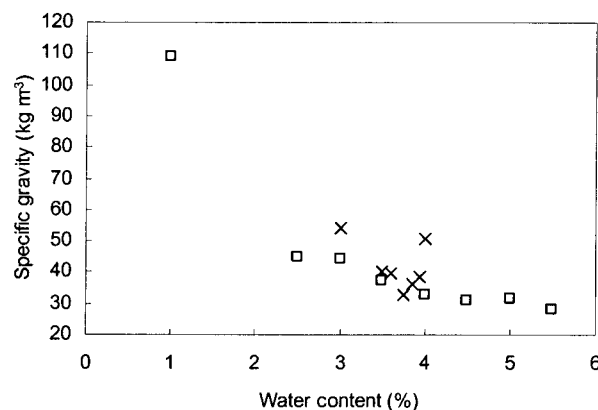


Figure 1 Foam specific gravity of the different formulation series (see Table I) of polyurethane foams as a function of the water content. The symbols represent the different formulation series: (□) series A and (×) series B.

RESULTS AND DISCUSSION

Specific gravity

A plot of the specific gravity as a function of the water content in the formulations of the synthesized foams is presented in Figure 1. Analyzing this figure, we must remember that the uncertainty of the method used is $\pm 2.5 \text{ kg m}^{-3}$ and that differences below this value must be interpreted with care. Generally, the specific gravity falls as the water content increases. In fact, the CO_2 formed by the reaction of water with the isocyanate originates and expands the cells, allowing, for each formulation series, some control over the specific gravity of the foam through variations in the water content. However, major differences, particularly in the way in which the specific gravity changes with the water content, were detected for the two formulation series, which, as shown in Table I, differ mainly in the type of isocyanate.

In series A (with TDI), the specific gravity of the foams decreases monotonically with increasing water content (Fig. 1) to an almost constant value near 30 kg m^{-3} for water concentrations in the formulation of greater than 4%. This could be a result of CO_2 escaping from the mixture, which was observed before the foam started to grow for water concentrations in the formulation of greater than 3.5%. The increase in the viscosity of the polymer during the synthesis of the foams is probably the reason for the main difference between these two series (the use of different isocyanates) and can be related to the differences in the expansion process.^{36,37} However, the surface tension can also play a significant role.^{36,38} Most likely, the minimum point of series B (with MDI) corresponds to the start of the foam collapsing, and the increase in the water content from this value increases this process; consequently, the specific gravity of the foam increases. The values of the specific gravity and their

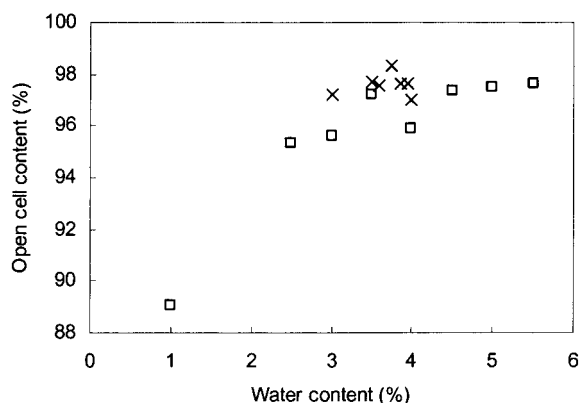


Figure 2 Open cell content of the foams, determined by gas pycnometry, as a function of the water content in the formulation. The symbols represent the different formulation series: (□) series A and (×) series B.

variation with the water content are comparable to those normally obtained in the synthesis of flexible polyurethane foams without the use of organic solvents.^{39,40}

Open cell content

The open cell content of the synthesized foams is presented in Figure 2 as a function of the water content. Similar behaviors for the dependence of the open cell content on the water content were observed for the two formulation series. The differences between some of the values are too small to be considered because they are below the 0.5% uncertainty of the method, which was estimated from the repeatability of the measurements. Also, the values of the open cell content are indistinguishable for foams with more than 3%. Figure 2 clearly demonstrates that the formulations with more than 3.5% water produce foams with an open cell content of more than 96% (except for one case in series A). Another interesting detail of the series is the asymptotical approach to an open cell content of 98% at high water contents in the formulations, which, in the limit, could be related to the volume occupied by the polymeric matrix, or it indicates the importance of other adjustments in the formulations.

TG-DSC

The TG-DSC experiments were performed with foams synthesized from different isocyanates (series A and B) to correlate the thermal properties with the chemical nature of the foams. The mass loss was calculated with the mass of the sample at 100°C as a reference. It was assumed that the mass loss at this temperature (always <0.5% in relation to the values at the ambient temperature) was from water or other vapors that

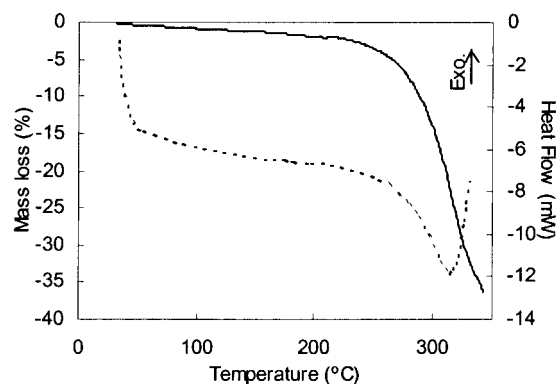


Figure 3 TG-DSC analysis of series A foams (TDI) with 4.50% water in the formulation. The mass loss is represented by the solid line, and the heat flow is represented by the dashed line.

could be absorbed by the polymeric matrix. The shapes of the curves for the mass loss and heat flux, obtained for all foams from series A and B (see Fig. 3 for an example), as well as the black residue obtained at the end of each experiment, indicate that thermal decomposition of the polyurethane occurred with the loss of volatile substances. In Figure 4, the mass losses at two temperatures, T_d and 250°C, for the foams of series A (synthesized with TDI) as a function of the water content in the formulation are given. A similar graph for the mass loss from the samples from series B (synthesized with MDI) is presented in Figure 5. In both figures, the mass losses at 250°C are minimal, always being lower than 4% for foams synthesized with TDI (Fig. 4) and lower than 2% for foams synthesized with MDI (Fig. 5). A comparison of Figures 4 and 5 shows better thermal stability for the foams formulated with MDI than for those formulated with TDI. The results of the mass losses, obtained at 250°C, do not show any clear relationship to the water content.

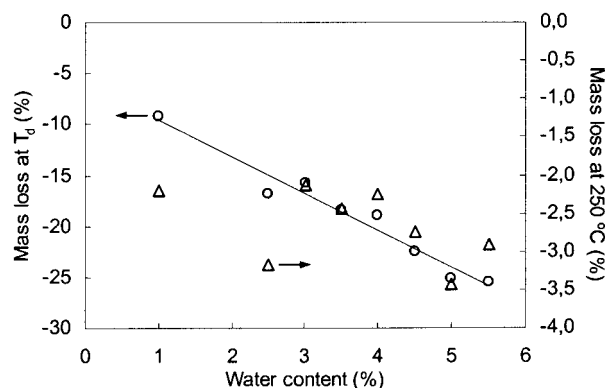


Figure 4 Mass losses of series A foams at different temperatures obtained by TG-DSC. The symbols represent the different temperatures: (○) T_d and (△) 250°C. The solid line represents the linear fitting of the points obtained at T_d .

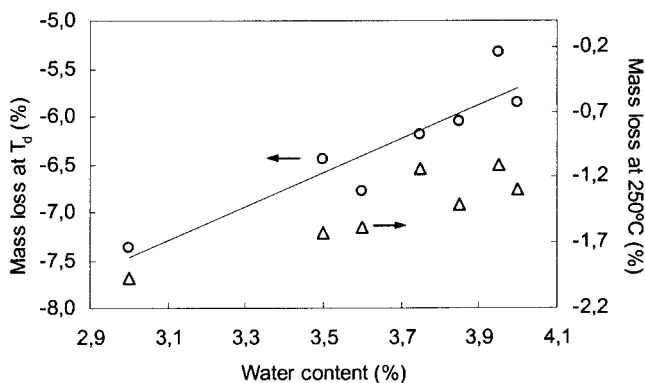


Figure 5 Mass losses of series B foams at different temperatures obtained by TG–DSC (see Fig. 4 for the notation).

The mass losses of the foams synthesized with MDI (Fig. 5) at T_d are much lower than the mass losses of the foams synthesized with TDI (Fig. 4), despite the T_d values being very close (Fig. 6). Another difference that can be observed in Figures 4 and 5 is that the mass losses of MDI foams at T_d decrease with increasing water content, whereas the mass losses of the TDI foams increase with increasing water content.

The dependence of T_d on the water content is shown in Figure 6 for both series. The foams obtained with MDI present slightly higher T_d 's than those prepared with TDI, although the differences never exceed 5°C for similar water contents. Figure 6 also shows an increase in T_d with increasing water content in the formulation for both series. These values are comparable to those obtained by other authors using similar polyurethane foams.^{41–43} Some authors reported that, for polyether polyurethanes, the initial thermal decomposition occurred around 250–275°C, and the main decomposition process occurred between 300 and 325°C.⁴² The information presented in Figures 4–6 allows us to conclude that the synthesized foams are thermally stable up to 250°C in a flux of an inert gas. This is an important aspect concerning the possibility of the thermal regeneration of adsorbent materials that could be supported on these polymeric matrices.

The decomposition enthalpies of foams from series A and B increase linearly as the water content in the formulation increases, corresponding to more endothermic reactions. The foams synthesized with TDI (series A) have more positive enthalpies of decomposition (between 80 and 260 J g⁻¹) than those synthesized with MDI (between 50 and 100 J g⁻¹). This indicates that the decomposition of the matrix is more endothermic with foams produced with TDI than with MDI.

The TG–DSC data clearly show that the series A and B polyurethane foams are good candidates for supports of adsorbent materials, particularly if the com-

posite materials to be obtained are to be regenerated by a temperature increase. The most favorable situation, in terms of thermal stability, is obtained with a foam synthesized with MDI.

Hydrophobicity

In a previous stage of the hydrophobicity studies, the adsorption of nitrogen at –196°C in selected samples of the synthesized foams was made. Because of the very low amounts adsorbed, it can only be stated that the surface areas of the foams are less than 2 m² g⁻¹. This implies that gases and vapors can be physically adsorbed on the foams only to a very limited extent. However, this information is important for analyzing the adsorption data of water in foams. In fact, the adsorbed amounts of the isotherms of water in various samples of the synthesized foams, presented in Figure 7, are not negligible and can only be attributed to a relatively strong interaction between the polymer matrix and the water molecules. The reversibility of the adsorption isotherms was also confirmed. The differences between the isotherms obtained in the different series of foams are very small and for some samples, particularly at low relative pressures, are within the uncertainty of the method. However, these differences show a trend that is in line with the relative content of urea bonds in the polymer because the foams with higher water contents in the formulation have more urea bonds in the matrix of the polymer. At a molecular level, the matrix has groups with urethane and urea bonds that are more hydrophilic (because of the polar carbonyl) than the more hydrophobic polyether chains that constitute the remaining structure of the polymer. The number of urethane bonds in the two series (A and B) of foams is probably almost constant because the same NCO index is maintained and the polyol is the same. Some differences could exist between the two series because of the different reactivi-

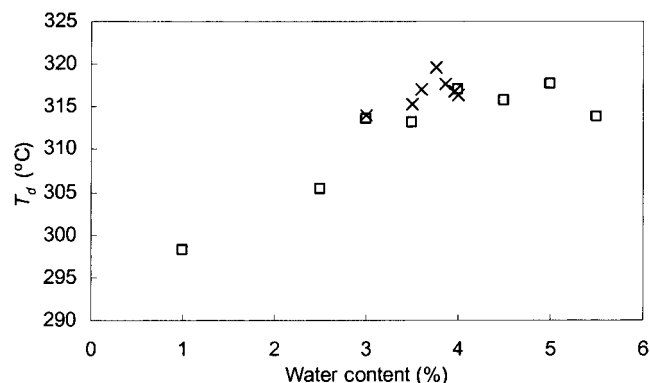


Figure 6 T_d 's of series A and B foams obtained by TG–DSC. The symbols represent the different formulation series: (□) series A and (×) series B.

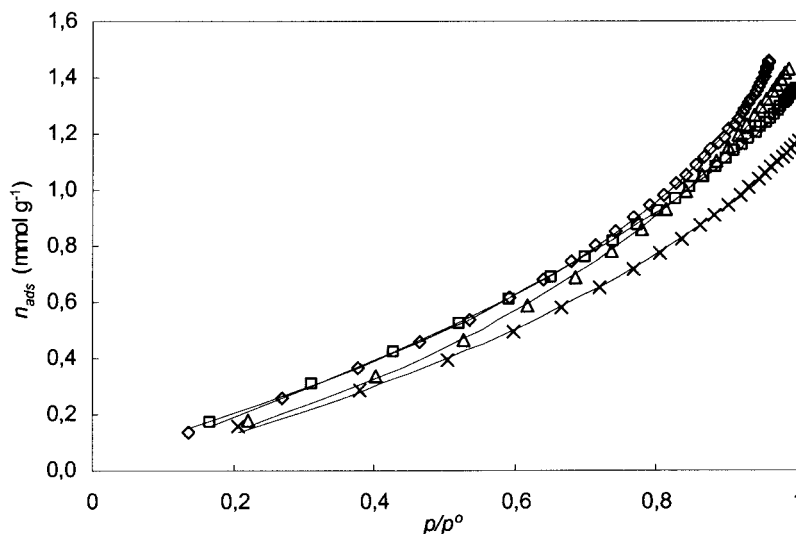


Figure 7 Water adsorption isotherms at 30°C for different foams: (\diamond) series A with 5% water, (Δ) series A with 2.5% water, (\times) series B with 3% water, and (\square) series B with 4% water. The solid lines represent the fittings of the DA equation to the adsorption data (see the text).

ties of MDI and TDI, and thus the differences between series A and B are more difficult to interpret. An increase in the content of urea groups in the matrix, due to the increase in the water content in the formulations, makes the polymer less hydrophobic. The isotherms in Figure 7 reflect this behavior, but not in a pronounced way. In series A, the isotherm corresponding to the foam with the highest water content (5%) presents higher adsorbed amounts than the isotherm corresponding to the foam with the lowest water content (2.5%). For the foams of series B, the same observation applies; that is, the isotherm corresponding to the foam with 4% water in the formulation is above the isotherm corresponding to the foam with 3% water.

To quantify these differences, we fitted two equations to the adsorption data. First, the Henry equation, which allows the determination of the Henry constant (K'),⁴⁴ was fitted between 0 and 0.6 p/p^0 ; within this range, the isotherms are relatively linear. These constants are presented in Table II. High values of K' mean high affinity between the solid and the adsor-

bate. Therefore, in this case, high values of K' correspond to less hydrophobic foams. The Dubinin–Astakhov (DA) method⁴⁵ was also fitted to the water adsorption results. Briefly, the DA expression is $w = w_0 \exp[-(A/E)^n]$, where the adsorption space w is related to the limiting adsorption value w_0 . A is the adsorption potential [$A = -RT \ln(p/p^0)$], and E (the characteristic energy of adsorption) and n are temperature-invariant parameters. R is the perfect gas constant and T is the absolute temperature. E could be related to parameters that are closely dependent on the energetics of adsorption, such as the heat of adsorption.⁴⁶ The fit of the DA model was made by the nonlinear least-squares method: the coefficients of determination of DA fits were between 0.9997 and 0.9994, and χ^2 was between 3×10^{-5} and 8×10^{-5} . The solid lines in Figure 7 represent the fitted curves. The trends for E , w_0 , and K' (Table II) agree with what has already been stated. In fact, comparing the foams of the same series, we find that the values of the parameters corresponding to high water contents are generally high, except for the E values for the foams of series A. The low values of K' for all the samples indicates the hydrophobic nature of all the synthesized polyurethane foams, and the differences among the values are significant and can also be correlated to the water content in the formulation. These observations are most likely related to the fact that foams with high water contents in their formulation are less hydrophobic, if all the other components remain unchanged, except that the amounts of isocyanate, as mentioned previously, have to be adjusted to obtain the same NCO index in all the formulations.

TABLE II
Fitted Parameters of DA and Henry Models to the Adsorption Data of Water at 30 °C, in Polyurethane Foams

Series	Water content (%)	Open cell content (%)	w_0 (mmol/g)	E (J/mol)	K' (mmol/g)
A	2.50	95.3	1.55	1.28	0.90
A	5.00	97.5	1.79	1.18	1.00
B	3.00	97.2	1.19	1.55	0.79
B	4.00	97.0	1.39	1.72	1.01

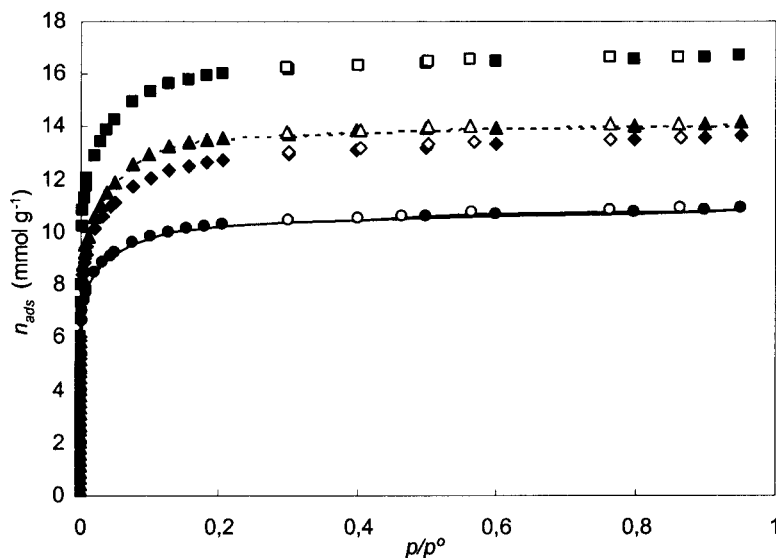


Figure 8 Nitrogen adsorption isotherms at -196°C in samples of two activated carbons: (\square, \blacksquare) RB3, ($\triangle, \blacktriangle$) supported RB3, (\diamond, \blacklozenge) CarbonTech, and (\circ, \bullet) supported CarbonTech. The dotted and continuous lines represent the broken pellets of RB3 and CarbonTech, respectively. The filled symbols are adsorption points, and the open symbols are desorption points.

Supported adsorbents

Two commercial activated carbons, CarbonTech and Norit RB3, were supported in a polyurethane matrix to evaluate the influence of the supporting process on the surface characteristics of the adsorbents. The polyurethane matrix was synthesized with MDI and 3.85% water with a formulation analogous to those described previously. This formulation was chosen because of the high open cell content, low apparent density, good thermal stability, and moderate collapse of the cellular structure, as previously discussed. The only modification was the addition of activated carbon (ca. 10% in polyol weight), which was mixed at the same time as the two components of the polyurethane formulation (formulated polyol and isocyanate). A possible correction in the formulation, to account for the water adsorbed on the activated carbons, could be neglected because of the highly hydrophobic nature of the samples used.⁴⁷ The two activated carbons used were cylindrical pellets, with a diameter of about 3 mm, which maintained their shape after the mixing, foaming, and curing of the foam. Their effectiveness for the retention of VOCs and a more detailed characterization are discussed elsewhere.⁴⁸

Nitrogen adsorption isotherms in the activated carbons, presented in Figure 8, were determined before and after they were supported on the polyurethane foam. For that purpose, samples of the supported pellets were collected from the polyurethane matrix. Figure 8 shows that none of the isotherms exhibit a significant hysteresis loop and that they are almost parallel to the pressure axis above $0.2 p/p^{\circ}$, showing that these materials have low mesopore volume. How-

ever, the large adsorbed quantities at small values of p/p° are characteristic of microporous materials. Figure 8 also shows that the shapes of the adsorption isotherms of the two activated carbons, before and after being supported, are similar, but a decrease in the adsorbed quantities can be noted. This decrease in the adsorption capacity can be attributed to the covering of the activated carbon with polyurethane during the reaction and foaming process. The possibility of that fraction being only blocked externally to nitrogen access, by the polyurethane film that covers the surfaces of the pellets, was tested by the determination of nitrogen adsorption isotherms in pellets that were broken after being supported in the polyurethane matrix. The resulting isotherms were indistinguishable from those determined for the supported pellets that were not broken, as confirmed by Figure 8. This allows the conclusion that the decrease in the adsorption capacity is not related to the hindrance of nitrogen transport to the interior of the pellets but is probably more related to the impregnation of the small fraction of the activated carbon on the surfaces of the pellets.

The Brunnauer–Emmet–Teller (BET) equation was used, between 0.01 and $0.15 p/p^{\circ}$, to calculate the apparent surface area (A_{BET}) of all the samples from the nitrogen adsorption data.⁴⁹ The micropore volume (V_{μ}) and A_{ext} values were calculated from the isotherms with the t -method.⁴⁹ These results are presented in Table III. The relative changes in these parameters (δA_{BET} , δV_{μ} , and δA_{ext}) of the supported adsorbents, in relation to the original ones, are also presented in this table. From these results, it can be confirmed that the differences between the broken and

TABLE III
Adsorbent Parameters Calculated from the Nitrogen Adsorption Data

	A_{BET} (m ² /g)	δA_{BET} (%)	V_{μ} (cm ³ /g)	A_{ext} (m ² /g)	δV_{μ} (%)	δA_{ext} (%)
RB3	1344 ± 16	—	0.532	65	—	—
Supported RB3	1148 ± 13	15	0.453	55	15	15
Supported RB3: broken pellets	1139 ± 13	15	0.450	54	16	17
CarbonTech	1065 ± 10	—	0.413	79	—	—
Supported CarbonTech	859 ± 10	19	0.338	52	18	34
Supported CarbonTech: broken pellets	854 ± 10	20	0.336	51	19	35

Apparent surface area A_{BET} calculated by the BET equation, and their relative change (δA_{BET}) in relation to the unsupported values. Micropore volume (V_{μ}) and external surface area (A_{ext}) calculated by the t -method, and their respective relative change ($\delta V_{\mu}, \delta A_{ext}$) in relation to the unsupported values.

unbroken pellets are within the uncertainty of the method for the two activated carbons used. Comparing the relative changes between the supported and original adsorbents for RB3 and CarbonTech, respectively, we find that A_{BET} and V_{μ} decrease about 15 and 19%, and the decreases in A_{ext} are about 16 and 35%. These values are comparable to others reported with a different supporting procedure.³⁰ It is clear that the significant change introduced by the supporting process is in A_{ext} of the CarbonTech sample and that the two adsorbents maintain their high surface areas and high V_{μ} values, which are characteristic of microporous materials. One factor that probably contributes markedly to this is the rapid rise in the viscosity of the polyurethane reaction mixture that avoids strong impregnation of the microporous fraction of the adsorbent pellets. Thus, the procedure used for supporting pellets of activated carbon does not introduce a significant change in their adsorbent nature and can probably be applied with success to other types of adsorbent materials.

CONCLUSIONS

Various types of polyurethane foams, prepared from two different isocyanates, were obtained. Physical properties, such as the specific gravity, open cell content, thermal stability, and hydrophobicity, were studied and related to the compositions of the foams. The results showed that the type of isocyanate and the water content in the formulation were the major factors influencing the thermal stability of the prepared foams. However, as for the specific gravity, open cell content, and hydrophobicity, similar properties were obtained with different formulations. It was confirmed that, with respect to the studied properties, the polyurethane-based foams presented appropriate characteristics for potential consideration as supports of granular solid adsorbents. The results obtained with two microporous activated carbons that were supported in a polyurethane matrix, with respect to their adsorption capacity evaluated by nitrogen adsorption,

revealed that only a fraction (between 15 and 20%) was lost with the supporting procedure used. It was concluded that this decrease in the adsorption capacity was probably related to the thin polyurethane film that impregnated the surfaces of the pellets and that the microporous characteristics of the two activated carbons were maintained. Therefore, further studies of these composite materials, adsorbent-polymer matrices, are very promising when, for instance, the preparation of new gas filter devices is envisaged.

One of the authors (M.L.P.) thanks Fundação para a Ciência e Tecnologia for a Ph.D. grant.

References

- Olson, D. H.; Haag, W. O.; Borghard, W. S. *Microporous Mesoporous Mater* 2000, 35, 435.
- Matsumoto, A.; Sasaki, T.; Nishimiya, N.; Tsutsumi, K. *Langmuir* 2001, 17, 47.
- Stoeckli, F.; Huguenin, D. *J Chem Soc Faraday Trans* 1992, 88, 737.
- Kraehenbuehl, F.; Quillet, C.; Schmitter, B.; Stoeckli, H. F. *J Chem Soc Faraday Trans* 1 1986, 82, 3439.
- Stoeckli, F.; Jakubov, T.; Lavanchy, A. *J Chem Soc Faraday Trans* 1994, 90, 783.
- Llewellyn, P. L.; Schuth, F.; Grillet, Y.; Rouquerol, F.; Rouquerol, J.; Unger, K. K. *Langmuir* 1995, 11, 574.
- Salame, I. I.; Bandosz, T. J. *Langmuir* 1999, 15, 587.
- Anderson, M. W.; Klinowski, J. *J Chem Soc Faraday Trans* 1 1986, 82, 1449.
- Giaya, A.; Thompson, R. W.; Denkwicz, R. *Microporous Mesoporous Mater* 2000, 40, 205.
- Standard Test Method for Water Absorption of Rigid Cellular Plastics; ASTM D 2842-01; American Society for Testing and Materials: West Conshohocken, PA, 2001.
- Rigid Cellular Plastics—Determination of Water Absorption; ISO 2896:2001; International Organization for Standardization: Geneva, 2001.
- Sabbahi, A.; Vergnaud, J. M. *Eur Polym J* 1993, 29, 1243.
- Sabbahi, A.; Vergnaud, J. M. *Eur Polym J* 1991, 27, 845.
- Sabbahi, A.; Bouzon, J.; Vergnaud, J. M. *Eur Polym J* 1994, 30, 657.
- Chang, V. S. C.; Kennedy, J. P. *Polym Bull* 1982, 8, 69.
- Chen, C. H.; Ma, C. C. M. *J Appl Polym Sci* 1992, 46, 937.
- Chen, C. H.; Ma, C. C. M. *Compos Sci Technol* 1994, 52, 427.
- Pisipati, J. S.; Godbey, J. A. *J Cellul Plast* 1996, 32, 108.

19. Pisipati, J. S.; Ball, E. E.; Galligan, P. L.; Gluck, D. G. *J Cellul Plast* 1996, 32, 62.
20. Xu, M. X.; Liu, W. G.; Gao, Z. X.; Fang, L. P.; Yao, K. D. *J Appl Polym Sci* 1996, 60, 1595.
21. Lu, X.; Xu, G. *J Appl Polym Sci* 1997, 65, 2733.
22. Schilling, B. *Kunstst Plast Eur* 1997, 87, 1004.
23. Li, F. K.; Qi, L. Y.; Yang, J. P.; Xu, M.; Luo, X. L.; Ma, D. Z. *J Appl Polym Sci* 2000, 75, 68.
24. Furtado, C. A.; de Souza, P. P.; Silva, G. G.; Matencio, T.; Pernaut, J. M. *Electrochim Acta* 2001, 46, 1629.
25. Ramirez-Garcia, S.; Cespedes, F.; Alegret, S. *Electroanalysis* 2001, 13, 529.
26. Mendes, R. K.; Claro-Neto, S.; Cavalheiro, E. T. G. *Talanta* 2002, 57, 909.
27. Richner, R.; Muller, S.; Wokaun, A. *Carbon* 2002, 40, 307.
28. Bunning, T. J.; Jeon, H. G.; Roy, A. K.; Kearns, K. M.; Farmer, B. L.; Adams, W. W. *J Appl Polym Sci* 2003, 87, 2348.
29. Bansal, R. C.; Donnet, J. B.; Stoeckli, F. *Active Carbon*; Marcel Dekker: New York, 1988.
30. Rivin, D.; Kendrick, C. E. *Carbon* 1997, 35, 1295.
31. Cagliostro, D. E.; Changtai, W.; Smith, J. M. *Ind Eng Chem Proc Des Dev* 1985, 24, 377.
32. Standard Test Method for Apparent Density of Rigid Cellular Plastics; ASTM D 1622-98; American Society for Testing and Materials: West Conshohocken, PA, 1998.
33. Cellular Plastics and Rubbers—Determination of Apparent (Bulk) Density; ISO 845:1988 International Organization for Standardization: Geneva, 1988.
34. Standard Method for Open Cell Content of Rigid Cellular Plastics; ASTM D 6226-98e1; American Society for Testing and Materials: West Conshohocken, PA, 1998.
35. Standard Test Method for Open Cell Content of Rigid Cellular Plastics by Air Pycnometer; ASTM D 2856-94; American Society for Testing and Materials: West Conshohocken, PA, 1998.
36. Hartley, F. D.; Cross, M. M.; Lord, F. W. In *Advances in Polyurethane Technology*; Buistand, J. M.; Gudgeon, H., Eds.; Elsevier: London, 1970; p 127.
37. Baillif, P. Y.; Tabellout, M.; Emery, J. R. *Macromolecules* 1999, 32, 3432.
38. Adamson, A. W. *Physical Chemistry of Surfaces*; Wiley: New York, 1990.
39. Villar, W. D. *Química e Tecnologia dos Poliuretanos*; Pronor: São Paulo, Brazil, 1990.
40. Woods, G. *The ICI Polyurethanes Book*; Wiley: New York, 1987.
41. Festel, G.; Eisenbach, C. D. *Angew Makromol Chem* 1998, 256, 89.
42. Lattimer, R. P.; Williams, R. C. *J Anal Appl Pyrolysis* 2002, 63, 85.
43. Lattimer, R. P.; Polce, M. J.; Wesdemiotis, C. *J Anal Appl Pyrolysis* 1998, 48, 1.
44. Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*; Wiley: New York, 1984.
45. Jaroniec, M.; Madey, R. *Carbon* 1988, 26, 107.
46. Dubinin, M. M. In *Characterization of Porous Solids*; Gregg, S. J.; Singand, K. S. W.; Stoeckli, F., Eds.; Society of Chemical Industry: London, 1979; p 1.
47. Pires, J.; Pinto, M.; Carvalho, A.; Carvalho, M. B. *Adsorption* 2003, 9, 303.
48. Pires, J.; Pinto, M.; Carvalho, A.; Carvalho, M. B. *J Chem Eng Data* 2003, 48, 416.
49. Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic: London, 1982.