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Review

Production, properties, and applications of hydrocolloid cellular solids

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Many common synthetic and edible materials are, in fact, cellular solids. When classifying the structure of cellular solids, a few variables, such as open *vs.* closed cells, flexible *vs.* brittle cell walls, cell-size distribution, cell-wall thickness, cell shape, the uniformity of the structure of the cellular solid and the different scales of length are taken into account. Compressive stress-strain relationships of most cellular solids can be easily identified according to their characteristic sigmoid shape, reflecting three deformation mechanisms: (i) elastic distortion under small strains, (ii) collapse and/or fracture of the cell walls, and (iii) densification. Various techniques are used to produce hydrocolloid (gum) cellular solids. The products of these include (i) sponges, obtained when the drying gel contains the occasionally produced gas bubbles; (ii) sponges produced by the immobilization of microorganisms; (iii) solid foams produced by drying foamed solutions or gels containing oils, and (iv) hydrocolloid sponges produced by enzymatic reactions. The porosity of the manufactured cellular solid is subject to change and depends on its composition and the processing technique. The porosity is controlled by a range of methods and the resulting surface structures can be investigated by microscopy and analyzed using fractal methods. Models used to describe stress-strain behaviors of hydrocolloid cellular solids as well as multilayered products and composites are discussed in detail in this manuscript. Hydrocolloid cellular solids have numerous purposes, simple and complex, ranging from dried texturized fruits to carriers of vitamins and other essential micronutrients. They can also be used to control the acoustic response of specific dry food products, and have a great potential for future use in countless different fields, from novel foods and packaging to medicine and medical care, daily commodities, farming and agriculture, and the environmental, chemical, and even electronic industries.

Keywords: Cellular solids / Drug release / Hydrocolloids / Novel foods / Review / Water treatment

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Abbreviation: SEM, scanning electron microscopy

1 Introduction

1.1 General aspects

The term 'cellular solid' can be traced back to the word, 'cell', which derives from the Latin word 'cella' – a small compartment, an enclosed space [1, 2]. The term 'cellular solid' refers to materials sharing structural similarities, which are nevertheless mechanically different. This review is primarily devoted to discussing material structures based on hydrocolloids (gums), filled with air or some other gas, and their mechanical properties. 'Cellular' vegetative tissues are not dealt with here. A few examples of cellular solids could include: wooden artifacts excavated from Egyptian pyramids; cork bungs used to seal wine bottles; structures built by communities of organisms, such as corals or insect nests; man-made honeycomb-like materials for use in the production of lightweight components for the packaging industry, and polymeric solid foams, the uses of which range from disposable coffee cups to the crash padding in aircraft cockpits; even metallic, glass and ceramic foams can be included in this list [1]. Cellular solids have a low density and markedly low mechanical strength, based on the cell wall and the entire cellular structure. Their structure can be classified according to the following characteristics: (i) flexibility *vs*. brittleness of the cell wall; (ii) distribution of cell size in the body of the cellular solid; (iii) open *vs*. closed cells; (iv) thickness and shape of the cell wall, and (v) structure uniformity, as measured on different length scales [3].

Cellular solids have many applications, thermal insulation for one: coffee cups or even booster rockets. Transport systems and ships are composed of various types of cellular solids. Other applications incorporate cellular solids into packing materials to absorb the energy of potential impacts, and into structural materials for buoyancy. They also function as fillers, carriers, water-repellent membranes, and non-slip surfaces, as well as being purveyors of damping capacity and specific electrical properties. Many food items are also cellular solids, perhaps the most common of all being bread (Fig. 1), and a few kinds of cakes with a spongy structure. Another familiar product is the meringue, made of foamed egg whites and sugar and later baked. The size of the cells created by gas distribution, the maximal included phase and the ease of processing are influenced by the content and character of the surface-active agents used in the process [4]. Foamed chocolate is a product which has been specifically expanded to change its texture (Lillford, 1989). Hard brittle candies are also often expanded to make them more appealing to consumers. Other examples of cellular solids in the food industry include edible sponges, made from a mixture of maltodextrin, eggs and water (Attenburrow, 1989). The most valued properties of cellular solids are their density, conductivity, Young's modulus and strength [5]. Cellular solids usually have relative densities of less than 0.3, but they may reach lower values. Different structures of cellular solids lead to a wide range of such properties and a much greater availability. A low-density substance translates to light, stiff, large portable structures that are able to float. Their low thermal conductivity brings about thermal insulation [5].

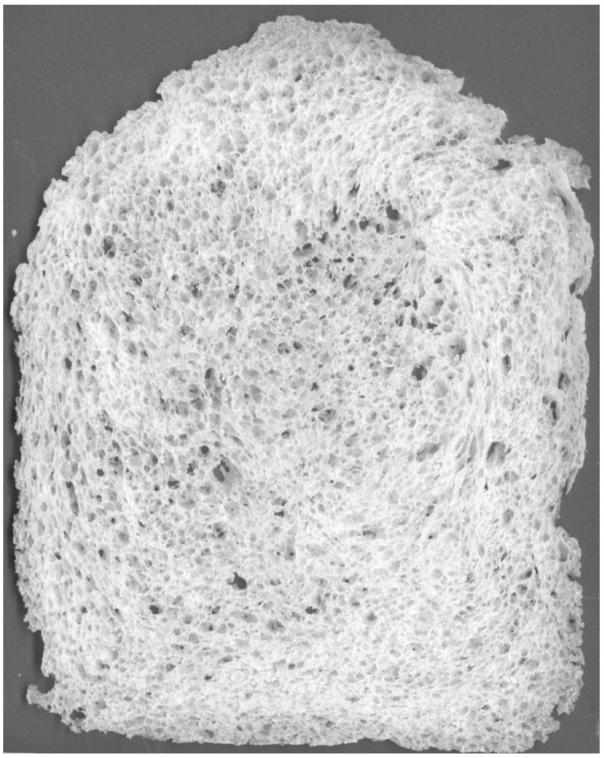

Figure 1. Cross-section through a bread slice (actual size). Bread consists of cells, expanded by either the fermentation of yeast or CO_2 from bicarbonate. Bread crumbs are an example of a cellular solid (courtesy of N. Kampf).

1.2 Evaluation of cellular solids

Cellular solids have unique mechanical, thermal, electrical, and acoustic properties. Many synthetic types of foam are used for thermal insulation due to the low-volume fraction of their solid phase, small cell size, and poor conductivity of enclosed gas. Many different types of products make use of foam's low thermal conductivity, such as insulation for liquid-oxygen rocket tanks and, at the other extreme, disposable coffee cups. The food industry takes advantage

of this low conductivity by filling refrigerated trucks and railway cars with foam. In general, the coefficients of thermal expansion of most foams are roughly the same as those of the solid materials from which they were produced. Their small moduli and the small thermal stresses generated by a temperature gradient give them good thermal shock resistance [1]. In principle, hydrocolloid-based cellular solids can be used for insulation; however, synthetic foams are preferred due to their lower cost. In addition, edible materials are prone to changes, especially if they absorb water. On the other hand, the biodegradability of edible sponges can be an advantage where ecological issues are involved, and may become even more important as the cost of their production decreases and ecological hazards increase.

Foams are remarkable for their good thermal insulation. Heat conduction in solids is characterized by thermal conductivity and thermal diffusivity. The thermal conductivity is defined by Fourier's law as the heat flux, *i. e.*, the amount of heat flowing across a unit area per unit time, induced by a temperature gradient. The thermal conductivity of foam has four contributing factors: conduction through the solid, conduction through the gas, conduction within the cells, and radiation through the cell walls and across the cell voids [1]. Electrical properties of foams, such as high electrical resistance, are important for the insulation of coatings and mounting panels of electrical components. These properties are derived from those of the solid from which they were made, and modified by the function of the relative density. We are not familiar with any characterization of such properties in the field of edible sponges. However, this issue could take on some importance in the future of induced drug release from digestible cellular solids, if said release were to be controlled by an electrical field. Cellular, porous solids can also be used to absorb sound. In combination with other materials, they can help in isolation. However, they are poor at providing insulation against sound. Nevertheless, the importance of their crunchiness and the characterization of their sound responses are much appreciated in the marketing and consumption of edible cellular solids (see further on).

2 Procedures for the production of tailored hydrocolloid cellular solids (sponges)

The term 'hydrocolloids' refers to a range of polysaccharides and proteins that can be used in many sectors for: thickening, gel formation, foam stabilization, emulsions and dispersions, the inhibition of ice- and sugar-crystal formation, and the controlled release of flavors [6]. The major hydrocolloids used in the production of cellular solids are summarized in Table 1.

2.1 Sponges containing or lacking internally produced gas bubbles derived from the drying of gels

There are many procedures currently used for the production of cellular solids, including: (i) sponge production *via* the drying of gels containing or lacking internal bubbles produced by the distribution of gases throughout the solid, (ii) sponge formation *via* the fermentation of immobilized yeasts, a process that occasionally includes the addition of oil emulsions to the gel prior to drying in order to control structure and porosity, and (iii) hydrocolloid sponge production *via* enzymatic reaction, among others [7]. Stable solid foams are often produced by freeze-drying, whereby the hydrocolloid gels are simply freeze-dried without any further treatment. Different textures can be obtained by the inclusion of gas bubbles in the gel prior to drying. Most hydrocolloid gels possess a low solid content and consequently, are considered a poor raw material for drying. Studies of gel dehydration were performed to model different food items: however, it is important to mention that in those studies, there was little or no interest in the properties of the dried product. In fact, dried gel products, such as hydrocolloid sponges, are economically feasible despite the high cost of the dehydration process. Such moieties can, theoretically, serve as internal or external absorbents to be used, for instance, after surgery or combined with burn treatment. If said sponge is made from a hydrocolloid that can decompose quickly and easily inside the human body, it could be left in place, eliminating the complications associated with the removal and replacement of conventionally used absorbing materials [8].

As already stated, mechanically stable sponges are produced by freeze-drying various types of hydrocolloid gels. Agar (2%), alginate (1%), and κ-carrageenan (1.5%) gel specimens, for example, were studied. These specimens originated from 'mother' solutions which also contained 0–2.5% sodium bicarbonate (agar and carrageenan) or calcium carbonate (alginate) (see Fig. 2). Upon immersion in a citric acid bath (0–2%), the carbonate reacts with the diffusing acid to produce an abundant amount of CO_2 bubbles. The acid's movement in the gel is controlled by diffusion, as evidenced by the linearity of the penetrated distance *vs.* $t^{0.5}$ plots. The slopes for all gels were about 0.7 mm · $min^{-0.5}$. This information suggests that the hydrocolloid species and the concentration, when tested over a certain range, has little effect on the acid-diffusion rate [9]. The number of bubbles formed depended entirely on the time of immersion and the concentration of the carbonate, with patterns varying between the three types of gels. In agar, after about 2.5 h, there were already about 4500 bubbles · cm^{-3}. The number slowly increased with time, reaching about 5500 bubbles · cm^{-3} after 54 h immersion. When compared to agar, the alginate gels had a considerably smaller number of

Table 1. Main classes of hydrocolloids for sponge production

Hydrocolloid (structure)	Principal function	Source
Agar E406 (repetitive units of D-galactose and 3,6 anhydro-L-galactose)	Gelling agent	Red seaweed
Alginate (sodium) E401 (a true block copolymer composed of homopolymeric regions of mannuronic and guluronic acid residues)	Gelling agent	Brown seaweed
Arabic (gum) E414 (complex polysaccharide containing a small amount of nitrogenous material that cannot be removed by purification)	Emulsifier, stabilizer, thickener	Tree gum exudate
Carrageenan E407 (repeating galactose units and 3,6- anhydrogalactose, both sulfated and non-sulfated)	Gelling agent, thickener, stabilizer, emulsifier	Red seaweed
Curdlan (repeating glucose subunits joined by a β-linkage between the first and third carbons of the glucose ring)	Gelling agent	Microbial
Dextran (containing 95% of 1,6-linked and stabilizer units of α-D-anhydro-glucopyranose and 5% of 1,3-linked units)	Emulsifier and stabilizer	Microbial
Carboxymethyl cellulose	Thickener	Cellulose pulp
Chitosan (deacetylated chitin)	Gelling	Animal
Hydroxypropylcellulose E463 (cellulose treated with aqueous sodium hydroxide followed by propylene oxide undergoes an alkoxylation reaction)	Thickener and emulsifier	Produced from vegetative material
Methylcellulose E461	Thickener, emulsifier, and gelling agent	Vegetative material
Microcrystalline cellulose	Thickener and gelling agent	Vegetative material
Gelatin (derived from the parent protein collagen)	Gelling agent	Animal
Gellan gum E418 (primary structure is composed of a linear tetrasaccharide repeat unit)	Thickener, gelling agent, and stabilizer	Microbial
Ghatti gum	Thickener	Tree gum exudate
Guar gum (see LBG)	Thickener	Seeds
Karaya gum (complex, branched, partially acetylated polysaccharide, containing galacturonic acid and L-rhamnose residues as the main chains)	Thickener	Tree gum exudate
Konjac mannan E425 (main chain consists of D-glucose and D-mannose linked by β-D-1,4 bonds)	Gelling and thickening	Tubers
Locust bean gum (LBG) E410 (Linear 1,4 β-D-mannan chains with varying amounts of single D-galactose substituents linked to the main backbone)	Thickener	Seeds
Pectin E440 (high-molecular-weight heteropolymer containing mostly galacturonic acid units. The acid group may be free or as a simple salt or naturally esterified with methanol)	Gelling agent	Plants
Pectin (low methoxy)	Gelling agent	Plants
Processed euchema seaweed (E407a)	Gelling agent, thickener, stabilizer, emulsifier	Seaweed
Propylene glycol alginate (E405)	Emulsifier and foam stabilizer	From alginic acid
Starch (linear and branched glucose polymers)	Thickener and gelling agent	Plants
Starch (modified)	Thickener and gelling agent	From starch
Tara gum (E417) (see LBG)	Thickener	Seeds
Tamarind (linked D-glucan backbone partially substituted at the *O*-6 position)	Thickener and stabilizer	Seeds
Tragacanth E413 (highly branched, heterogeneous hydrophilic carbohydrate polymer. Methoxyl groups are also presented)	Thickener	Tree gum exudate
Xanthan gum E415 (a linear 1,4-linked, β-D-glucose backbone with a trisaccharide side chain on every other glucose at C-3)	Thickener	Microbial

bubbles, only 900 cm^{-3} after 2.5 h. As time elapsed, the amount of bubbles increased to about 2000 cm^{-3} after 24 h, or 2700 cm^{-3} after 36 h, depending on the carbonate concentration [9].

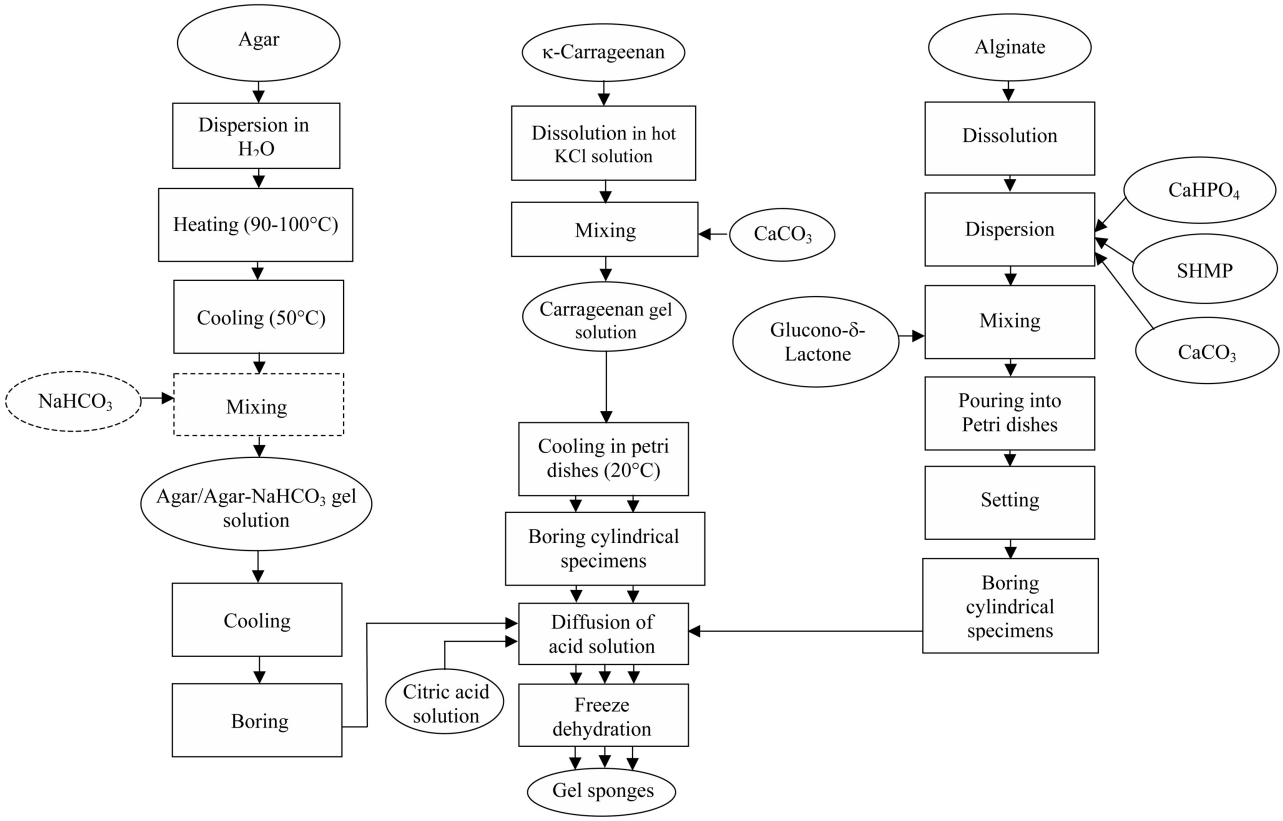

Figure 2. Production of sponges based on agar, carrageenan, and alginate.

The compressive strength and deformability of the gas-filled gels produced in this manner were determined using a universal testing machine (UTM) and then compared to those of pure gels, and gels that had not been subjected to the diffusion process but contained the same concentration of carbonate, after various times of immersion. While the agar and alginate retained considerable mechanical integrity, even after several hours, the carrageenan gels disintegrated after about 2 – 5 h [9]. Mechanically stable dry solid sponges are produced by drying the gels with or without internally produced gas bubbles. The sponges' characteristic compressive stress-strain curves can be described by the three-parameter model originally developed for polymeric sponges and baked goods (see below). Internally produced bubbles, formed by immersing biocarbonate-containing gels in an acid bath, resulted in a considerable loss of mechanical integrity in the dry agar sponges but not in those made of alginate [8].

2.2 Sponges produced by fermentation of immobilized yeast

A mixture is lightened through aeration, caused by a leavening agent. The leavening action can be triggered by physical, chemical, or biological means. In the food industry, commonly used leavening agents are air, steam, and CO_2 [10]. The method described above (gas-filled gel) calls for the presence of CO_2 in the gel prior to freeze-dehydration, resulting in a reaction between the acid component and the carbonate. The most obvious choice for CO_2 production in a gel is fermentation, in which the action of yeast enzymes converts sugars into alcohol and CO_2. Agar-yeast sponges are made by immobilizing yeast in agar gels and immersing them in a 5% sucrose solution for 3 or 7 days, followed by drying. The higher the initial concentration of the microorganisms in the gel, the more the resulting situation affects its integrity. During the slow fermentation process, CO_2 bubbles and ethyl alcohol are produced, lowering the gel's pH. The longer the fermentation time and the higher the yeast concentration, the less strong and stiff the gels [11]. After drying, such sponges were compressed and showed a characteristic sigmoidal curve, identical to the one observed in cellular solids, the curve being a manifestation of the three aforementioned deformation mechanisms. Electron microscopy revealed the apparent distribution of yeast cells inside the cell walls, as well as on their surface (Fig. 3). Agar-yeast sponges have properties resembling those of rice cakes, and they could be used as carriers of vitamins and minerals, thereby potentially serving as diet-

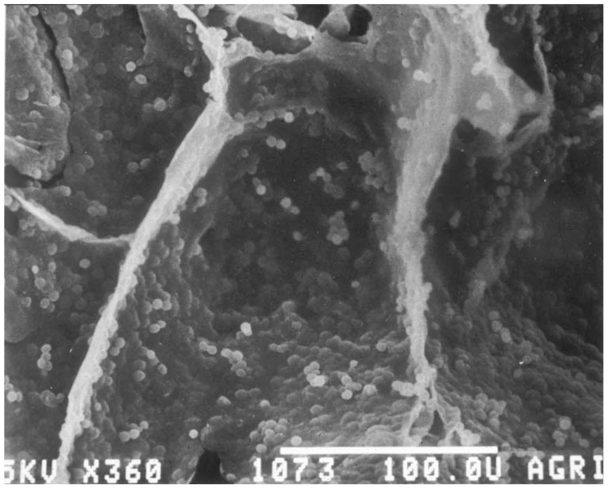

Figure 3. SEM-generated micrograph of a sponge containing yeast, both on the surface of the sponge walls and entrapped within them.

ary supplements. Considering the vitamin and mineral content of dry yeast, even without food additives this biological sponge could be a nutritious food source, with a unique structure and taste [11].

2.3 Sponges produced by drying gels containing oil emulsions

A lipid that is liquid at room temperature is called an 'oil', while one that is solid or semisolid under the same conditions is referred to as a 'fat'. Vegetable oils are distinguished by either the name of the vegetable from which they are derived or their commercial brand name. The most popular edible oils are soybean, canola, olive, corn, and peanut. Oils are used for frying and cooking due to their characteristic flavor, as well as in the manufacturing of many food products, such as commercial salad dressings [10]. However, a less-known use is the inclusion of emulsified oils in gels before setting. Image analysis of freeze-drying clearly shows the encapsulated oil droplets in various areas of the produced cellular solid. A Gaussian distribution of these areas was found with a maximum of 54% for the $(1-10) \times 10^{-12}$ m^2 area range. The properties of the resultant cellular solids depend on relative humidity and storage conditions [12].

Another study described the inclusion of oil within cold-set alginate gels. It was found that to change the properties of the sponges produced by drying them, a few parameters had to be considered: (i) the higher the oil content in the gel, the lower its stress at failure and its stiffness, as reflected in the deformability modulus; (ii) the higher the oil content, the more brittle the gel formed; (iii) the higher the oil content in the dried sponge, the smoother the curve representing its stress-strain relationships. Even with a high proportion of oil embedded and well-dispersed within the hydrocolloid matrix, sponge integrity was maintained. Thus sponges represent an alternative way of encapsulating oils; as such, they could potentially be used as carriers for vitamins, minerals and perhaps even colors, to serve, for example, as high-energy rations for the military [13].

2.4 Sponges produced by enzymatic activity

Sponges with a cellular structure were created by subjecting agar-starch gels to α-amylase activity prior to freeze-dehydration. A variety of starch concentrations (0.5–1.5%), enzyme concentrations (1000–1500 ppm) and exposure times changed the structure and mechanical properties of the hydrocolloid cellular solids produced. The influence of the duration of the enzymatic treatment on the cellular structure of freeze-dried 2% agar-1.5% starch gel specimens (sponges) was studied in depth. The enzyme solution (1500 ppm α-amylase) combined with the agar-1.5% starch gels was incubated at 55°C for 0, 24, and 72 h (Fig. 4). Initially, the enzyme began to decompose the substrate on the gel surface. Hydrolysis of the starch caused enlargement of the pores located on the gel's outer matrix, resulting in sponges with major structural changes. The longer the exposure to the enzyme, the larger the surface pores were, possibly contributing to a change in the sponges' mechanical properties. The effect of increasing enzyme concentration was only slightly detectable at the highest enzyme concentration (1500 ppm): the stress-strain curve was located only slightly lower than those of the control and 1000 ppm enzyme-containing sponges [14].

The influence of 1500 ppm α-amylase on agar gels containing 1.5% starch, at incubations of 0, 24, and 72 h, was examined: the longer the gel was immersed in the enzyme solution, the greater the possibility of starch decomposition and the higher the likelihood of forming a weaker sponge. In addition, the sponges became slightly more porous after 24 and 72 h of immersion (~0.93–0.96) than the sponges in the control group (~0.87–0.91). It should be noted that incubation at 55°C for 72 h led to a decrease in the sponge's mechanical properties. This was also observed by comparing the stress measured at a strain of ~0.2 at the shoulder with its equivalent measured in the control group. Starch degradation was established by HPLC analysis. For agar-1.5% starch, the gels were incubated without the presence of enzyme for 72 h at 55°C and only traces of glucose and raffinose were found. In comparison, when a 1500 ppm enzyme concentration was used to decompose the starch embedded in the agar gels, starch-degradation products such as glucose, raffinose, maltose, and maltotriose were found in the sample, along with other unidentified oligosac-

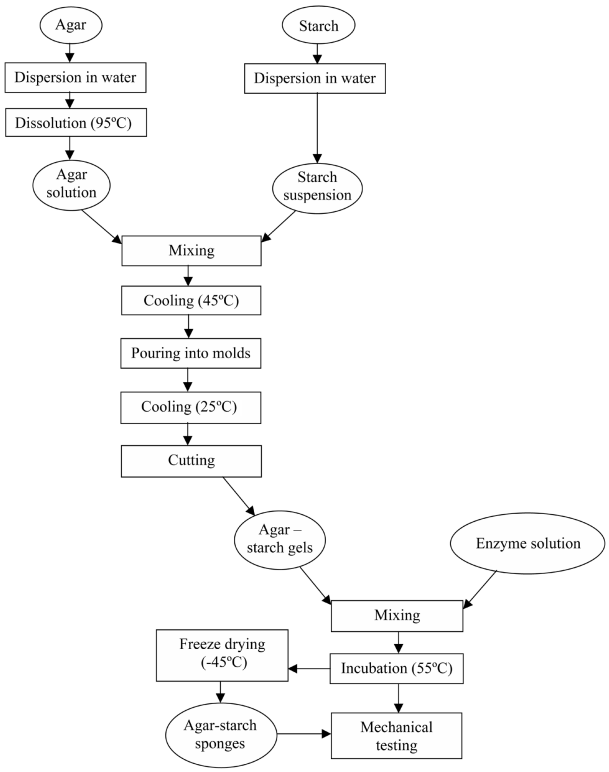

Figure 4. Flow chart for the production of agar-starch gels and sponges.

charides. It was concluded that the embedded starch can be used, in principle, as an ingredient slated for subsequent degradation. Such a process could influence, and possibly even control, the porosity and mechanical properties of the resultant sponge. In a further experiment, applying the same conditions (identical temperature, time, substrate, and enzyme concentrations), an enzyme solution decomposed a nonembedded starch solution with greater efficiency than its embedded counterpart; this was substantiated by a chromatograph of the degradation components [14].

Additional procedures used to manufacture hydrocolloid cellular solids include the entrapment of gas, produced or distributed, inside the gum solution, followed by gelation of the solution and drying. Substrates are broken down by a particular enzyme entrapped in the gel as part of its ingredients then, the gel is dried. It is important to note that the choice of drying method has an effect on the cellular solid's mechanical properties, structure and porosity [4].

2.5 Porosity control in cellular edible sponges

The single most significant structural characteristic of a cellular solid is its relative density (ρ^*/ρ_s), *i.e.*, the density, ρ^*, of the foam divided by that of the solid from which it is made, ρ_s. The porosity, or the fraction of pore space in the solid foam is calculated using $[1-(\rho^*/\rho_s)]$. Controlling the porosity enables production of the desired mechanical and structural properties, as well as extended stability. The porosity of starchy products depends on their moisture content and the way in which they are produced. Porosities of 0.06 and 0.27 have been calculated for regular and puffed pasta, respectively [15]. White bread and butter cookies have porosities of 0.90 and 0.55, respectively [16]. The distribution of pore size and the porosity in general have a major influence on diffusion efficiency [16, 17]. Accordingly, porosity control serves as a fundamental parameter with respect to diffusion processes and permeability [18].

Alginate gels were immersed in sucrose solutions of 10–60° Bx to attain a wider variety of porosities in the resulting hydrocolloid cellular solids. After drying, gel porosity decreased from 0.85 to 0.42 and 0.07 after immersion in the 30 and 60°Bx solutions for 183 and 158 h, respectively. Similarly, after immersing gels containing 5% soy oil in addition to the other components, the porosity decreased to 0.36 and 0.04 after 165 and 158 h, in 30 and 60°Bx solutions, respectively. Preparation and formulation play important roles in determining porosity and can both be utilized to control porosity values in the range of 0.85 – 0.04. Scanning electron microscopy (SEM) micrographs revealed changes in the novel cellular solid, originally characterized by numerous large void spaces, and now exhibiting a denser and more uniform appearance, after immersion in a 60°Bx sucrose solution. The dry gel system described above, combined with porosity control, offers a novel tool for the creation of tailor-made cellular solid food items [19].

Structural characterization of a cellular solid, such as a slice of bread (Fig. 1), is a significant factor in that solid's mass production given that customer acceptance and willingness to purchase highly depend on its visual appearance and 'bite texture' [20]. These equivalent concepts have wide application in science since they can be used to define and characterize the structure of porous edible and nonedible bodies and materials such as ceramics, bone, and natural hydrocolloid cellular solids. Kaye [20] suggests using a mathematical procedure to model the fractal structure of porous systems, namely, the Sierpinski carpet. (The Sierpinski carpet is named after the Polish mathematician Waclaw Sierpinski (1882 – 1969) who taught mathematics in Warsaw. The carpet consists of the withering (elimination) of portions of a surface *via* a process of geometrical removal.) However, ideal Sierpinski fractal carpets are symmetrically structured, whereas natural systems do not necessarily behave that way. It was therefore concluded that in the case of fractal boundaries, many porous bodies are statistically self-similar versions of an ideal Sierpinski carpet [20].

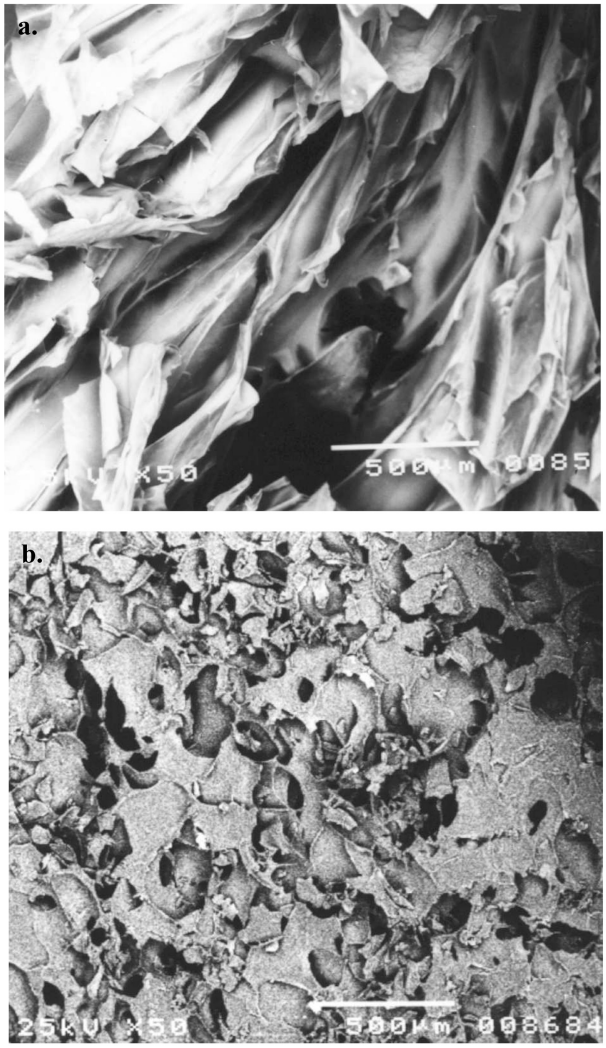

Figure 5. SEM-generated micrographs of agar-orange concentrate-based cellular solids. (a) No concentrate included; (b) 25% concentrate (courtesy of M. Gililov).

Another approach was exemplified in a study of freeze-dried texturized fruit prepared by freeze-drying gels made of fruit concentrate or puree. The resultant cellular solids were dry and crunchy, with a high fruit content (Fig. 5). Dried texturized fruit products can be characterized by their porosity and internal pore-size distribution, among other parameters. One of the objectives of this study was to examine the possibility of assessing the porosity of diverse edible products by modifying a technique first suggested by the Czech scientist Korcak, ~65 years ago, and used by him in the fields of geography and cartography. In 1938, Korcak declared that all the islands of the world can be described using a single numerical relationship. It was of interest to see whether this procedure would be suitable for describing the size distribution of pores in a certain section of a dried texturized fruit or other cellular solid. It was hypothesized that instead of dealing with 'pieces' of land (islands or in this case archipelagos) suspended in great bodies of water such as seas and oceans, as is done in cartography, it might be possible to invert the picture: the "holes" or "pores" are regarded as suspended in a solid matrix, thus developing a new way of estimating porosity. The other goal of this research was to test the calculated fractal index for sensitivity to certain conditions used in food processing. It was observed that the average fractal dimension of the circumscribing silhouette of the pores was about twice the measure of the size distribution of a set of pores as estimated by Mandelbroth when dealing with randomly selected, sufficiently large pores in the freeze-dried texturized fruit. It is important to note that fractal dimensions were introduced to the English-speaking scientific community in 1977 by Benoit Mandelbroth, their inventor, in a book entitled *"Fractals: Form, Chance, and Dimensions."* The fractal dimension of the pore "coastline" was a property of the individual pores, whereas the fractal index deduced from the Korcak plot was a property of the group of pores. The measure of cell distribution according to size was also found to be related to the porosity of the texturized fruit. The suggested approach can be used to identify general changes in the porosity of a cellular solid, regardless of its origin or whether it is edible or not, and it can serve as a simple tool to judge product development [21].

2.6 Conclusions

Many different hydrocolloids can be used for the preparation of cellular solids. Gelling agents are preferable, since gel production and drying is all that is needed to prepare sponges. However, foamed, thickened gum solutions that can pass through the drying stage can also successfully serve as a source for the production of such moieties. The properties of the final sponge product can be modified during the production stage. For example, to manipulate sponge porosity, gas bubbles from different sources can be trapped (included) within the gel prior to its drying. The gel can also include fillers, oils, or substrates that can be enzymatically decomposed, in order to tailor its mechanical responses, taste, ingredient diffusion into its matrix and slow-release properties to a particular application (see Section 4.7).

3 Description of stress-strain behavior of hydrocolloid cellular solids and multilayered products using models

Cellular solids are highly compressible materials. Their cross-sectional area remains nearly unaffected, even after compression or substantial deformation. Thus, an engineer-

ing stress-strain relationship can legitimately be used. The engineering stress, σ_E, and strain, ε_E, are defined as:

$$\sigma_E = F/A_0 \quad (1)$$

$$\varepsilon_E = \Delta H/H_0 \quad (2)$$

where F is the force, A_0 and H_0 are the specimen's initial area and height, respectively, and ΔH is the absolute deformation. Figure 6 illustrates a typical stress-strain curve for a compressed cellular material, containing three regions. The first region is linear-elastic, the second is seen as a plateau with a roughly constant stress leading to the third and final region, where there is a steep increase in stress. Each region can be associated with an exact deformation mechanism. When a specimen is loaded, the cell walls bend, giving way to linear-elastic behavior if the cell wall is made of a linear-elastic material. When the critical stress is reached, the cells begin to collapse. Eventually, at high strains, this sort of collapse is all it takes for opposing cell walls to touch or for their broken fragments to pack together. Further deformation compresses the cell-wall material itself; this causes the final, steeply rising segment of the stress-strain curve, and has come to be known as densification [4]. The typical sigmoidal shape of the curve is maintained when the strain is presented as Hencky's (natural) strain:

$$\varepsilon_H = \ln [H_0/(H_0 - \Delta H)] \quad (3)$$

This is an indication of the true compressibility of the cellular solid [3].

An array of empirical mathematical models can be used to portray the compressive stress-strain curve up to about 80% deformation [22]:

$$\sigma(\varepsilon) = C_1\varepsilon/[(1 + C_2\varepsilon)(C_3 - \varepsilon)] \quad (4)$$

and

$$\sigma(\varepsilon) = C_1/[\varepsilon/(C_3 - \varepsilon)]^{C_2} \quad (5)$$

$$\sigma(\varepsilon) = -(1/C_1)\ln [1 - (\varepsilon/(C_3)^{C_2}] \quad (6)$$

and

$$\sigma(\varepsilon) = C_1\varepsilon^{C_2} + C_3\varepsilon^{C_4}(C_2<1, C_4>1) \quad (7)$$

where *Cs* represent the constants. When calculated, these constants can stand for a quantitative comparison factor between curves of different solid foams, as well as between those from the same material subjected to repeated compression-decompression cycles [22]. They can also serve as a means of calculating the compressibility pattern of

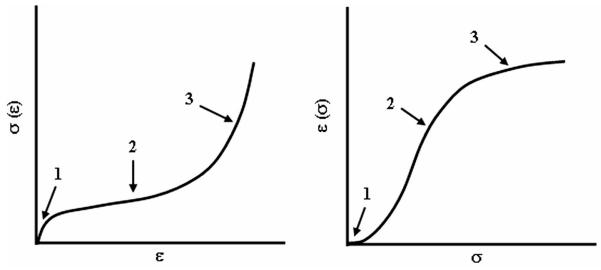

Figure 6. Schematic representation of the typical compressive stress-strain relationships found in sponges. 1. Deformation of the original matrix; 2. densification; 3. compaction of the collapsed cell-wall material.

layered collections of sponges [23–25]. Constants are subject to change in parallel to processing. They supply a sensitive tool for studying the effects of drying, storage, heating, and humidification on the texture of the spongy product.

An easy technique to generate the appearance of different textures and tastes in the same bite of food is to create a multilayered product. When an array of different cellular materials are layered and then flattened, each with its own distinct thickness, then compressed uniaxially, the cross-sectional area, which is the same for each individual layer, can be assumed to be virtually unchanged [3]. The applied stress is considered to be the same in all the layers and the total deformation is represented as the sum of the deformations detected in each layer [5].

$$\sigma_{total} = \sigma_i \quad (8)$$

where σ_{total} is the array's stress and σ_i is the stress in an individual layer, represented by the variable *i*.

$$\varepsilon_{total} = (1/Ho_{total})\sum Ho_i\, \varepsilon i(\sigma) \quad (9)$$

where ε_{total} is the array's strain, Ho_i is the thickness of each individual layer *i*, and εi is the strain found in each layer as a function of the stress. The array's initial overall thickness is the sum of that of the individual layers, *i. e.*,

$$Ho_{total} = \sum Ho_i \quad (10)$$

Equations (3) and (4) are simple to apply since they can be used to express the strain as an explicit algebraic function of the stress $\varepsilon(\sigma)$. Inserting the terms $\varepsilon i(\sigma)$ and the corresponding Ho_i into Eq. (7) allows a calculation of the stress-strain relationships of any layered array of sponges, as long as the assumption of same cross-sectional area remains basically valid. Equations (4)–(6) call for a determination of their constants by nonlinear regression. This requires the use of close guesses as initial values. This need can be avoided if Eq. (7), or a polynomial model, is used in the cal-

culation [3]. Finding initial values that are close enough for use and will give the proper results is fairly easy, since we know that $C_2 < 1$, and $C_4 > 1$.

Constants of a polynomial model, such as:

$$\sigma(\varepsilon) = C_1\varepsilon + C_2\varepsilon^2 + C_3\varepsilon^3 + C_4\varepsilon^4 \quad (11)$$

can be determined by a generalized linear regression computer program with no need for any guesswork at all [3]. Once all the $\sigma_i(\varepsilon)$ values are expressed in terms of the model under discussion, and the Ho_i values are known, the stress-strain relationships of that array can be numerically calculated using any type of standard equation-solving software.

In conclusion, the mechanical properties of cellular solids are important in terms of: (i) the stability required from these products for use in foods (see Section 4.1) or as carriers of food ingredients (see Section 4.2), (ii) their influence on the acoustic response of edible products (see Section 4.3), (iii) the stability required for multilayered food products (see Section 4.4), and (iv) the endurance required from these products in continuous operations, such as water and waste-material treatment (see Section 4.5) and biological control of pests (see Section 4.6). Here, we chose to concentrate on empirical mathematical models, since they are beneficial in portraying the stress-strain curve over its deformation to about 80%.

4 Simple and complex applications of cellular solids

4.1 Dried texturized fruits

Hydrocolloid cellular solids have many applications, one of which is in the creation of dried texturized fruits, used as vitamin carriers or as a crunchy addition to confections. These novel structured fruit products are most commonly made from pulp or fruit puree. A wide range of hydrocolloid gels and other additives have been the subject of a number of patents and commercial applications of texturized fruit [26–29].

Dried hydrocolloid cellular solids were composed of a variety of hydrocolloids, such as agar, agarose, and gellan, with or without the inclusion of orange concentrate or banana puree. The fruit content in the formed gels before drying ranged between 0 and 25%. The inclusion of fruit pulp influenced the density of the resultant cellular solids: the higher the fruit content, the higher the density of the solid. The bulk density of a cellular solid composed solely of agar was 0.029 g · cm^{-3}. After the inclusion of 25% orange concentrate, the density rose to 0.214 g · cm^{-3}. However, when the same amount of banana puree was added instead, the density of the cellular solid rose to only 0.106 g · cm^{-3}. A major increase in ΔE^*, a parameter representing color differences, was noted when the content of fruit pulp was less than 15%. In contrast, no major difference in ΔE^* was found when the fruit pulp content exceeded 15%. The type of hydrocolloid used in the manufacture of the cellular solids did not affect their color at all. After inclusion of the fruit pulp, the cellular solids were denser, had smaller pores and a more homogeneous structure (Fig. 5).

At the same time, an increase in fruit-pulp content led to an increase in the number of pores with smaller area, whereas the number of pores with larger area decreased. There were no significant differences between the number of medium-sized and large pores following the different treatments. Generally, pore number was higher after the inclusion of orange concentrate than after that of banana puree. The dried texturized fruits were compressed to ~90% deformation: the higher the content of the fruit pulp, the higher the final product's mechanical strength. The cellular solid was found to be harder, and it densified at a lower strain than before (no fruit inclusion). The inclusion of orange concentrate had a more extensive influence on the strength of the cellular solid than the inclusion of banana puree. These conclusions were validated in sensory-evaluation tests demonstrating that a cellular solid prepared only from agar and containing 10% orange concentrate is simply harder than the cellular solid produced from the same ingredients under the same conditions, without the inclusion of pulp. Different amounts of calcium were added to the dry texturized fruits. An increase in the amount of added calcium produced a cellular solid with a denser structure and smaller pores. The addition of calcium caused the cellular solids to become less brittle, and had a negative affect on their sensory characteristics [30].

In conclusion, the possibility of including a very high proportion of fruit pulp in such products could help minimize the percentage of fruit that are not harvested in order to keep market prices at a level that is beneficial to both growers and sellers.

4.2 Vitamin carriers

Vitamins can be defined as organic substances, vital to the normal functioning of the body when consumed in diminutive amounts. Vitamins usually find their way to our body from food; some are produced by the body itself and others can be consumed in the form of a synthetically manufactured food supplement. Vitamins and minerals are known as micronutrients. The addition of synthetically produced vitamins to food products such as milk, margarine, bread,

and cereal, in order to improve their nutritional value, is now widely accepted in many places worldwide [10, 31].

Bread, as well as other baked goods [32], being regarded as edible cellular solids, have the potential to be used as vitamin carriers. Results from a study on the fortification of bread described the addition of vitamin E as a nutrient and antioxidant in the form of DL-α-tocopheryl acetate at 200, 400, 800, or 1600 IU/lb of bread. (Tocopherol was the name given to the vitamin E-containing isolate of wheatgerm oil. D-α-Tocopheryl is the most highly biologically active of all the forms: of the eight tocopherols, D-α-tocopheryl accounts for 80% of the vitamin's activity. DL-α-Tocopheryl is the name given to synthetic derivatives which are composed of equal amounts of all the stereoisomers.) The control product had no added vitamin E. The bread was prepared using the standard sponge-and-dough procedure [33]. The stability of the vitamin in the freshly baked bread was evaluated and later, it was compared to the data collected from stored breads. Dough characteristics, baking quality, and bread sensory properties (grain, texture, crumb body, crumb color, taste/aroma, and mouthfeel) were monitored as well. The results indicated that DL-α-tocopheryl acetate could be added to breads at relatively high levels without no undesirable effect on quality; regardless of the concentration applied. Approx. 33% of the supplement was lost during baking; however, no further loss occurred during the typical shelf-life of the bread [33]. Because the importance of this type of addition to breads and other baked goods is on the rise, special methods need to be established for accurate vitamin determinations [34, 35]. One study showed a 15% decrease in native folate content in dough from the sponge stage to the proofed stage, and another 20% decrease from the proofed dough to the finished bread. (Folate is one of the B vitamins, essential for the formation of red and white blood cells in bone marrow. The best way to make sure you get enough folate is to take a folic-acid supplement or eat folic-acid-fortified foods, such as soft-grain breads and breakfast cereals.) The collected data indicated good relative stability of added folic acid and native folates when added to the baking process; the additions also helped increase endogenous folate contents in the dough and the finished bread when compared with the flour they were made from [34].

Since sponges are basically dried-gel products, they are ideal carriers, simply due to the ease of inclusion of various vitamins. Cold-set 1% alginate gels containing vitamin A were produced. All the gels were either freeze-dried and kept over silica gel to avoid rehydration prior to testing, or packed in laminate before any clinical testing was performed. After the gelation process was complete, the gels were freeze-dried, forming a crunchy, chewable, cellular solid specifically designed to package the vitamin A in it. It is important to note that vitamin A was chosen for this study since it is an essential micronutrient that plays a major role in growth, epithelial maintenance, vision and reproduction in humans [36]. Moreover, vitamin A deficiency is a well-known, widespread problem, primarily affecting developing countries. Eighty children from a rural area in northern Ethiopia were fed edible, fortified hydrocolloid sponges carrying 4000 IU of vitamin A, over the course of 3 months. As a result of the addition of this supplement, vitamin A levels increased significantly following regular intake of the edible cellular solid, providing proof of its effectiveness as a vitamin A carrier for children. Due to its lack of flavor, odor and color, these characteristics can be added later and controlled, ensuring broad acceptance by the target subjects [37].

Hydrocolloid cellular solids can be used not only as vitamin carriers, but for any food ingredient that is soluble in water or oil, and can be blended into a gum solution before its setting and gellification or foaming, prior to drying.

4.3 Designing acoustic responses in hydrocolloid cellular solids

Crunchy foods emit noise during their mastication. Acoustic aspects of foods have been studied since the 1960s [38, 39]. These studies focused mainly on the properties of the acoustic signature and on its relationship with the perceived textural attributes [40 – 44], as well as on the development and use of instruments to record signals and build mathematical models for analytical studies [45 – 48]. Further work discussed the effect of moisture content on the intensity of the noise emitted during the chewing process [49], characterized the acoustic signatures of selected food items [50], and even dicussed the apparent fractal dimension of sound bursts in the acoustic signature of certain crunchy foods [51].

Available information sources on the acoustic signatures of hydrocolloid cellular solids are limited. The moieties tested in one such analysis were freeze-dried gels, some with and some without the addition of sucrose or starch. Agar, κ-carrageenan and gellan gels (2%), with and without infused sucrose (5, 10, and 12.5%), were freeze-dried, and the mechanical and acoustic signatures of the resultant solid sponges were recorded. The presence of sugar or starch in the dried gels increased their density in ways that could not have been foreseen from the corresponding stoichiometric relations between the gum and additives. This indicated that the sugar, or starch, were not inert fillers. In general, the presence of sucrose in the gels' solid matrix increased the brittleness of the sponges, and the addition of sucrose or starch altered the acoustic properties of the produced cellular solids (Figs. 7, 8).

Figure 7. Device used for the compression of cellular solids and for an acoustic recording of their response (courtesy of N. Jaffe).

The effect of the sucrose or starch addition can be quantified in terms of the increase in the mechanical signature's apparent fractal dimension [52–54]. The more brittle sponges had a "richer" acoustic signature and required the use of a "blanket" algorithm to determine their apparent fractal dimension. (An automated fractal analysis technique particularly appropriate to jagged lines and surfaces is the 'blanket algorithm'. The essence of this technique is that the digitized image or waveform is progressively covered by a 'blanket', the thickness of which at any point is proportional to the difference in height between that point and the one immediately preceding it. Effectively, large blanket thicknesses are initially applied to rugged images in which substantial differences exist between adjacent points, but the blanket thickness decreases with subsequent iterations as the coated image is progressively smoothed.) A clear correspondence can be found between the jaggedness of the mechanical signature of the product and its acoustic signature. The conclusion drawn from these findings was that the more brittle the samples, distinguished from the others as such by the apparent fractal dimension of their stress-strain relationship, the more 'noisy' their acoustic signature. This suggests that the same fracture events that are noticeable in force deformation during a specimen's compression are responsible for the characteristic sound emission that people associate with a sense of 'crunchiness' in a food item [52]. This also strengthens the concept defining the perception of 'crunchiness' or 'crispiness' as the simultaneous response to the mechanical and acoustic stimuli [40].

Another study discusses the effects of starch, sucrose and their combination in different concentrations on the mechanical and acoustic properties of freeze-dried alginate gels [53]. In this study, alginate gels (2%), with or without starch and/or sucrose incorporation, were freeze-dehydrated to produce an array of cellular sponges. The stress-strain relationships observed in these dried gels were irregular and jagged, typically associated with the more brittle cellular solids. The presence of starch in the dried solid matrix did indeed increase the stiffness of the sponges. In contrast, sucrose had the opposite effect, suggesting that its presence in the matrix may interfere with the mechanical integrity of the dried gel. All the dried gels produced a 'rich' acoustic signature upon compression, in agreement with the estimation made by judging the magnitude of their apparent fractal dimension, determined by the 'blanket' algorithm. If there were any differences between the dried gels' acoustic signatures, they were too faint to be detected by the apparent fractal dimension alone, and they were therefore not taken into account in the results [53].

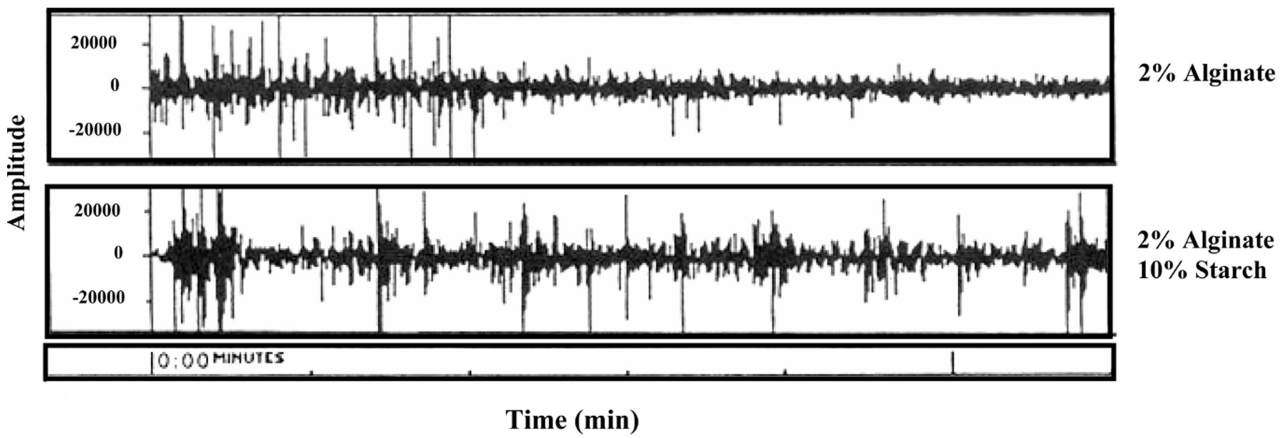

Figure 8. Typical acoustic response of a cellular solid: alginate-based product (top) and alginate-starch-based product (bottom).

4.4 Multilayered hydrocolloid cellular solids and related composite materials

A simple method of generating the appearance of different textures and tastes in the same bite is the use of layers. A few multilayered items are available to the public and they are no longer an unusual sight at the local supermarket. Crunchy wafers, for instance, are a multilayered, sweetened confection for children. These wafers often consist of a sweet vegetable-fat-based chocolate- or vanilla-taste filling between layers of brittle wafers [5]. The characteristic sigmoid compressive stress-strain relationships of sponges and their layered arrays are illustrated *via* two kinds of mathematical models, utilizing three parameters (see Eq. 5–7). Since compression does not result in any significant expansion of the sponge's cross-sectional area, it can be assumed that the stress in a multi layered array is equal in all layers of the product. This enables a prediction of the array's stress-strain relationships based on the parameters of the individual layers and their known thicknesses. Consequently, when the subject is an array consisting of only two sponge layers, the compressive behavior can be calculated using the following equation:

$$\varepsilon_E(\sigma) = \frac{H_{01}\varepsilon_{E1}(\sigma) + H_{02}\varepsilon_{E2}(\sigma)}{H_{01} + H_{02}} \quad (12)$$

where subscripts 1 and 2 are interchangeable, referring to the top and bottom layers, accordingly. ε_{Ei} is the strain of each individual layer and H_{oi} (i = 1, 2 ...) is the thickness of each layer. The array's compressive behavior can be predicted in a satisfactory manner, irrespective of the mathematical form of the model and of whether the strain is expressed in the form of engineering or Hencky's strain [55].

Composite materials are made up of two or more components, each of which is manufactured from a different material. Each individual component can be considered as the matrix or particulate part of the system. Water-soluble polymer beads embedded within a hydrocolloid cellular solid complex are an example of a particulate composite system. Testing included two model systems, the first built from an agar matrix (2%) with embedded alginate beads, the second from a carrageenan matrix (3%) with entrapped chitosan beads. A variety of quantities, sizes and concentrations of the beads embedded in the matrices were used in order to study their influence on the physical properties of the composite systems and to determine their ability to control these properties (Fig. 9).

The maximum percentages of beads introduced into the matrices throughout this research were 80% in the agar-alginate system and 60% in the carrageenan-chitosan system. The higher the percentage of beads in the matrix, the stronger the resulting dry composite material. In addition, it

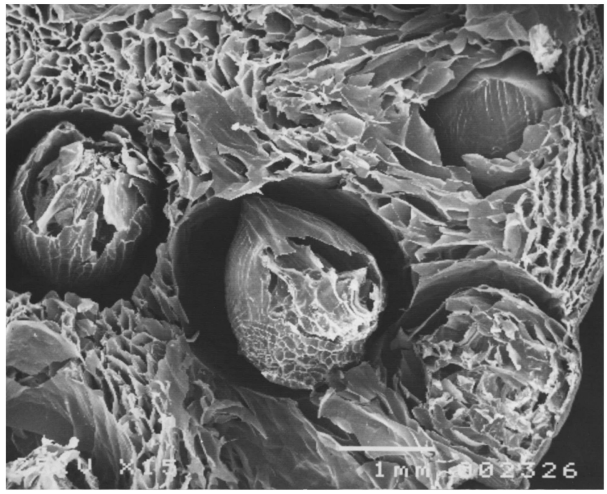

Figure 9. SEM-generated micrograph of a dry hydrogel matrix, showing hydrocolloid beads embedded within its structure (courtesy of Y. Ungar).

was found that the higher the proportion of beads in the dried matrix, the more influence they have on the mechanical properties of the composite. When the diameter of the bead was increased from 2 to 5 mm while keeping the percentage of beads in the matrix at a constant 20, it was found that the composite sponge systems were, in fact, strengthened by the addition of these larger beads. Increasing the gum concentration from 1 to 2% strengthened the resultant cellular solid system. The inclusion of beads in the matrix also afforded control of the porosities of the new cellular composite. The type of matrix, bead quantity and size and the interaction between the two components are what characterized the resulting physical properties. These types of composite systems have the potential to be used in slow release, as immobilization and packing materials, or in the production of composite dry foods with novel textures [56].

When building such composite cellular hydrocolloid matrices, the dependence of the modulus on the composite system can be portrayed by a simple mathematical model. It is important to note that this model can be fitted to a more rigid system, that is, a system containing rigid particles in a rigid matrix.

$$Ec = x(E_p\phi_p + E_m\phi_m) + (1-x)(E_pE_m)/(E_p\phi_m + E_m\phi_p) \quad (13)$$

E and ϕ in the equation represent the modulus and volume fraction of particle p and matrix m, respectively. In the sponge specimen, there was no apparent interaction between the particles and the matrix. As a result, x = 0, changing the expression so that it can be rewritten as:

$$Ec = (E_pE_m)/(E_p\phi_m + E_m\phi_p) \quad (14)$$

4.5 Water treatment

Water treatment can be defined as the use of chemicals or techniques to improve water quality for human consumption or industrial applications. Sponges, hydrocolloid-based and others, are often used as matrices for the immobilization of microbial cells in water-purification processes. Free and immobilized microalgal cells of *Chlorella sorokiniana*, for example, were immobilized using a biostructural matrix of *Luffa cylindrica* for the purpose of sequestering cadmium from a contaminated aqueous medium [57]. The same vegetative sponge was used as the matrix in ferrous iron removal from strongly acidic industrial wastewater [58].

4.5.1 Wastewater from olive-oil mills

Olive-oil mill wastewater (OMW) was remediated biologically by using polyurethane sponges to immobilize *Aspergillus niger* cells, leaving the water significantly less toxic. The results proved that the addition of rock phosphate and ammonium sulfate has a positive effect on the growth of the immobilized mycelium and its degradation of OMW phenols [59]. Polyurethane foam sponge media were examined to verify their ability to control filamentous bulking in a sequencing batch-reactor process. A microscopic study performed under these conditions revealed that the sponge media were capable of cutting or even breaking the biomass up into shorter filaments and smaller flocs, mitigating the severe bulking condition. More aerobic conditions in the flocs were only some of the indirect effects derived from the physical breakdown of the biomass. As expected, favorable conditions were created for the suppression of filamentous bulking [60].

4.5.2 Nitrate removal

Nitrate contaminants in the environment are rapidly becoming of international concern. Wastewater from the food and agricultural industries may be a major source, causing the sudden increase in prevalence of this phenomenon. Bacterial denitrification is the most common method used to get rid of biological nitrate. Alginate beads containing a denitrifying isolate and starch were freeze-dried before incubation under denitrifying conditions. The physical properties and denitrification abilities of the complex were compared to those of untreated alginate beads. Dried alginate beads were found to possess physical properties similar to those of porous, sponge-like matrices. A comparison to conventionally prepared alginate beads showed a considerable reduction in the physical damage incurred by gas accumulation under denitrifying conditions with the freeze-dried beads. Those beads, in turn, were stronger and more capable of sustaining the denitrification activity over prolonged periods of time, relative to regular beads [61]. Freeze-dried beads containing 40% granular starch were shown to have better mechanical and denitrifying properties than beads containing lower concentrations of starch [62].

4.6 Biological control

Biological control is characterized as the reduction in activity and viability of a pathogen as a result of another organism's activity. The importance of biological control lies in its potential to reduce crop losses and to alleviate environmental damage caused by the excessive use of pesticides over time. The major problem with biological control is its nonreproducibility under field conditions. All formulations aimed at providing control of the immobilization of bacteria or spores, such as peat, coal, clay, compost, and polyacrylamide or alginate nondried gels, have been found inefficient [63]. The improved viability of Gram-negative bacteria through freeze-dehydration, storage, and soil inoculation is of crucial significance to the efficiency of their application. Entrapping 10^9 cells per alginate bead produced from a solution containing 30% glycerol and 1% chitin showed significant improvement in survival prospects (95%) during freeze-drying, relative to other studies. Furthermore, immobilization of the bacterium improved its survival in nonsterile irrigated and dry soils relative to bacteria placed in a water suspension. The results suggested that optimal conservation of Gram-negative bacteria in alginate-based cellular solids is not only possible but applicable to a wide range of practices [64].

Freeze-dried alginate sponge carriers can also be used as packaging materials and as protectors of spores and bacteria against UVC (254 nm UV radiation), as well as improving the antifungal activity of biocontrol agents [65]. Microorganisms found in the soil in general, biocontrol agents in particular, are extremely sensitive to UV light. Methods of packaging biocontrol microorganisms in cellular solids for convenience of use have been further developed to reduce loss by exposure to UV radiation from the environment. The bacterial and fungal biocontrol agents *Pantoea agglomerans* and *Trichoderma harzianum* were immobilized in freeze-dried alginate beads (Fig. 10) and later subjected to UVC radiation. Cells immobilized in freeze-dried alginate-glycerol beads showed an even greater rate of survival after exposure to UV irradiation. Adding chitin, bentonite or kaolin as fillers to the alginate-glycerol combination further increased bacterial survival significantly [65], with the alginate-glycerol-kaolin beads conferring the highest levels of survival. The level of protection provided by the cell carrier was influenced mainly by the transmissive properties of the dried hydrocolloid cellular solids from which it was made. The control group, consisting of a dried alginate matrix, transmitted an average of 7.2% of the radiation. Incorporation of a filler in the matrix drastically reduced UV trans-

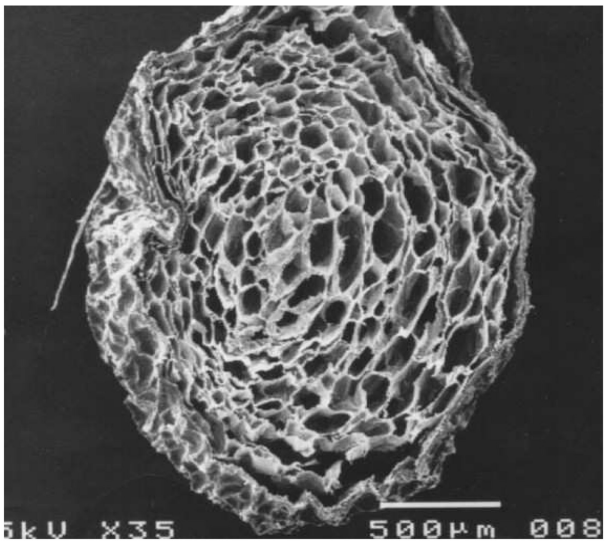

Figure 10. Dried gum beads revealing physical properties similar to those of porous, sponge-like matrices. Dried beads can be used in the building of cellular composite materials. When immobilized microorganisms are included in them, they can be used for biological control, water treatment and other environmental purposes (courtesy of C. Zohar-Perez).

mission. Alginate-kaolin, -bentonite, or -chitin combinations transmitted an average of 0.15, 0.38, and 3.4% of the radiation, respectively. The inclusion of a filler had a considerable effect on the bead's average wall thickness as well, resulting in a 1.5- to 3-fold increase as compared to beads solely based on alginate [66]. The results led to the conclusion that the degree of protection of entrapped microorganisms against UVC radiation is determined by the cellular solid's structure, as well as by the UV-transmission properties of the dried matrix. It was also observed that in order to achieve the maximum protection against UV-radiation-induced cell loss, biocontrol microorganisms need to be immobilized in alginate-glycerol beads containing kaolin [65].

4.7 Hydrocolloid sponges for drug delivery

Over the past couple of decades, the area of drug delivery systems using controlled release has seen considerable progress. An important role in the development of such systems has been played by hydrogels [67, 68]. A substance is considered a hydrogel when the material is already swollen in water. The water can be easily removed through freeze-drying (lyophilization) or, in some cases, by extraction using organic solvents. The water is removed with only the slightest disturbance to the polymer network. The dehydrated hydrogel is exceptionally light and has high porosity. These substances are called aerogels or sponges [69, 70]. Such materials have lower thermal conductivities and are capable of absorbing at least 10 – 20% their weight in water [71].

Because of their bulk and surface properties, hydrogels have been extensively researched; as a result of their various potential uses in pharmaceutical, agricultural, biomedical, and consumer-oriented applications, their development is expected to progress rapidly. Most research performed on biodegradable drug delivery has engaged the use of polymers that are insoluble in water. Biodegradable hydrogels should, therefore, be applicable in the development of new and improved drug-delivery systems [67]. Freeze-dried sponges made of sodium alginate and chitosan are an interesting example, since they hold great potential for wound dressings/bandages or even matrices for use in tissue engineering. In this case, the sponge preparation would involve the dissolution of both polymers, either individually or in combination, in 1% acetic acid, followed by freeze-drying of the corresponding solutions [72]. The dissolution of the model drug paracetamol was assessed and is believed to be a function of polysaccharide composition. Systems composed of chitosan alone showed the slowest release profile, whereas mixed systems displayed a relatively rapid dissolution profile. The combined use of chitosan and alginate appeared to be a crucial factor in allowing the formulator to manipulate both mechanical and drug-release properties of the sponges [72].

Sponges destined to be used in bone generation involved the inclusion of chitosan in their preparation: porous sponges made of radiolabeled becaplermin (platelet-derived growth factor BB), containing chitosan and chondroitin sulfate A (chondroitin 4-sulfate), were prepared for use in bone generation. *In vitro* release of becaplermin from the sponges could be controlled by having a variety of initial drug loadings and changing the concentration of chondroitin sulfate A. The becaplermin sponges enhanced osteoblast migration and proliferation [73]. Chitosan-gelatin sponges were also used to control drug delivery using ionic and nonionic plasticizers in order to facilitate foaming of polymer solutions and softening of the sponges produced from low-viscosity chitosan [74]. Chitosan sponges prepared using partial *N*-acetylation or cross-linking were evaluated as sustained-release drug carriers using triamcinolone acetonide as the model drug. The drug content was found to be uniform in both types of chitosan sponges. The incorporated drug was in a crystalline form. Both chitosan sponges had water uptake abilities that amounted to more than 20 times their weight. The pH of the dissolution media and drug content of the sponges had an effect on the drug-release rate. The release rate at pH 1.2 was faster than at pH 7.4. The drug release at pH 7.4 was a function of the square root of time over 52 h from sponges prepared by *N*-acetylation and over 36 h from cross-linked sponges. Slower release times were seen as the drug content

increased. The appearance of delayed drug release was due to a decrease in poliglusam solubility by *N*-acetylation or cross-linking [75].

Alginate gel formation in the presence of calcium ions, as well as other cross-linking agents, with poly-L-lysine formed sponge-like nano- and microparticles. Variation in particle size was controlled by adjusting the final concentrations and proportions of the components. Particles formed in the region located between 0.04 and 0.08% w/v alginate. In the case of the final formulation, the change from the nanometer to the picometer size range took place at a concentration of approx. 0.055% w/v. Oligonucleotide-loaded microparticles were prepared using two different methods: absorption of the drug through the cross-linked polymeric matrix or incorporation of an oligonucleotide/poly-L-lysine complex in a calcium alginate pre-gel [76]. The release of oligonucleotide from microparticles made by absorption of the drug in the cross-linked polymeric matrix was higher. Increasing the amounts of poly-L-lysine used in each trial resulted in larger particles, higher oligonucleotide loads and an overall slower drug release. An increase in the final solid content found in the formulation caused the appearance of larger particles, with an especially high concentration of calcium alginate pre-gels. Microparticles produced from alginate and poly-L-lysine have the potential of becoming carriers for antisense oligonucleotides [76].

Another review discusses some of the more recent developments and applications of collagen as a biomaterial used in drug-delivery systems carrying antibiotics, specifically gentamicin [77]. Due to its biocompatibility and well-established safety profile, collagen was found to be a favorable matrix for quick, on-site drug delivery. Some of the main clinical and experimental applications focused on the treatment and prophylaxis of bone and soft tissue infections, wound healing, and ophthalmic and periodontal treatment. Recent efforts have concentrated on the use of collagen-based diffusion membranes for prolonged drug release [77]. Collagen-based sponges and polymethylmethacrylate beads used as carrier systems for local gentamicin (GS) treatment were proven to have pharmacokinetic disadvantages with respect to their GS-release profiles. Therefore, poly(lactic-*co*-glycolic acid) (PLGA) microparticles were devised to replace them. None of the five poly(α-hydroxy) acids tested resulted in the desired antibiotic release over a time period of approximately 1 week. However, an attempt to produce microparticles from a blend of different resomers yielded the targeted liberation profile [78]. Collagen microparticles are now being prepared using marine sponge collagen rather than the previously used, standard collagen. Marine sponge collagens loaded with retinol were incorporated into hydrogels and tested for drug stability. The *in vitro* penetration of retinol from this formulation into the hairless mice test subjects' skin was compared to retinol formulations that did not include microparticles. The existence of sponge collagen microparticles (SCMPs) had no influence on the chemical stability of the retinol found in the hydrogel. The dermal penetration of retinol showed a significant, approximately twofold increase [79]. There are some reports in the literature on the manufacture of collagen-based ointments, suppositories and sponges that also contain vitamin U, as well as other mechanisms used to treat skin wounds [80]. ('Vitamin U' is not a vitamin. Some manufacturers and retailers use the name to describe '*S*-methyl-L-methionine', a putative derivative of methionine. This term was derived from methionine's use as an unproven treatment for ulcers by naturopathic doctors.)

An ocular device based on a gelatin sponge (Gelfoam) was used to control the systemic delivery of bovine insulin zinc. *In vitro* drug release from the ocular device was performed *via* a flow-through dissolution method. After the insertion of ocular devices into New Zealand white rabbits, measurements of blood dextrose (glucose) levels were taken and later analyzed. The results indicated that the *in vitro* release of insulin zinc from the gelatin sponge-based ocular device depended on flow rate. The *in vivo* data suggested a direct relationship between the decrease in blood dextrose levels and the rate of insulin zinc released from the ocular device [81]. Drug release from the gelatin sponge took place through diffusion and was affected by the pH of the external solution and the charge and molecular weight of the drugs used [82]. Gelatin sponges were also reported for use as an ophthalmic carrier for pilocarpine hydrochloride. Prolonged drug release was successfully attained by embedding a retardant in the matrix pores. The device, embedded with acetyl ester wax, released the drug in a zero-order pattern for up to 5 h, with a release exponent of 0.93 [83].

Hydrocolloids are useful in drug delivery due to their various amenable properties: their ease of use, their potential inclusion of drugs that differ in nature and reactivity, the option to include different active ingredients, their reasonable price based on the high proportion of water used to solubilize the polymer, and their stability over a wide range of temperatures and moistures, especially with properly designed packaging.

5 Conclusions

There are a large variety of methods enabling the manufacture of mechanically stable solid sponges. Their characteristic compressive stress-strain relationships can be effectively illustrated by means of empirical mathematical models which were originally developed for polymeric sponges and baked goods, but have been successfully adapted for use in these cases. The structure, porosity, shape, and

mechanical properties of cellular solids can be modified for potential uses in countless fields, such as foods, drug carriers, agriculture, packaging, water treatment, and biological control.

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