# Oxidation of Encapsulated Oil in Tailor-Made Cellular Solid

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A cellular alginate solid containing oil was prepared by freeze-drying. The oil was incorporated in the matrix by emulsification in the pre-gel state. The alginate−oil gels were immersed in 60 °Brix sucrose solution for various periods, before freeze-drying. The extent of the collapse expressing the reduction in sample volume was affected by immersion duration and freeze-drying conditions. Sucrose diffusion during immersion followed an exponential pattern. Effective diffusivity calculated using nonlinear regression gave a value of $3.64 \times 10^{-10}$ m$^2$/s. The effect of relative humidity on water content calculated on a dry basis excluding sucrose showed a significant increase in water content at 75% RH. Image analysis was utilized to quantify the area of the encapsulated oil droplets. The area of the droplets was divided into four subregions defined as $(0.02-0.1) \times 10^{-12}$, $(0.1-1.0) \times 10^{-12}$, $(1-10) \times 10^{-12}$, and $(10-100) \times 10^{-12}$ m$^2$. A distribution resembling a Gaussian bell distribution with a maximum of 54% for the $(1-10) \times 10^{-12}$ m$^2$ area range was found. The number of oil droplets was almost constant for the first three area regions, and then decreased markedly. Oxidation index was not effected by porosity at 0 and 22% RH. A 75% RH and porosity above a critical value of ca. 0.45 was found to increase oxidation significantly. Samples immersed for less than 5.5 h in sucrose solution were mechanically stronger after equilibration at 0 and 22% RH when compared to their counterpart equilibrated at 75% RH. Immersion for more than 24 h resulted in similar mechanical strength irrespective of the RH.

**Keywords:** *Porosity; diffusivity; permeability; oxidation; encapsulated oil; deformability*

## INTRODUCTION

Cellular solids are made of interconnected networks of solid struts or plates forming the edges and faces of cells (Gibson and Ashby, 1988). The cells can be of different shape and size. Three-dimensional cellular materials are called foams, and polymeric foams could be used for cushioning, packaging, and insulation. Cork, softwood, and corals are naturally occurring cellular solids. Many foods have this kind of structure including bread, morning cereals, foamed chocolate, and meringue.

Cellular solids can be produced by freeze dehydration of hydrocolloid gels (Nussinovitch et al., 1993; Rassis et al., 1997, 1998). Different procedures of gel preparation yield sponges of distinct structural and mechanical characteristics. Diffusion of α-amylase into agar-starch gels for different times resulted with sponges that were mechanically weaker as diffusion time lengthened (Nussinovitch et al., 1998). Oil incorporation (10−40%) into alginate gum solution revealed cellular solids with decreasing stress at failure, stiffness (as reflected by the deformability modulus), and Hencky's strain at failure as oil concentration increased (Nussinovitch and Gershon, 1997). Sucrose diffusion into alginate−starch gels produced decreasing porosity and mechanically stronger cellular solids with immersion time (Rassis et al., 1998).

Stress−strain relationship of cellular solids change as the environmental relative humidity is alternated. Sponge cakes after vacuum dehydration and equilibration to 0.33 $a_w$ collapsed by brittle fracture. Sponges conditioned to water activities of 0.57 or 0.75 collapsed by elastic buckling. However, compression occurred without fracture up to 50% strain with samples exposed to higher water activity (Attenborrow et al., 1989). Compression curves of a corn meal extrudate conditioned at 11%, 43%, and 75% RH, revealed at the low moisture irregular and jagged response curve. Increasing the relative humidity resulted in smoother response curves (Barrett et al., 1992; Harris and Peleg, 1996; Peleg, 1997).

Oil oxidation is a major concern for food stability during storage. Freeze-drying of a mixture of lactose−gelatin−methyl−linoleate revealed two kinds of oil, surface and encapsulated (Shimada et al., 1991). While surface oil oxidized quickly, the encapsulated oil deteriorated very slowly (Karel, 1979; Shimada et al., 1991). Elevating the temperature of the freeze-dried powder above the glass transition temperature of the lactose caused its crystallization and matrix changes, resulting in the release and oxidation of the encapsulated oil (Shimada et al., 1991). Oxidation of a freeze-dried emulsified mixture of $\beta$-carotene with maltodextrin was faster after 2, 3, and 6 weeks at 45, 35, and 25 °C, respectively. However, the faster initial oxidation rate due to the existence of surface $\beta$-carotene leveled off, showing only little difference between the different storage temperatures. These oxidation rates were not affected by the relative humidity of 11 and 32% (Desobry et al., 1997). Oxidation of methyl linoleate encapsulated in gum Arabic and stored under 12% and 44% RH was similar, and increased significantly at 75% and 96% RH (Minemoto et al., 1997). Squid oil oxidation after emul-

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sification and spray drying was influenced by the wall materials. The latter affected the oxidation rate, which was reduced by casein, lecithin, and Avicel (emulsifying agents) which were added to the gelatin−maltodextrin wall matrix (Lin et al., 1995). Significant differences in oxygen uptake were observed between anhydrous milkfat and microencapsulated system containing the fat in whey protein isolate as wall material. Oxygen uptake was evident after 1 week for the first system and increased with time, while the encapsulated milk fat was stable after 6 weeks at 50 °C (Moreau and Rosenberg, 1996).

Structural collapse during drying affects products quality by reducing porosity, rehydration ability and texture (Karel et al., 1994). Freeze-drying is used as a process that reveals excellent products, with high porosity and little shrinkage or collapse. In freeze-drying, a glassy matrix of food solids that is formed does not allow structural changes, and the initial volume can be maintained (Roos, 1995b). Collapse during freeze-drying may occur when the temperature that is governed by the chamber pressure is above the $T'_g$ of the concentrated amorphous solution (Roos, 1995a; Krokida et al., 1998). A viscous flow of the concentrated amorphous solution occurs due to the decreasing viscosity in the vicinity of the onset temperature of ice melting above $T'_g$ (Roos, 1995a; Krokida et al., 1998). Glass transition temperature of the maximally freeze-concentrated solution of sucrose is −46 °C (Roos, 1993). However, significant collapse could occur above −32 °C due to melting.

The objectives of this research were to determine the oxidation of oil encapsulated within a dry cellular solid produced from alginate gels immersed for various duration in sucrose solution, and to study the effect of porosity, relative humidity, diffusion, and mechanical properties.

## MATERIALS AND METHODS

**Preparation of Cellular Solids**. Cellular solid materials were prepared on a magnetic stirrer by mixing 2% (w/w) sunflower oil with double-distilled water and a few drops of Twin 80 until an emulsion was created. Sodium alginate powder (LV, mol. weight $7 \times 10^5$ to $8 \times 10^5$ 61% manuronic acid, and 39% guluronic acid; Sigma, St. Louis, MO), 2.5% (w/w), was added, mixed (magnetic stirrer) overnight (15 h) at ambient temperature (25 ± 2 °C). Sodium hexametaphosphate (SHMP, BDH, Poole Dorset, UK), 1.5% (w/w), was added, and the mixture was further stirred for 60 min and heated to ca. 40 °C, prior to the addition of $CaHPO_4$ (Riedel-de Haen, Seelze, Germany), 1.5% (w/w), and incorporated for 60 min. The mixture was cooled to 20 ± 1 °C and homogenized to incorporate the oil as small droplets with an Ultra Turrax (Ultra Turrax T25, IKA Labortechnik, Staufen, Germany), for 4 min at 23 500 rpm. Freshly prepared GDL (glucono-δ-lactone, Sigma) solution, 3% (w/w), was added to reduce the pH and enhance the setting of the gel and mixed in. The GDL volume was ca. 10% of the overall gum solution. The mixture was poured into glass cylinders 2 × 2 cm (diameter × height) and left covered for overnight (15 h) at 4 °C for gelation. The gel samples were immersed in 60 °Brix sucrose solution at ambient temperature. The volume of the sugar solution was approximately 70 times that of the gel. Immersion periods ranged from 0 to 72 h; samples were removed from the sucrose solution, wiped gently, weighed, and stored at −18 °C. The samples were freeze-dried using a pilot plant unit (model 15 RSRC-X, Repp Industries Inc., Gardiner, NY), operating at 33.3 Pa and −45 °C.

**Diffusion Measurements**. Diffusion of sucrose concentration into the gels was measured on a table refractometer (Carl Zeiss, Berlin, Germany), by removing the samples from the sugar solution and wiping them carefully with a paper towel. An inner disk (3 mm height × 8 mm diameter) was taken from the center of the gel, crushed by a mortar and pestle, and diluted with two weights of distilled water, and total soluble solids (°Brix) were determined. Refractometric values within the gel and the surrounding sucrose solution were also determined vs time of immersion. The results are the mean of two experiments, with at least triplicates.

**Relative Humidity**. Samples were equilibrated for ca. 4 weeks at ambient temperature (25 ± 2 °C) in a desiccator over the following salt solutions: 0% RH ($CaSO_4$, W. A. Hammond Drierite Co., Xenia, OH), 22% RH ($K(CH_2COO)$, Merck Darmstadt, Germany), and 75% RH (NaCl, J. T. Baker, Phillipsburg, NJ).

**Particle and Bulk Density and Porosity Determination.** The particle density of the cellular solid was determined on a multipycnometer (Quanta Chrome Corp., Syosset, NY). Helium gas was used at a working pressure of 103.4−110.4 kPa. The bulk density was determined by volumetric displacement using glass beads (425−600 μm, Sigma), and porosity was calculated as (Marousis and Saravacos, 1990)

$$\epsilon = 1 - \frac{\rho_b}{\rho_p} \quad (1)$$

where $\epsilon$ is the porosity, $\rho_b$ bulk density, and $\rho_p$ particle density. The relative density was derived from the ratio $\rho_b/\rho_p$. Each determination was done in triplicate.

**Microscopic View of Oil Containing Cellular Solids**. Sudan Red B (Fluka, Buchs, Switzerland) was used to color the oil before its incorporation into the solution gum. The dried cellular solids were cut with a new blade into thin layers. Cells shape and oil location were studied on a microscope (Olympus AX70, Olympus Optical Co. Ltd., Tokyo, Japan) with a mounted camera (Olympus, PM-10, SC 35, Type 12). Photographs magnification was ×100 and ×200.

**Oil Location**. Freeze-dried samples were rinsed with hexane (HPLC grade, Frutarom, Haifa, Israel), attempting to extract the oil. After crushing, the samples were again stirred with hexane first and with petroleum ether (60−80 °C, Frutarom) later on, for the same reason. All the rinses were collected. This procedure was applied only for determining the location of the encapsulated oil.

**Oil Extraction**. Specimens were kept at the above relative humidities for 6 weeks prior to oil oxidation tests. Each determination was done in duplicate. For complete oil extraction, dry cellular solid samples were cut into small pieces and stirred with 40 mL 1% (w/w) EDTA (ethylaminetetraacetic-acid, BDH) and 10% (w/w) trisodium citrate (BDH), for 1.5−2 h until all the sample was dissolved. An antioxidant solution (1.5 mL of 0.8% BHT (Sigma, Steinheim, Germany) in hexane (Frutarom)) was added to the samples prior to stirring. The sample solution was poured into a separatory funnel, NaCl (ca. 2 g; J.T. Baker) and petroleum ether (40 mL) were added, and the separatory funnel was shaken vigorously. The organic phase was poured through a cotton layer with a small amount of $Na_2SO_4$ (anhydrous, Frutarom), into a flask. This procedure was repeated three times and all the organic fractions were collected and evaporated to dryness on a laboratory evaporator (Rotavapor, Type RE−111, Buchi, Flawil, Switzerland), and the remaining oil was weighed.

**Oxidation Index**. Oil (0.02−0.06 g) was transferred into a glass tube containing 4.95 g of hexane (HPLC grade, Frutarom) and mixed by a vortex, followed by a volumetric dilution of 1:20 with hexane. Oxidation was determined spectrophotometrically (UV/Visible, Philips Cambridge, U.K.) at 234 nm (Shimada et al., 1991). An extinction coefficient of 29 000 $mol^{-1}$ $L^{-1}$ (Privett and Blank, 1962) was utilized to quantify the concentration of the hydroperoxides formed during oxidation. The results are the mean of two experiments, and duplicate samples.

**Electron Microscopy Micrographs (SEM) and Image Analysis.** Dry gels after sucrose diffusion were the subject for the SEM study. SEM micrographs were obtained by cutting

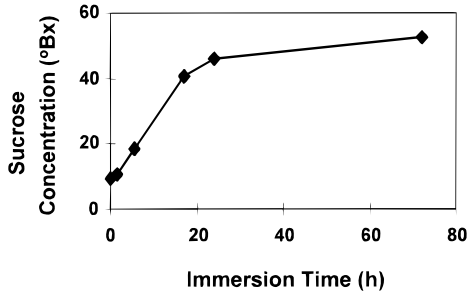


**Figure 1.** Sucrose diffusion into gels during immersion in 60 °Brix solution.

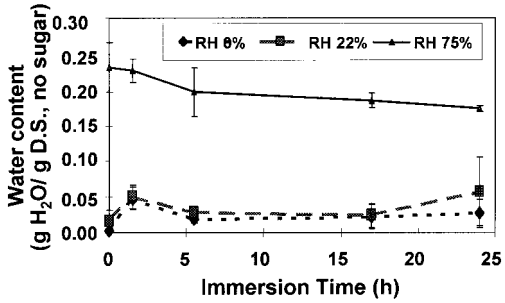


**Figure 2.** Water content of cellular solids as a function of relative humidity and immersion time.

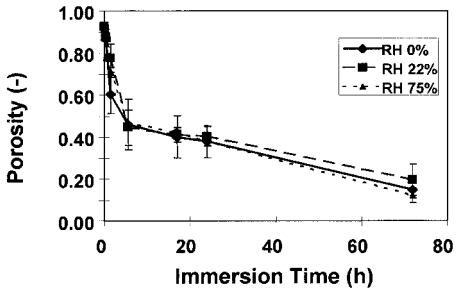


**Figure 3.** Cellular solid porosity as a function of immersion time and relative humidity.

through the dry cellular solid with a double-edged razor blade and exposing the internal surface features. Single ducts were used to produce 2−4 mm slice thickness. A 1:1 mixture of colloidal graphite in isopropyl alcohol and Ducco household glue was used as a conductive mounting adhesive and was mounted on 10 × 10 mm aluminum SEM stubs coated with approximately 50 nm Au/Pd (60:40, w/w) in a Polaron E5100 unit (Polaron Equipment, Holywell Ind. Watford, UK) fitted with a Peltier cooling stage. Samples were examined on an electron microscope (JEOL JSM 25S SEM, Tokyo, Japan) at an accelerating voltage of 15 kV and a working distance of 48 mm. Micrographs were magnified at 500, 1000, and 1500.

Electron micrographs were scanned (Astra 1220P Umax Technologies Inc., Union City, CA) and analyzed using the public domain NIH image program (written by Wayne Rasband, U.S. National Institutes of Health, Springfield, VA). This program determined the oil drops area, measured in pixels and translated into metric units. Four samples were checked and the results were calculated and plotted using a software package (Excel97, Microsoft Corp., Seattle, WA).

**Mechanical Tests**. Specimens equilibrated at 0, 22%, and 75% RH prior to mechanical tests were compressed to 80% deformation between parallel lubricated plates, at a constant deformation (displacement) rate of 10 mm/min, using an Instron Universal Testing Machine model 1011 (Instron Corp. Canton, MA). The Instron was connected to an IBM-compatible personal computer by an analog to digital conversion interface card. A program developed at the Instron Corp. (Canton, MA) and modified in our laboratory performed the data acquisition and deformation conversion of the continuous voltage of Instron vs time output into digitized deformation vs force. The results are typical representatives of two experiments.

## RESULTS AND DISCUSSION

**Sucrose Diffusion**. Diffusion of sucrose into the gel containing 2% sunflower oil immersed in sucrose solution of 60 °Brix followed an exponential behavior (Figure 1). Sucrose concentration in the center of the gel leveled off after ca. 20 h and had an asymptotic trend up to 72 h (the duration of the immersion). Sucrose penetration was described according to a diffusion equation for a semiinfinite solid in one direction (Gross and Ruegg, 1987), yielded an effective diffusivity, $D_{eff}$ of $3.64 \times 10^{-10}$ $m^2/s$ ($R^2 = 0.984$; $P < 0.05$). A similar value ($4.6 \times 10^{-10}$ $m^2/s$) was reported for alginate−starch gels immersed in sucrose solution (Rassis et al., 1998). During immersion, sucrose and water diffused in opposite directions, resulting in a weight decrease due to water loss. Water diffusion from the gel into the surrounding sucrose solution predominates sucrose diffusion into the gel and is due to osmotic pressure difference between the surrounding solution and the gels (Rassis et al., 1998; Tanaka, 1981; Trelea et al., 1997). Weight loss due to agar and carrageenan immersed in acetone solution and weight gain due to gels submerged in sucrose solution (0−30%) was discussed previously (Nussinovitch and Peleg, 1990; Nussinovitch et al., 1995). The diffusion of sucrose and water had a significant effect on the mechanical properties, structure, and porosities of the resultant cellular solids after freeze dehydration of the gels. These effects are discussed below.

**Water Absorption**. The cellular solid specimens were equilibrated at three relative humidities (0, 22, and 75%) for ca. 4 weeks until a constant weight was observed. The effect of relative humidity on water content calculated on a dry basis (excluding sucrose) showed only a slight difference at 22% RH and a significant increase in water content at 75% RH in comparison with 0% RH (Figure 2). The data also indicated that at 75% RH water content decreased slightly with sucrose concentration. The decrease is probably due to two main effects: reduction in volume of the cellular solid by shrinkage of the gel during the immersion in sucrose solution, and the physical state of the sucrose in the dry matrix. In the cellular solid, sucrose is mostly in an amorphous state after the freeze dehydration process. The sucrose state could change into a crystalline form during equilibration as a function of relative humidity and time (Karel, 1975; Roos, 1995a). We therefore suspect that at 75% RH a major part of the sucrose is in the crystalline state, which caused a decrease in water content. Another explanation for the lower water content at 75% relative humidity and high sucrose concentration is due to the reduced free space (e.g., porosity) available for the water to penetrate into the samples (Rassis et al., 1997, 1998). This is verified later by the mechanical properties of the dry matrices. Sucrose crystallization is expected to increase non encapsulated oil (Shimada et al., 1991). However, as in this case, the oil was encapsulated in the alginate matrix and no changes in the encapsulation of the oil were observed.

**Porosity**. The porosity of the cellular solids decreased with immersion time due to sucrose diffusion into the wet gels (Figure 3). Porosity changed from an initial value of 0.93 to 0.12 after 72 h immersion in 60 °Brix sucrose solution. It is worth noting that the three RH

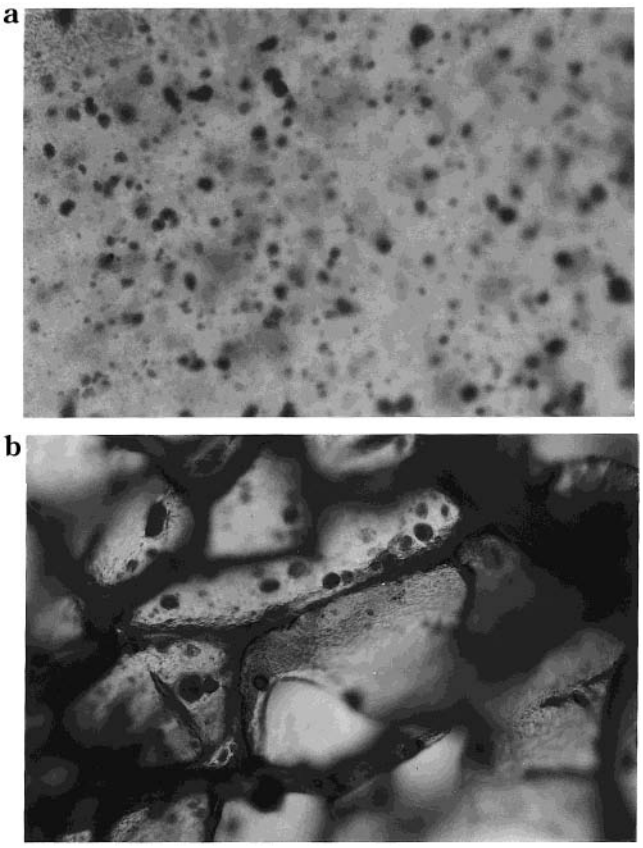


**Figure 4.** Microscopic view of cellular solids containing oil colored with Sudan Red: (a) equilibrated to 0% RH, magnification ×100; (b) equilibrated to 75% RH, magnification ×200.

used to equilibrate the sample had no apparent effect on the porosity. However, relative humidity affected the specimens' structure as was evident in the mechanical properties.

**Oil Location**. Sunflower oil (2%) was emulsified within the gum solution before gelation and freeze dehydration. At this concentration, oil is totally encapsulated during the alginate matrix gel formation followed by entrapment within the cellular solid matrix after freeze dehydration (Nussinovitch and Gershon, 1997). To verify complete encapsulation, the oil was mixed with Sudan Red prior to its incorporation in the gum solution. The resultant cellular solids had a light pink color. However, when rinsing the cellular solids with hexane no pigment could be extracted. Less than 60% of the oil could be recovered when the samples were pulverized and stirred with hexane for ca. 5 min. Additional 10% oil could be extracted when hexane was replaced with petroleum ether (60−80 °C), thus indicating full oil encapsulation. Further support for this finding is the fact that complete oil recovery was only possible when the alginate matrix was disintegrated with EDTA (1%) and trisodium citrate (10%).

The cellular solid containing oil colored with Sudan Red was inspected on a light microscope. The small droplets of oil (i.e., the darker spots) are visible throughout the slide (Figure 4a), indicating as well the existence of different oil size droplets. The structure of the cells of the cellular solid as could be seen by the darker color of the cells walls indicated that oil droplets were more concentrated in this region (Figure 4b). As the oil was fully encapsulated in the dry matrix, the visible oil drops are a part of the wall matrix that formed the cells. The

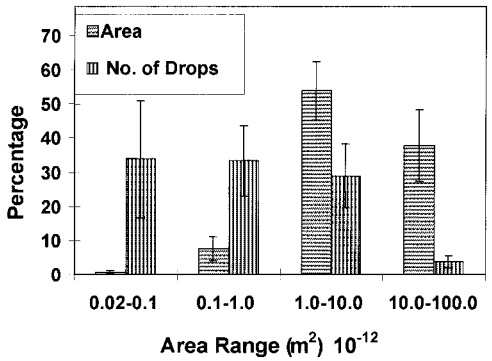


**Figure 5.** Oil drops intersect area and drops number image analysis (see text for explanation).

slight pink color of the photographs (observed originally) was probably due to pigment smearing while slicing the cellular solids during the microscopic preparation.

It is worth noting that oil encapsulation occurred during the alginate matrix formation. Hence, sucrose diffusion during immersion thickened probably the encapsulated oil matrix in a nonspecific way. However, shrinkage or collapse during immersion or freeze-drying had no effect on the encapsulated oil.

The area of the oil droplets encapsulated in the cellular solids was measured utilizing image analysis of the SEM micrographs. The droplets area was divided into four subregion ranges, namely, (0.02 (i.e., the lowest detection level set by the capabilities of the equipment utilized) to 0.1) $\times 10^{-12}$, (0.1−1.0) $\times 10^{-12}$, (1−10) $\times 10^{-12}$, and (10−100) $\times 10^{-12}$ m$^2$. The relative weights (%) of either the sum of area drops or the number of drops in each specific range were compared to the overall drops area, or number of drops (Figure 5). These data indicated that the area of the droplets was distributed unequally resembling somewhat a Gaussian bell distribution with a maximum of 54% for the (1−10) $\times 10^{-12}$ m$^2$ area range. The number of oil droplets was almost constant (ca. 30%) for the first three area ranges and decreased markedly in the last area range. These data showed that there were less large droplets ((10−100) $\times 10^{-12}$ m$^2$) that occupied a significant area, and the emulsified oil was maintained its original sizes. In other words, only ca. 4% (Figure 5) of the embedded oil drops coalesced during processing. Similar diameter of oil drops were reported previously (i.e., 1.26 $\times 10^{-6}$ m or 1.24 $\times 10^{-12}$ m$^2$, Xu et al., 1992; and 2.13 $\times 10^{-6}$ m or 3.56 $\times 10^{-12}$ m$^2$, Matsumura et al., 1993).

**Oil Oxidation**. The cellular solid specimens were kept at three different relative humidities (0, 22, and 75%) for 6 weeks at ambient temperature of 25 ± 2 °C. After this period, the oil was extracted from the samples and the oxidation index was determined (Shimada et al., 1991). Prior to its incorporation into the cellular solid, the initial oil oxidation index was 7.3 mmol/L. Oil oxidation levels of samples at high porosity (0.92) equilibrated to 0 and 22% RH were significantly lower compared with those at 75% RH (Figure 6). As these samples were not immersed in sucrose solution, it could be concluded that oxidation was controlled by a limiting factor not related to sucrose. An exponential relationship between aroma transport and moisture content of hydrophilic films was reported (Schwartzberg, 1986), and aroma permeation through polymers could be correlated with their oxygen permeability (DeLassus, 1994). Alginate films were described as poor moisture barriers but good oxygen barriers at low moisture levels

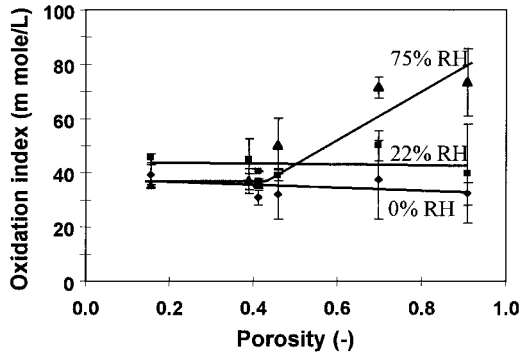


**Figure 6.** Oil oxidation index as a function of porosity and relative humidity.

(Krochta and Mulder-Johnston, 1997). Hence, the data suggest that water content in the alginate matrix could increase oxygen solubility resulting in higher permeability. Similar RH effect was reported at higher temperatures when D-limonene permeability was measured in whey protein films (Miller and Krochta, 1997; Miller et al., 1998).

At low water activity, oxidation of oil is expected to be accelerated through a free-radical mechanism (Karel, 1975). However, in this case, oil was encapsulated within the solid matrix, and the oxygen could reach the close proximity of the oil only by permeating through the solid wall matrix. Oxygen permeability depends both on solubility and diffusion. Therefore, water content is an important factor affecting both solubility and diffusivity. The rate constant of a diffusion-limited reaction could be related to the diffusivity and was shown to affect oxidation rate (Karel and Saguy, 1993; Karel, 1993).

Porosity above a critical level of ca. 0.45 and 75% RH had a profound effect on oxidation of the encapsulated oil (Figure 6). Below this critical porosity value, and at all RH studied, oxidation remained constant. Porosity above 0.4 was found to increase permeability, due to higher interconnections between the pores (Goedeken and Tong, 1993), which could also be the case in this study. The issue that needs to be addressed is whether oil oxidation was influenced by porosity of the samples equilibrated to 75% RH, or that moisture was the predominant factor. It is quite evident that water activity was not affecting the porosity (Figure 3), therefore, it could be concluded that the limiting factor was oxygen permeation through the dry calcium alginate wall matrix. The barrier efficiency against oxygen transfer through the alginate matrix depends mainly on both sorption and diffusion, in which moisture content plays a significant role.

**Mechanical Tests**. Cellular solids with no sucrose included within their dry matrix were compressed to ca. 80% deformation (Figure 7a). Such specimens resembled almost complete cylindrical shapes and suffered from no or a very limited shrinkage during the freeze dehydration (Figure 8,a and b, left). Force deformation curves of such cellular solids equilibrated to 0 and 22% RH showed no significant difference behavior. At 75% RH a weaker structure was formed due to water absorption by the dried matrix. Sucrose diffusion for 5.5 h into the gels followed by their freeze dehydration yielded similar results (Figure 7b) with the exception that dried gels equilibrated to 0 and 22% RH were somewhat stronger than their counterparts, and the rate at which force increased was much higher. The

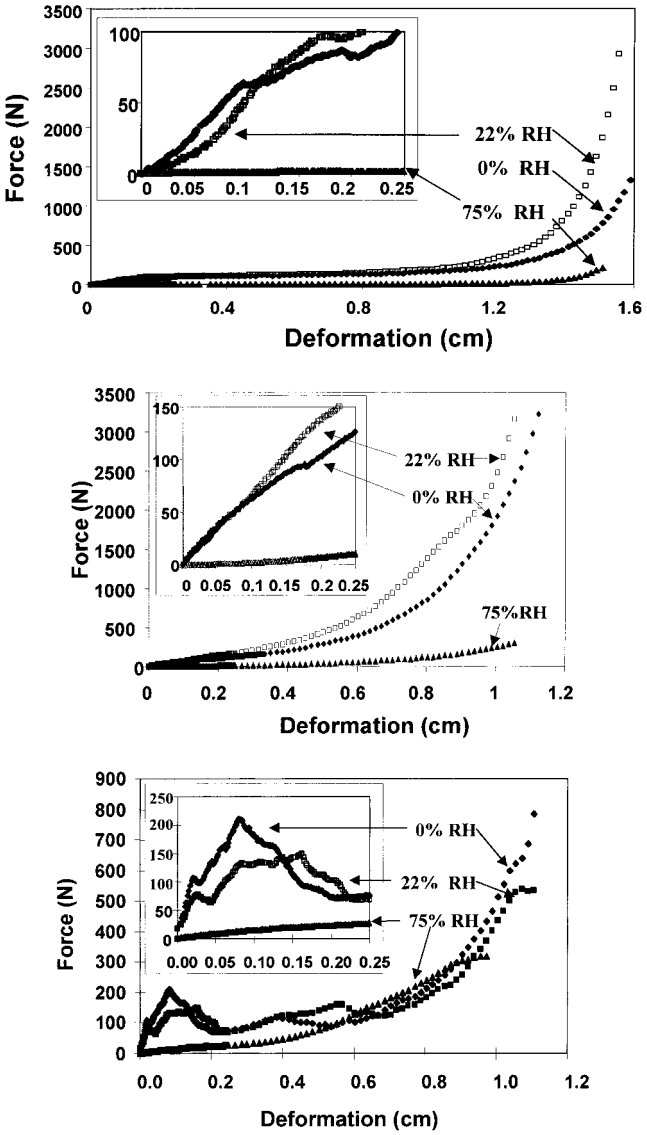


**Figure 7.** Force vs deformation as a function of relative humidity and immersion time: (a, top) 0 h; (b, middle) 5.5 h; (c, bottom) 24 h.

slopes of the curves for ca. 50% deformation were 587.7 and 300.0 N/cm for 0 and 22% RH at time zero, respectively, and 682.7 and 662.9 N/cm for the same RH and 5.5 h of immersion, respectively.

This increase is due to the sugar gain within the dried matrix, and the relative densities of the resultant specimens ($0.07 \pm 0.00$ and $0.62 \pm 0.13$, for 0 and 5.5 h of immersion, respectively). The relative density was also affected by the reduction in sample volume (collapse, Figure 8 in the middle). After longer period of diffusion this trend of strengthening stopped. In fact the force deformation curves (Figure 7c) are different since the instance at which changes in the volume occur are different. After 5.5 h of immersion the main reduction in volume is a result of collapse during the drying. After 24 h the main changes occurred throughout the immersion in the sucrose solution. Since less sucrose is present in the dried gels after 55 h immersion, the collapse is more catastrophic (i.e., walls of matrix touch each other) and as such the specimen is more compact and strong. After 24 h, less compaction of matrix walls occurs, and therefore they are weaker. It is important to note that the gels behave in an opposite way before drying, i.e., gels after 24 h of immersion are much stronger than

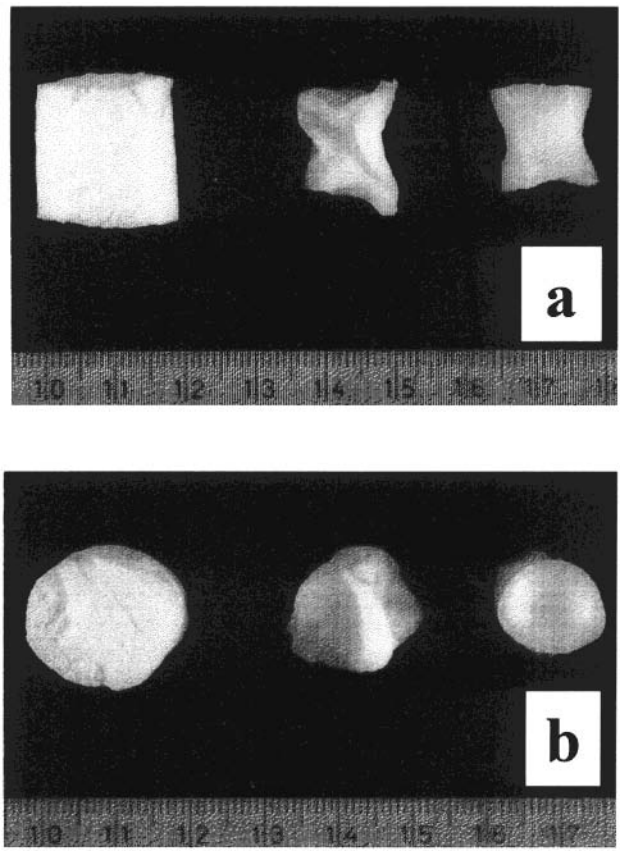


**Figure 8.** Photograph of cellular solids after (from left to right) 0, 5.5, and 24 h of immersion: (a) front view; (b) upper view.

those immersed for5.5 h (data not shown). Thus, the instant at which drying took place will have a major influence on specimens texture and shape.

The collapse during freeze-drying was a result of the temperature of the samples during freeze-drying. The collapse would occur if the temperature was above the $T'_g$ of the matrix. In a maximally freeze-concentrated sucrose solute matrix $T'_g$ is known to be −46 °C (Roos, 1993; Schenz, 1995). The collapse influenced samples that were immersed for up to 5.5 h. Specimens that were immersed for longer periods changed their cylindrical shape to a shrunken configuration and did not collapse during freeze-drying.

The mechanical properties of the cellular solids were affected by the RH. The porosity influenced the mechanical behavior probably through the sample structure. The porosity was markedly affected by sucrose diffusion. Sucrose diffusion was strengthening at the beginning and then weakening the mechanical properties of the cellular solids. The sugar had also a part in oil oxidation, by possibly more than one mechanism involving viscosity, mobility, and permeability affecting oxygen permeation.

## CONCLUSIONS

Sucrose diffusion into the gels had an exponential behavior. Water content of the samples stored at 0 and 22% RH was very low compared to 75% RH. Water content at 75% RH slightly decreased with immersion time. The porosity of the cellular solids was an outcome of its structure and decreased with increasing immersion time and was only slightly affected by relative humidity. Oil emulsified in the gel solution was encapsulated in the alginate dry matrix as tiny droplets. Oil droplets intersect area was between 0.02 and 100 × $10^{-12}$ $m^2$, the largest area was occupied by drops with intersect area of (1.0−10) × $10^{-12}$ $m^2$. The oxidation index increased above a critical porosity of ca. 0.45 and 75% RH. Samples that were immersed for short time in sucrose solution (5.5 h) were mechanically stronger than samples that were submerged for longer period (24 h).

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