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Dimensional changes of alginate dental impression materials

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Abstract The weight loss and corresponding dimensional changes of two dental alginate impression materials have been studied. The weight loss kinetics indicate this to be a diffusion controlled process, but with a boundary condition at the surface of the concentration decreasing exponentially with time. This is in marked contrast to most desorption processes, where the surface concentration becomes instantaneously zero. The appropriate theory has been developed for an exponential boundary condition, and its predictions compared with experimental data; the agreement was satisfactory. The diffusion coefficients for two thicknesses of the same material were not identical as predicted by theory; the possible reasons for this are discussed.

1 Introduction

Alginate polymers are one of the polysaccharides whose general chemistry is very well documented [1–3].

Alginate dental impression materials are one of the group often referred to as "elastic impression materials"; they are characterised by the high compliance associated with elastomeric materials, and strictly speaking are viscoelastic. Alginate impression materials were first patented in 1940 by the then Amalgamated Dental Company [3], with a number of patents subsequently, for example [4–10]. Since then alginate impression materials have been exhaustively studied. Dental materials textbooks describe their general composition, chemistry of setting, dimensional stability, strength, and other properties [11–16]. In particular their relatively poor dimensional stability compared with elastomers is well known, and in recent years, a considerable body of publications have appeared on the dimensional stability of alginates in sterilising solutions, for example [17–21].

In this paper further aspects of weight and associated dimensional changes have been considered.

2 Materials and methods

2.1 Materials

One proprietary material, Neocolloid (Zhermack) and one experimental material have been studied, the composition of which is listed in Table 1

2.2 Methods

2.2.1 Sample preparation

Neocolloid. The alginate impression powder container was first shaken to ensure even dispersion of the constituents. One level scoop of the powder (9 g) was added to one measure of tap water at 23°C(18 ml) and mixed with a spatula in a rubber bowl for 45 seconds. wax moulds were used to make rectangular samples measuring 10 × 60 mm that were either 1.5 mm or 3 mm thick. To make a sample, a wax mould was placed on to a glass slab, and the rectangular cavity of the wax was filled with the mixed alginate, covered with a glass slide, and then left to set for 3 min once the material had set, the glass slide was removed, and the alginate sample carefully cut out of the mould using a scalpel.

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Table 1 Composition of an experimental alginate

Ingredient	Supplier	%w/w
Manugel® DJX	ISP (Alginates(UK) Ltd.	14.0
Potassium Fluorotitinate	Rose Chemicals Ltd.	3.0
Diatomaceous earth	Sigma Aldrich Co. Ltd.	63.0
Crystacast Plaster $2CaSO_4,H_2O$	CFS Partnership	9.0
Tetrasodium pyrophosphate	Sigma Aldrich Co. Ltd.	0.42
Magnesium oxide	Aldrich Chemical Co.	10.0

*Formulation supplied by ISP (UK) Ltd.

Experimental materials. The ingredients in Table 1 were first thoroughly blended, and 10 g of the resulting powder mixed with 23 ml of water. Samples were then prepared as above.

2.2.2 Weight change measurements

After preparing a sample, it was weighed (±0.0001 g) immediately, then at the following time intervals during an eight hour period:

- Every five minute for the first hour
- Every fifteen minutes for the second hour
- Every thirty minutes for the remaining six hours.[23pc]

The samples were kept in a polytetraflourethylene (PTFE) trough between weighings, and measurements were made on both 1.5 and 3 mm thick samples, five repeat measurements being carried out in each case. These measurements were done on both Neocolloid and the experimental alginate.

2.2.3 Linear shrinkage measurements

A travelling microscope was used to measure the dimensional changes occurring in the alginate samples. A sample was placed in a PTFE trough and secured at one end by a fixed pin. A movable pin was then placed inserted in the other end of the sample. The distance (±0.0001 cm) between the fixed pin and the sample edge closest to the movable pin was measured. Readings were taken at the same time intervals as before.

3 Results

3.1 Weight change measurements

Figures 1 and 2 shows typical weight change plots for two sample thicknesses (1.5, 3 mm) of Neocolloid and the Experimental Alginate. Figures 3 and 4 show the same data plotted as a function of $t^{1/2}$; note that after a lead in, the plot is substantially linear. This will be discussed in 4.1.

3.2 Linear shrinkage measurements

Figure 5 shows the linear shrinkage in air for the experimental material; very similar plots are obtained for Neocollloid.

3.3 Relationship between linear dimensional changes and weight changes

A priori dimensional changes are linked to the loss of water. Given that the relative density of water is unity, it might be

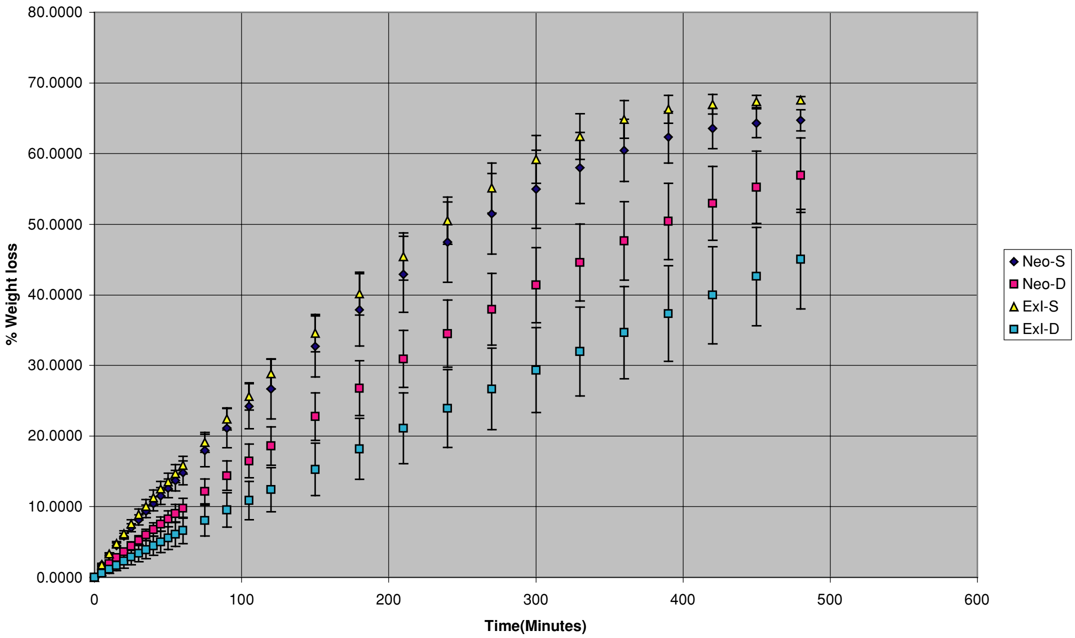

Fig. 1 % Weight loss as a function of time: Neo-Neocolloid, Exl-Experimental alginate, S-1.5 mm thickness, D-3.0 mm thickness

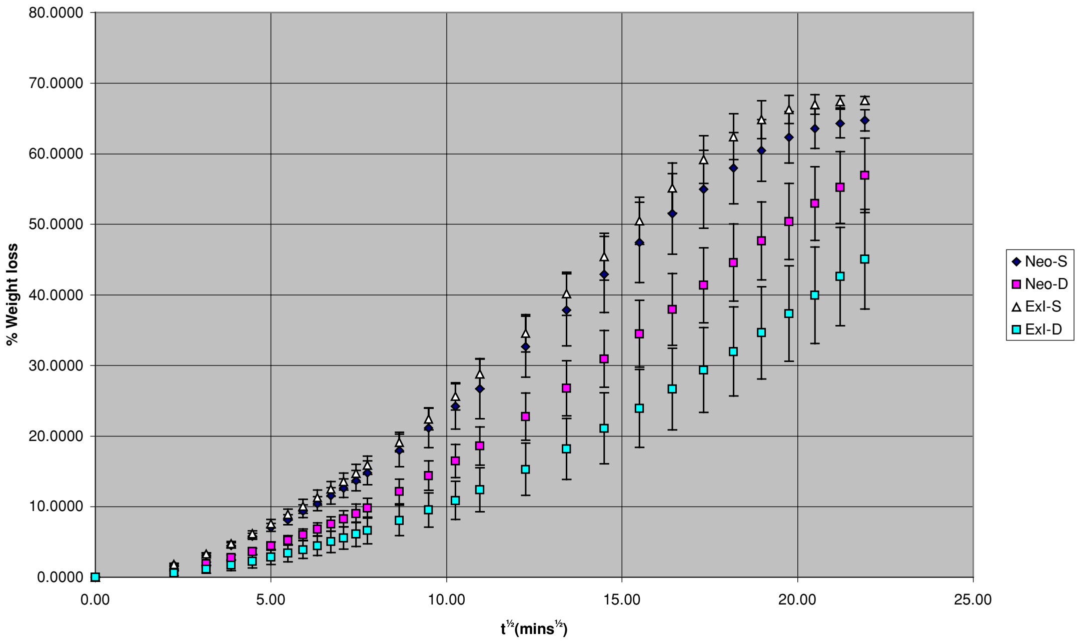

Fig. 2 Data from Fig. 1 replotted as a function of $t^{1/2}$

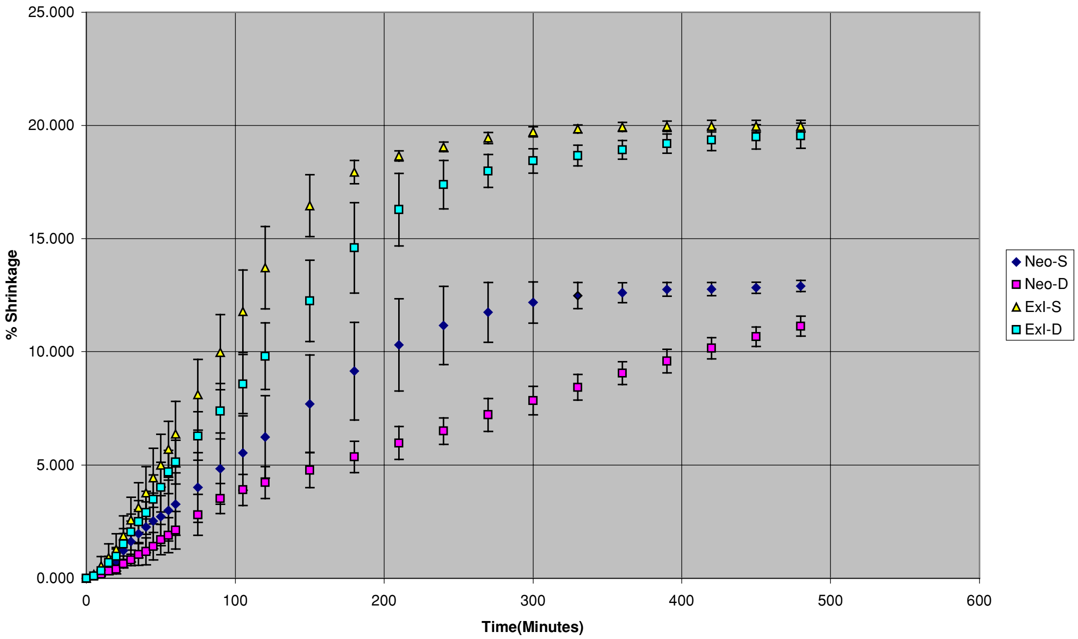

Fig. 3 % Linear Shrinkage as a function of time for the materials in Fig. 1

expected that:

$$\Delta L/1 = 1/3\Delta M/M \qquad (1)$$

This of course assumes that the water loss is isotropic, and uniform; the latter is unlikely because the process is diffusion controlled (*viva infra*). Figure 6 shows the relationship in air for two thicknesses of Neocolloid, compared with the predictions of Eq. (1).

4 Discussion

4.1 Weight changes

Changes in air. Much of the dental literature refers to the process of water loss as a process of Synerisis. This term is not strictly true. Synerisis, a term used for gels, is "water loss without dimensional change" [24]. It is constructive to consider the mechanism of water loss. Taking Experimental

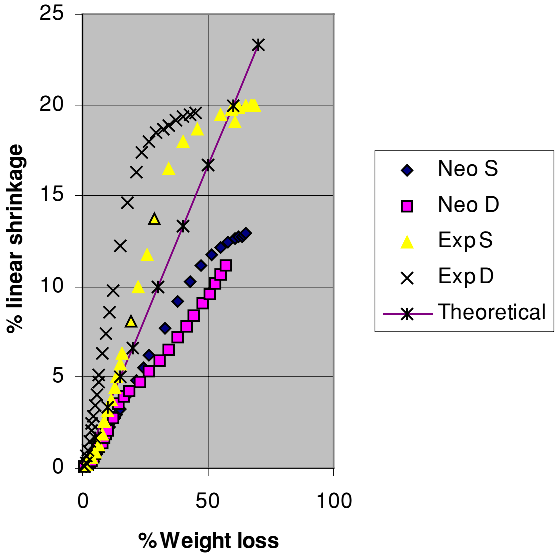

Fig. 4 Plot of % linear Shrinkage versus % weight Loss compared with the predictions of Eq. (1)

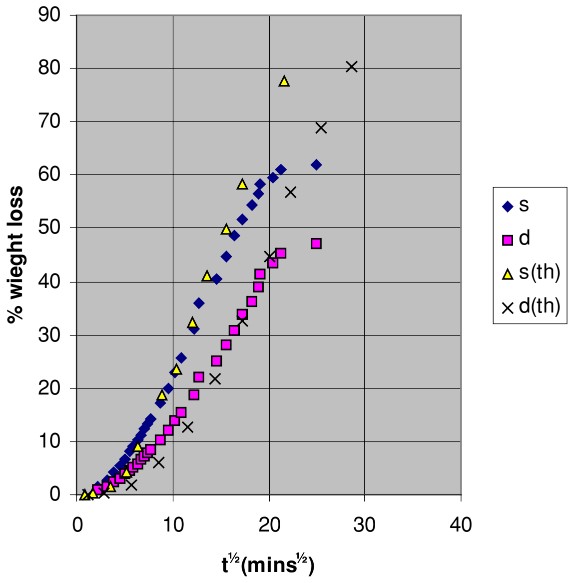

Fig. 5 Experimental weight loss-t$^{1/2}$ data compared with the predictions of equation 4-experimental alginate

Alginate A as an example, when it is mixed, 1.4 g sodium alginate is mixed with 23 ml water, ~6.1%w/v, an amount which should be soluble, although it is a moot point whether complete solution occurs in the usual time scale.

The alginate is soluble, because in the Gibbs Free Energy (ΔG) is negative:

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

because $T\Delta S > \Delta H$, where H is the Enthalpy (Total Heat) of the process, S Entropy, and T Tenperature (K).

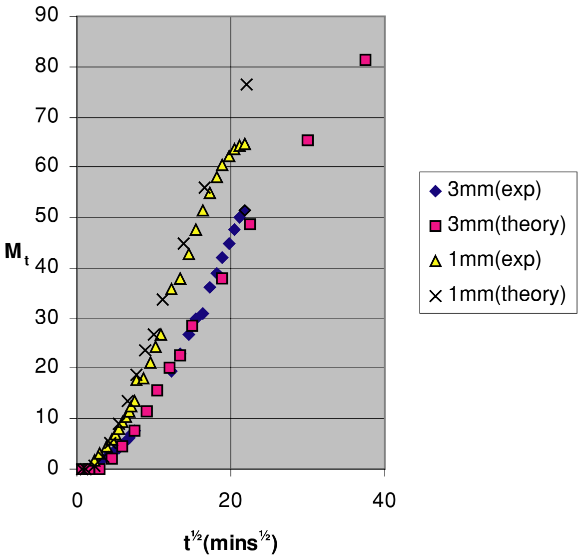

Fig. 6 Experimental weight loss-t$^{1/2}$ data compared with the predictions of equation 4-Neocolloid

However, when setting commences, i.e cross linking, then the Entropy reduces considerably, and ΔG becomes positive, and the system is now unstable, and the resulting Chemical Potential drives the water out.

The kinetics of water loss appear to be diffusion controlled, given the linear $t^{1/2}$ plots. However, most desorption plots are $t^{1/2}$ linear, going through the origin; this is consistent with the usual theoretical assumption that the surface concentration becomes instantaneously zero. The obvious inference from Figs. 3 and 4, is that this assumption is no longer true. The "lead in" noted above is often represented by the assumption that the surface concentration decays exponentially:

$$C_{\text{surface}} = C_0\exp(-kt) \tag{2}$$

The solution to Fick's Second Law in one dimension with this boundary condition, and subsequent integration to give mass loss as a function of time, is given by Crank [25] as:

$$M_t/M_\infty = 1 - \exp(-kt)\mathrm{Tan}(kL^2/D)^{1/2}/(kL^2/D)^{1/2}! \\ -8/\pi^2 \sum_{n=0}^{\infty} \frac{\exp[-(2n+1)^2\pi^2 Dt/4L^2]}{(2n+1)^2[1-(2n+1)^2(D\pi^2/4kL^2)]} \tag{3}$$

Unfortunately, this series is cumbersome, and converges slowly at short times, the region of interest in the current work. Also, the function is not continuous, having singularities, with the Tan term being ∞ when $(kL^2/D^{1/2}) = \pi/2$.

Hence for short values of time, the two major surfaces are treated as being of a semi-infinite medium. Solution of Fick's Second Law, and subsequent integration (see Appendix for

Table 2 Diffusion coefficients (D) and values of the exponential parameter (k) for Neocolloid and the Experimental Alginate

Material	Thickness (mm)	D (10^{-11}m^2 sec^{-1})	k (10^{-3} sec^{-1})
Neocolloid	1.5	3.82	1.46
	3.0	7.24	1.46
Experimental	1.5	2.46	2.0
	3.0	5.33	1.46

detailed theoretical treatment) gives:

$$M_t/M_\infty = (Dt/\pi L^2)^{1/2}[1 - \surd\pi/2\mathbf{V}(\surd(kt), 0)/\surd kt] \quad (4)$$

$\mathbf{V}(\surd kt, 0)$ is one of two functions, **U**(X.Y), **V**(X,Y), first defined and tabulated by Faddeeva and Terentev, to deal with error functions of complex argument [26]. They can be found in the test-book by Carslaw and Jaeger [27]. Further use of these functions is described in detail by Rabinovitch [28].

With a suitable choice of *k*, it is found that Eq. (4) fits the data surprisingly well, for example Figs. 5 and 6. Diffusion coefficients and *k* values are listed in Table 2.

It would be expected that for a given material, the *D* values obtained would be independent of thickness. However in both cases above, the *D* values are roughly twice as much for the thicker specimens. However, it should be borne in mind that as water is lost from the outer layers, shrinkage occurs, hence strains are set up. Neither of these factors are accounted for in simple diffusion theory. The two materials studied have similar diffusion coefficients.

The *k* values obtained are similar, although the reasons are not clear why the water loss from alginates should have this surface boundary condition. It could be of some practical importance, because if it could be substantially reduced, then the shrinkage of the alginate would likewise be reduced.

Linear shrinkage

Clearly linear shrinkage (Figs. 7 and 8) generally reflect weight changes.

If the shrinkage is isotropic, it might be expected that linear shrinkage will be 1/3 that of weight loss, given the relative density of water is unity.

Conclusions

(i) The loss of water from alginates in air on setting is due to a major decrease in entropy consequent on the cross linking reaction, and a change of the Gibb's free energy to a positive value. The system is then unstable.

(ii) Water loss is a diffusion process. In air the results are consistent with the surface concentration of water decreasing exponentially with time.

(iii) Linear shrinkage in air only follows the theoretical prediction of 1/3 of the corresponding weight loss in the early stages; thereafter there are departures, from the theoretical prediction, possibly due to sample distortion during shrinkage.

Appendix

Diffusion with an exponential boundary condition

It is required to solve Fick's Second Law:

$$\partial C/\partial t = D\partial^2 C/\partial x^2 \quad (1)$$

subject to

$$C = C_0 e^{-kt} \quad \text{at}\, x = 0 \quad (2)$$

for a semi-infinite medium. (In practice, this corresponds to the early stages of diffusion, where the diffusing fronts from each surface do not interact.)

Solving by standard Laplace Transform methods [ ] gives:

$$\begin{aligned} C/C_0 = {} & \mathrm{erf}(x/2\surd Dt) + 1/2\mathrm{e}^{-kt} \\ & \times e^{-kt}/2.\big[e^{-i(\surd k/D)x}\mathrm{erfc}(x/2\surd Dt - i\surd kt) \\ & + e^{i(\surd k/d)x}\mathrm{erfc}(x/2\surd Dt)\big] \end{aligned} \quad (3)$$

where $i = \surd{-1}$, and erf and erfc are error functions [ ]

The mass uptake will be given by:

$$M_t = 2A\int_0^\infty C(x, t)dx \quad (4)$$

where A is the area of one major surface.
The following integrals may be noted:

$$\int_0^\infty \mathrm{erf}(x/2\surd Dt)dx = 2(Dt/\pi)^{1/2} \quad (5)$$

$$\begin{aligned} & \int_0^\infty e^{i\surd(k/D)x}\mathrm{erfc}(x/2\surd Dt + i\surd kt)dx \\ & = i(D/k)^{1/2}e^{-kt}\mathrm{erfc}(i\surd kt) + i(D/k)^{1/2} \end{aligned} \quad (6)$$

$$\begin{aligned} & \int_0^\infty e^{-i\surd(k/D)x}\mathrm{erfc}(x/2\surd Dt - i\surd kt)dx \\ & = -i(D/k)^{1/2}e^{-kt}\mathrm{erfc}(-i\surd kt) - i(D/k)^{1/2} \end{aligned} \quad (7)$$

Hence

$$\begin{aligned} M_t = {} & 2AC_0\{2(Dt/\pi)^{1/2} - i(D/k)^{1/2}e^{-kt} \\ & \times [\mathrm{erf}(i\surd kt) - \mathrm{erf}(-\surd kt)]\} \end{aligned} \quad (8)$$

Faddeva and Terent'ev expressed complex error functions in the form

$$U(X,Y) + iV(X,Y) = \exp(-z^2)\left[1 + 2i \Big/ \sqrt{\pi} \int_0^z \exp(-s^2)ds\right] \quad (9)$$

whence

$$U(X,Y) - iV(X,Y) = \exp\left(-z_1^2\right)\left[1 - 2i \Big/ \sqrt{\pi} \int_0^{zl} \exp(-s^2)ds\right] \quad (10)$$

where $z = X + iY$

where z_1 is the complex conjugate of z.

(9)–(10), and noting $z = \sqrt{kt} + ix/2\sqrt{Dt}$, and $M_\infty = 2C_0$ AL, and that there are two major diffusing surfaces gives:

$$M_t/M_\infty = 2(Dt/\pi L^2)^{1/2}\{1 - \sqrt{\pi}/2.\mathbf{V}(\sqrt{kt}, 0)/\sqrt{kt}\} \quad (11)$$

a full treatment of complex error functions can be found in [28].

It will be noted that the term in front of the {} brackets is the normal form of the equation for weight loss during sorption/desorption.

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