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Journal of the European Ceramic Society 23 (2003) 2265–2272
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# Drying of gelcast ceramic parts via the liquid desiccant method

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Received 20 August 2002; received in revised form 15 December 2002; accepted 5 January 2003

**Abstract**

Conventional methods in drying ceramic parts, using dry air or gas with particular conditions of humidity and temperature, is usually confronted with many difficulties. Non-uniform and differential drying in various regions due to the solvent gradient, induces structural and residual stresses which cause defects, such as cracking, warpage, bending and the other malformations, which make the articles useless. These malformations can be minimised or eliminated by using the liquid desiccant drying method due to the release of residual stresses. In this work, gelcast green parts have been brought in contact with an appropriate liquid desiccant with the purpose of withdrawing above 30 wt.% solvent in a reasonable period of time, i.e. 3 h. The effects of factors such as loading level of ceramic powders, liquid desiccant concentration and its gradient, effective thickness and geometry of parts and type of liquid desiccant solution (aqueous or non-aqueous), on the drying rate were studied. Lower solid content in the gel, higher liquid desiccant concentration and lower effective thickness of parts, increase the drying rate. Decrease of aspect ratio in cylindrical parts changes the diffusion mechanism from radial to longitudinal direction. Drying of parts in aqueous solution of PEG1000 is more homogeneous than the non-aqueous one, but drying rate of parts in non-aqueous solution of PEG1000 is greater than the aqueous one.


*Keywords:* $Al_2O_3$; Diffusion; Drying; Gelcasting; Desiccants; Shaping

## 1. Introduction

Gelcasting is a relatively new near-net-shape ceramic forming process that is used in manufacturing advanced structural ceramic parts for various industries.[1–4] The gelcasting process involves the preparation of fluid, castable slurry of ceramic powder, which contains small quantities of mono and bifunctional monomers, catalysts, initiators and other additives. Gelation is initiated after the slurry is cast in a mould. The result is a homogeneous wet cast part, which contains moisture about a quarter of its mass that should then be removed by drying. After drying, binder removal and sintering are carried out as in the other ceramic process.

Removal of moisture is the longest stage in the gelcasting process due to the slow transport of liquid through the porous solid medium and can become troublesome in a manufacturing operation.[5] Hence, it is necessary to employ new drying method whereby the drying period is minimised without causing any damage to the part.

Cross-linked polymer gels, which have three-dimensional network structures, can swell and collapse reversibly when they are immersed in the solvents. The gel volume change is usually brought about by altering the conditions of the solvent; i.e. its temperature,[6] composition,[7,8] pH,[9] salt content [10] or free polymer content.[11,12]

In this work, the liquid desiccant drying method [13] has been used as a new method in drying gelcast ceramic parts. In this method, the wet green parts are brought into contact with an appropriate liquid desiccant by immersion. The reason for the effect of the liquid desiccant on a gelcast part is the chemical potential difference between the polymeric chains in the liquid desiccant and the solvent in the polymeric network in the part.[14]

Using the liquid desiccant has the following important advantages:[13]

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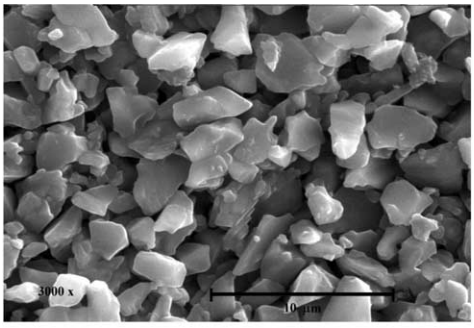
doi:10.1016/S0955-2219(03)00045-1

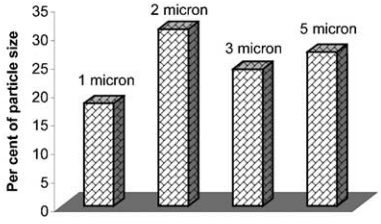
Table 1
Characteristics of materials

| Material | Function | Chemical formula | Mean particle size (micrometre) | Supplier |
|---|---|---|---|---|
| Silicon | Ceramic powder | Si | 5 | Good Fellow[a] |
| Alumina | Ceramic powder | $Al_2O_3$ | 4 | Commercial |
| Acrylamide (AM) | Monofunctional Monomer | $C_2H_3CONH_2$ | – | Merck[b] |
| *N,N′*-Methylene Bisacrylamide (MBAM) | Bifunctional monomer (cross linker) | $(C_2H_3CONH_2)_2CH_2$ | – | Sigma[c] |
| Ammonium persulfate | Initiator | $(NH_4)_2S_2O_8$ | – | Merck[b] |
| *N,N,N′,N′* Tetra methyl ethyl diamine | Accelerator (catalyst) | $C_6H_{16}N_2$ | – | Merck[b] |

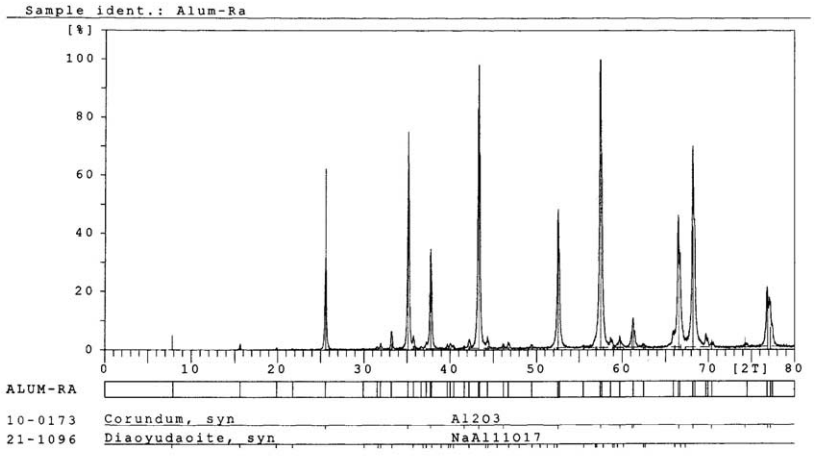
[a] Cambridge Science Park, Cambridge CB4 4DJ, UK.
[b] E. Merck, D6100 Darmstadt, F.R. Germany.
[c] Sigma Chemical Co., PO Box 14508 St. Louis, MO 63178, USA.




(a)




(b)




(c)

Fig. 1. (a) Shape, (b) particle size distribution and (c) X-ray diffraction of as-received α-alumina powder.

- Liquid desiccant provides a more uniform medium in comparison with conventional air drying methods.
- The water extraction capacity of the liquid desiccant is more significant than that of air having any relative humidity and temperature.
- By providing buoyant support on the part, malformations such as bending, warping, cracking and other defects can be minimised or completely eliminated during drying.
- Using liquid desiccant allows no region of the part to be dried too quickly, so the reductions of the residual stresses are developed during drying.
- In this method, the part loses safely about 20–30 wt.% of interior solvent (water) in a very short time, which is considered a breakthrough in the critical stage of the drying.

The present work reports the drying of pure acrylamide gel and gelcast alumina or silicon parts via liquid

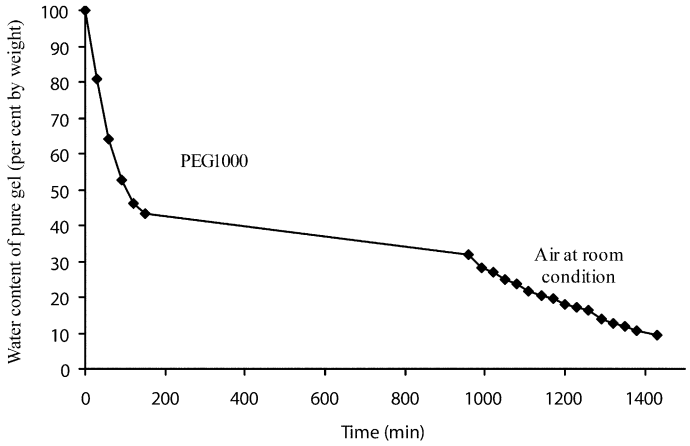



Fig. 2. Drying of cubic pure gel in aqueous solution of PEG1000 followed in air at room condition.

Table 2
Experimental design for determining the effects of various factors on the rate of drying and shrinkage of parts

| Set number | Number of experiments | Ceramic loading level (vol.%) | Liquid desiccant concentration (wt.%) | Effective thickness (diameter) (mm) | Aspect ratio ($L$ / $D$) | Type of solution |
|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 20 | 7 | 4 | Aqueous |
| | 2 | 10 | 20 | 7 | 4 | Aqueous |
| | 3 | 20 | 20 | 7 | 4 | Aqueous |
| | 4 | 30 | 20 | 7 | 4 | Aqueous |
| | 5 | 40 | 20 | 7 | 4 | Aqueous |
| | 6 | 45 | 20 | 7 | 4 | Aqueous |
| 2 | 7 | 40 | 20 | 7 | 4 | Aqueous |
| | 8 | 40 | 40 | 7 | 4 | Aqueous |
| | 9 | 40 | 60 | 7 | 4 | Aqueous |
| 3 | 10 | 40 | 20 | 7 | 4 | Aqueous |
| | 11 | 40 | 20 | 9 | 4 | Aqueous |
| 4 | 12 | 40 | 20 | 7 | 4 | Aqueous |
| | 13 | 40 | 20 | 7 | 0.5 | Aqueous |
| 5 | 14 | 40 | 20 | 7 | 4 | Aqueous |
| | 15 | 40 | 20 | 7 | 4 | Non-aqueous |

Table 3
Specifications of pure gel samples dried in air and liquid desiccant

| Sample identification | Shape of sample | Dimensions (mm) | Type of drying |
|---|---|---|---|
| $A_1$ | Cubic | 5×30×5 | Air at room condition |
| $A_2$ | Cubic | 50×30×5 | 60 wt.% of aqueous solution of PEG1000 |
| $B_1$ | Cylindrical | Diameter = 7 mm with $\frac{L}{D}=4$ | Air at room condition |
| $B_2$ | Cylindrical | Diameter = 7 mm with $\frac{L}{D}=4$ | 60 wt.% of aqueous solution of PEG1000 |

Table 4
Variation of linear shrinkage for cubic pure gel after dried in desiccant liquid

| | Dimensions of cubic gel (mm) | | Calculated linear shrinkage (per cent) |
|---|---|---|---|
| | Before drying | After drying | |
| Length | 50.00 | 37.00 | 26.00 |
| Width | 30.00 | 22.00 | 26.66 |
| Height | 5.00 | 3.90 | 22.00 |

Table 5
Variation of linear shrinkage for cylindrical pure gel at various times

| Time (min) | Dimensions of cylindrical gel | | Calculated linear shrinkage (per cent) | |
|---|---|---|---|---|
| | Height (mm) | Diameter (mm) | Height | Diameter |
| 0 | 40.0 | 10.0 | 0 | 0 |
| 180 | 31.4 | 7.4 | 21.50 | 26.00 |
| 1140 | 26.0 | 6.2 | 35.00 | 38.00 |
| 5100 | 23.5 | 5.5 | 41.25 | 44.50 |

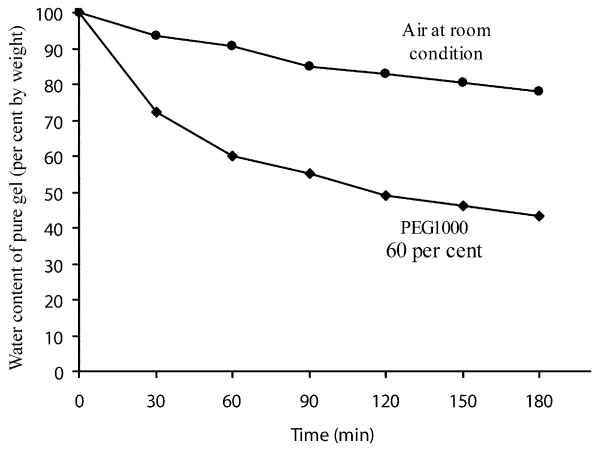



Fig. 3. Comparison of drying for cylindrical pure gel in air at room condition and in 60 wt.% aqueous solution of PEG1000.

desiccant drying technique. In this work, the effects of loading level of ceramic powders, concentration of liquid desiccant solution and its gradient, effective thickness, i.e. dimension of the part in which direction diffusion takes place, and geometry of parts and type of liquid desiccant solution (aqueous or non-aqueous) on the drying rate and shrinkage of parts were studied in details.

## 2. Experimental details

### 2.1. Materials

The specification of the materials used in this work are summarised in Table 1.

### 2.2. Experimental procedures

Commercial grade alumina powder that consists of particles of 4 μm in size is used to produce the gelcast parts (Fig. 1). Green gelcast parts of cylindrical shape with 7 and 9 mm diameter and $\frac{L}{D} = 0.5$ and/or $\frac{L}{D} = 4$ were prepared based on conventional aqueous gelcasting methods.[1] After casting, the samples were remoulded and immersed in an aqueous or non-aqueous

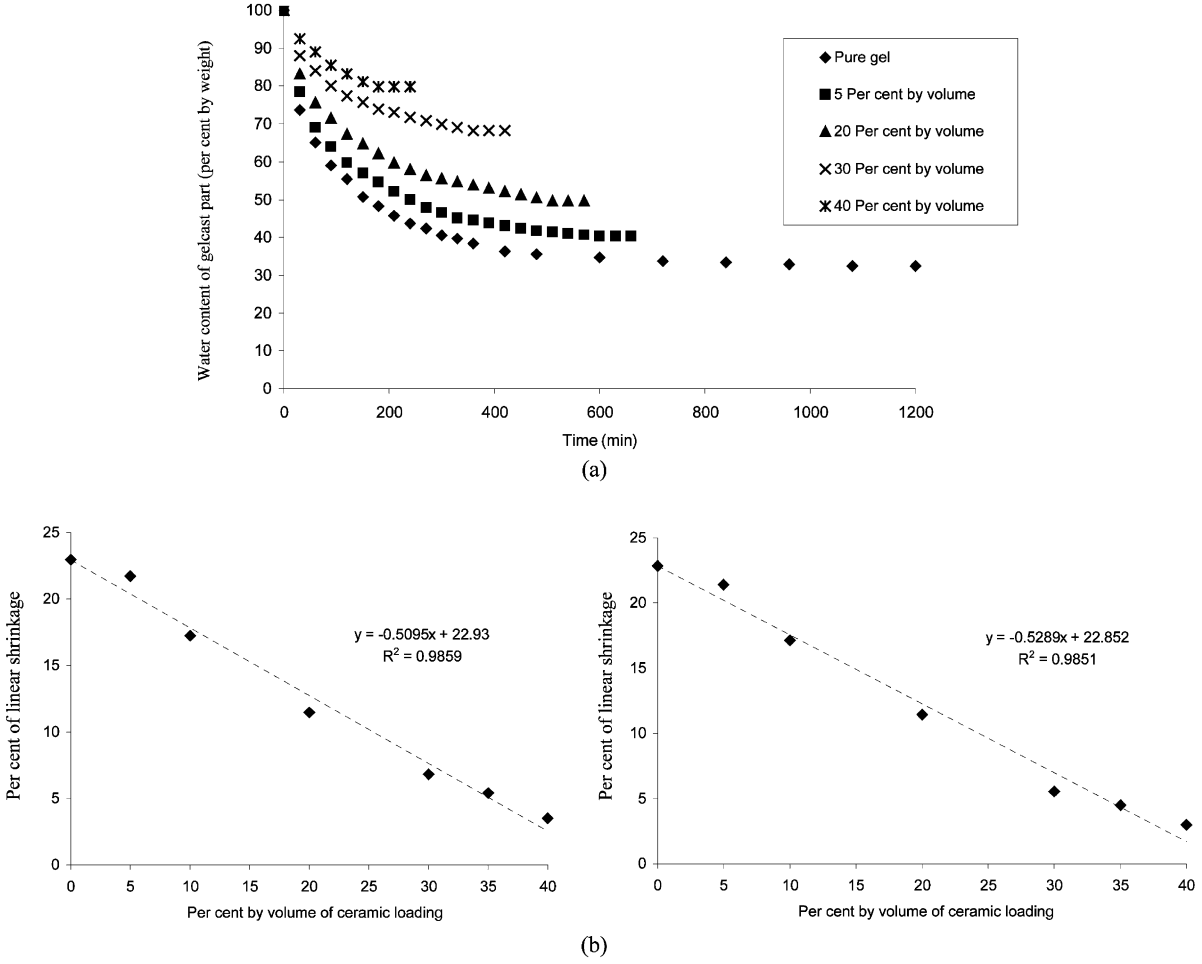



Fig. 4. (a). Comparison of drying for gelcast parts with various loading level of alumina. (b). Comparing the variation of linear shrinkage of gelcast parts in various loading level of ceramic (a) in the length, (b) in the diameter directions.

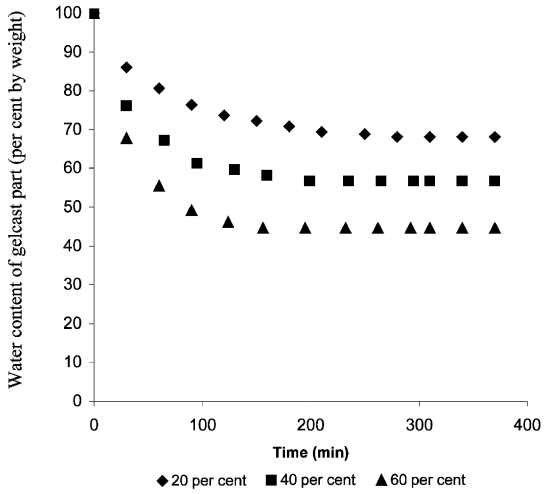



Fig. 5. Comparison of drying for gelcast parts in various concentration of liquid desiccant.

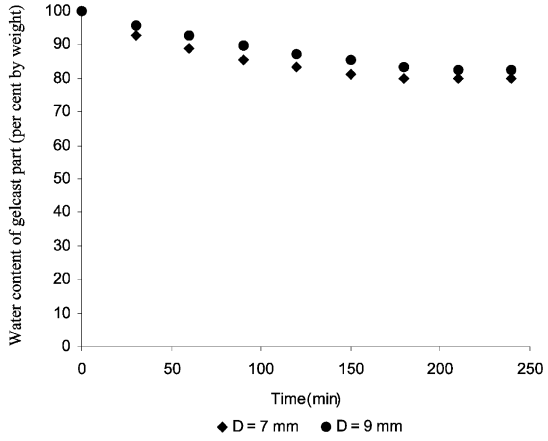



Fig. 6. Comparison of drying for gelcast parts with different thicknesses.

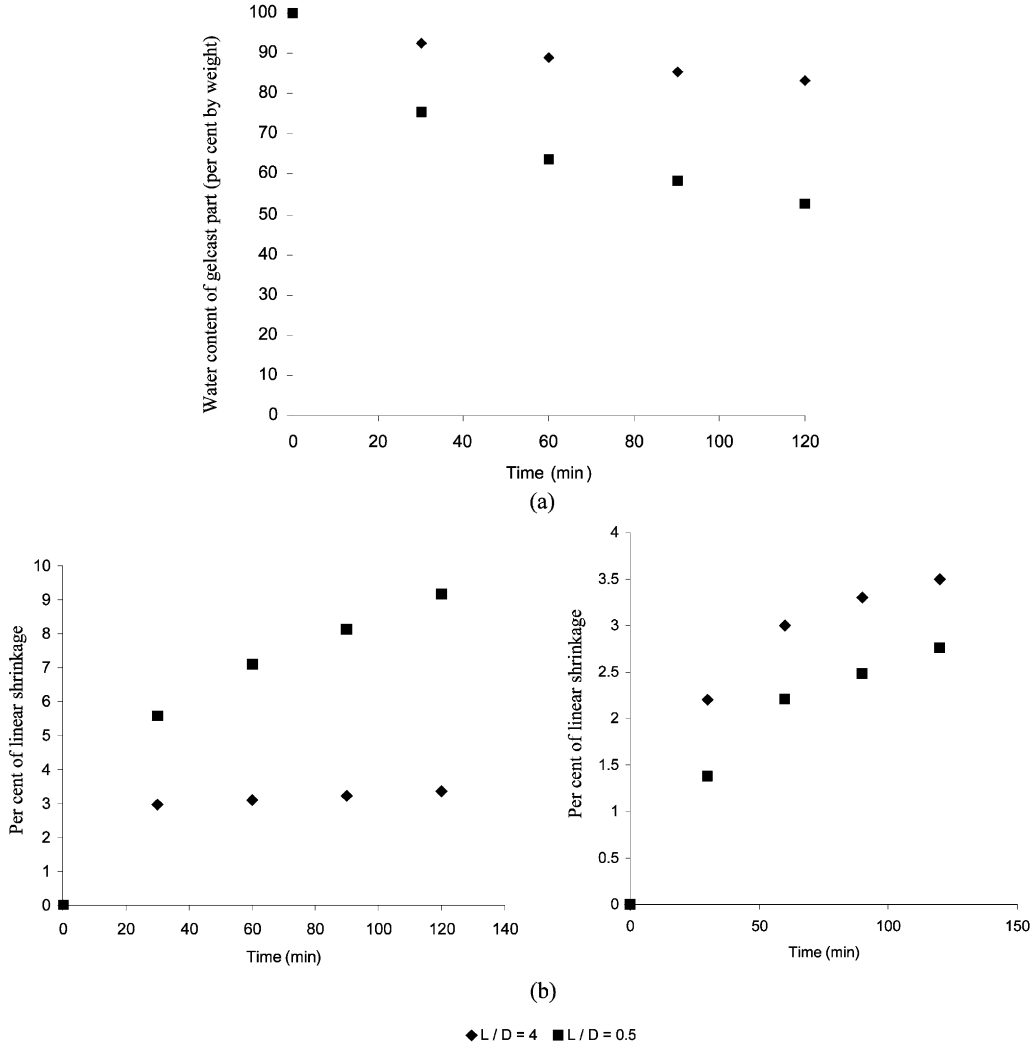



Fig. 7. (a). Comparison of drying for gelcast parts with different aspect ratio. (b). Variation of linear shrinkage of gelcast parts with different aspect ratio (a) in the length, and (b) in the diameter directions.

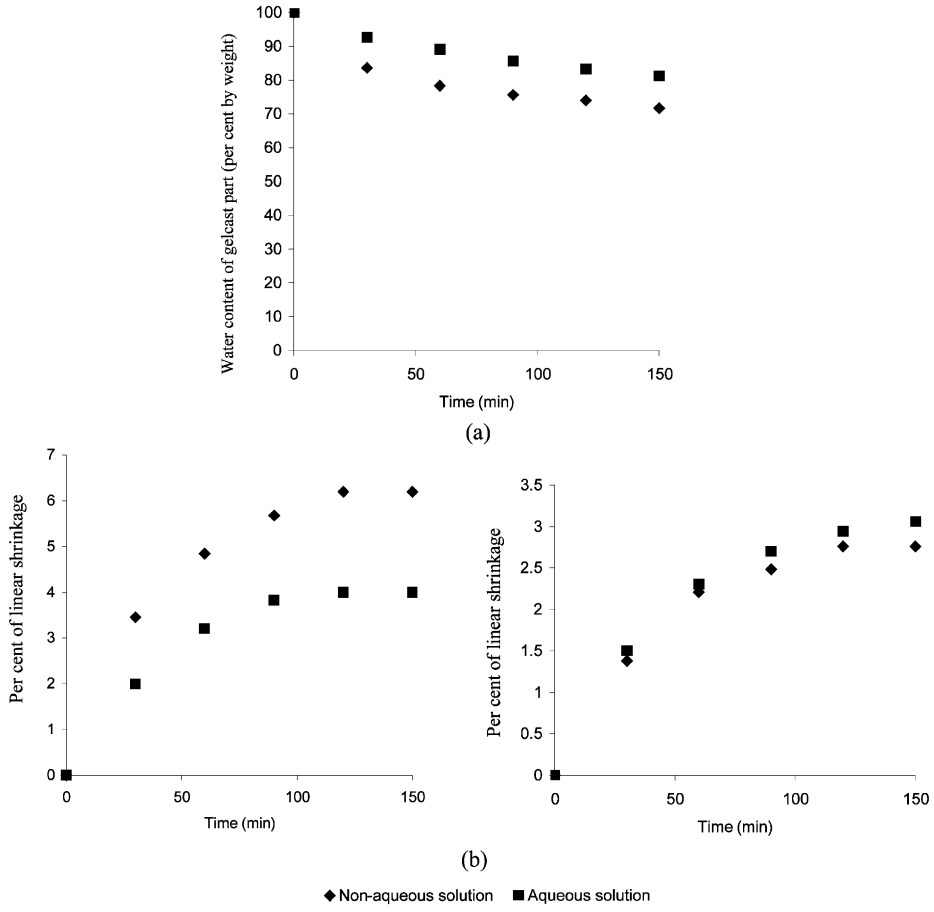



Fig. 8. (a). Comparison of drying for gelcast parts in different types of liquid desiccant solutions. (b). Variation of linear shrinkage of gelcast parts in different types of liquid desiccant solution (a) in the length, and (b) in the diameter directions.

solution of PEG1000 as liquid desiccant solution. Every 30 min, the sample was removed from the container and washed with deionized water. Excess water on the surface of the sample was drained off with tissue and then weighed. Five sets of drying experiments have been conducted on cylindrical shaped alumina gelcast samples and pure acrylamide gels. In each set, one of the parameters (i.e. ceramic loading level, effective thickness and geometry of parts, liquid desiccant concentration and type of liquid desiccant solution) varied while the other parameters were kept constant. These experiments revealed the relative sensitivity of the drying rates to the above parameters. Experiments based on above sets were designed as follows:

All of the samples were in cylindrical shape. Ethanol was used as solvent in non-aqueous type of liquid desiccant solution. Additional drying experiments were performed on gelcast silicon parts, for comparison.

Before starting the experiments, based on Table 2, a simple test was performed to determine whether or not a prospective liquid is a suitable liquid desiccant. Hence, identical hydrogel samples in the shape of cubes or cylinders were prepared and dried in the container of 60 wt.% PEG1000 aqueous solution and in air at room conditions to provide comparative data. Experiments based on above description were performed as given in Table 3.

## 3. Results and discussion

As shown in Table 3, pure gelled samples were cast with a monomer ratio of $\frac{AM}{MBAM} = 8$. The sample $A_1$ dried at room conditions. After 5 min, the part was cracked across the width, and 24 h after remoulding deformed completely and lost its shape and dimensional stability. The other cubic sample ($A_2$) was dried in a bath of liquid desiccant solution. After 960 min, the part was removed from the bath. It kept its shape while lost 65 wt.% of its interior solvent (Fig. 2). Some crazes were observed on the surface, which penetrated to some extent across the depth. Edges were fully sharp and no warpage or longitudinal crack was observed. Shrinkage of the part was measured using vernier calliper (0.02 $\frac{mm}{mm}$ accuracy), Table 4. Finally, drying was continued in the air at room temperature and humidity (Fig. 2).

The results obtained from drying samples $B_1$ and $B_2$ are compared in Fig. 3. After 10 min, sample $B_1$ was deformed grossly so that the determination of shrinkage

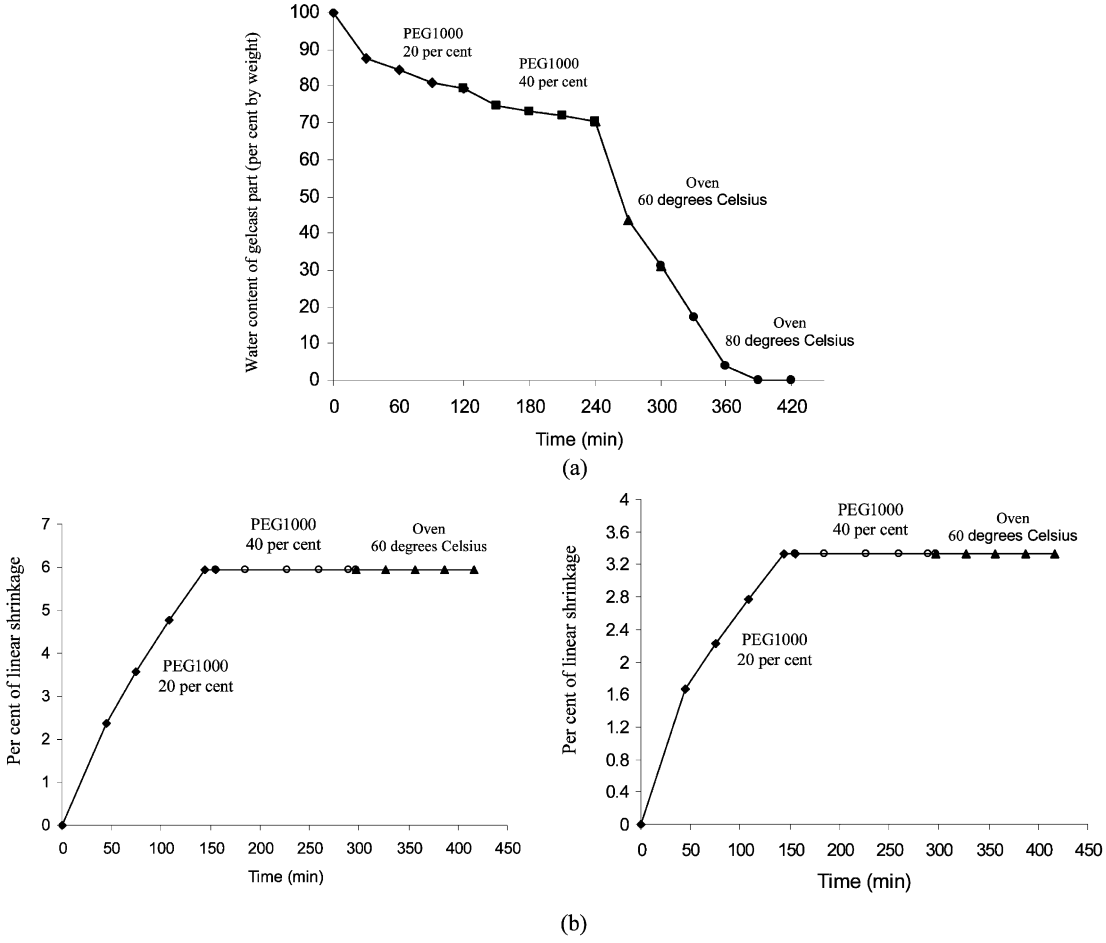



Fig. 9. (a). Drying of cylindrical alumina gelcast part in aqueous solutions of PEG1000 with various concentrations followed in an oven at 60 and 80 degrees of Celsius. (b). Variation of linear shrinkage of cylindrical alumina gelcast part in aqueous solutions of PEG1000 followed in an oven (a) in the length, and (b) in the diameter directions.

was not possible. The shrinkage of sample $B_2$ after 180, 1140 and 5100 min, is shown in Table 5.

After assuring the performance of the PEG1000 as the liquid desiccant in drying pure gels, experiments continued on alumina gelcast samples mentioned in Table 2.

Changing ceramic loading level in the gel, set 1, has a significant effect on the drying of ceramic gelcast parts. The rate of drying and shrinkage of parts decreases with the increasing the ceramic loading level in the gel (Fig. 4), which is desirable.

As shown in Fig. 5, by increasing the concentration of aqueous solution of liquid desiccant, set 2, the rate of drying increased considerably. This could be attributed to the concentration difference between the solvent in the gel and the PEG solution. This difference results in a gradient of osmotic pressure between two media. The higher the gradient the more is the diffusion of solvent from gel to the bath.

As seen in Fig. 6, by increasing the sample effective thickness (diameter), set 3, the rate of drying decreased. The thickness of the sample will increase the length of solvent diffusion and its drying time.

Another affective on the rate of drying is the geometry of the part. As shown in Fig. 7, with a decrease in the aspect ratio (length to diameter ratio) of the part from 4 to 0.5, the rate of drying was increased significantly. Also, the one dimensional diffusion mechanism of solvent was changed from radial to longitudinal direction.

As shown in Fig. 8, type of solvent in PEG1000 solution has considerable effect on the time and the rate of drying. Drying of parts in aqueous solution of PEG1000 is more homogeneous than non-aqueous one and the shrinkage in three dimensions is approximately equiaxial, but drying rate in non-aqueous solution of PEG1000 is greater than the aqueous one.

As seen in Figs. 9 and 10 alumina and silicon gelcast parts, lose 25–30 wt.% of their moisture content, respectively. Also they shrink safely and release their stresses during drying. Therefore one could easily dry them in an oven at higher temperature to increase the rate of drying of the part nearly ten times higher than the conventional drying (at higher humidity and lower temperature), without any defects.

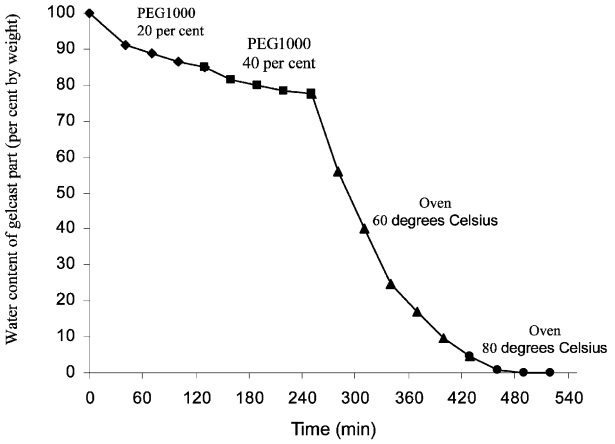



Fig. 10. Drying of cylindrical silicon gelcast part in of aqueous solutions of PEG1000 with various concentrations followed in an oven at 60 and 80 °C.

## 4. Conclusion

In this work, drying of gelcast parts via the liquid desiccant method was studied. By using this method, all of the defects during conventional drying are removed and also drying time is effectively reduced i.e. 10 times. Using this method, the parts lose safely about 20–30 wt.% of interior solvent (water) in a very short time which is a breakthrough in the critical stage of the drying. The linear shrinkage of the part is nearly uniform in all dimensions and no region is dried faster than the other. Lower ceramic loading level, higher concentration of liquid desiccant solution and lower effective thickness of the part, increase the rate of drying and decrease the time which is needed for sample to stop shrinking. Geometry of the part and type of solvent in liquid desiccant solution (aqueous or non-aqueous) have significant effects on the rate of drying. Decrease of aspect ratio in cylindrical parts, increases the drying rate and changes the diffusion mechanism from radial to longitudinal direction, too. Drying of parts in aqueous solution of liquid desiccant is more homogeneous than non-aqueous solution but rate of drying in non-aqueous solution is greater than aqueous solution of PEG1000.

Consequently, by using liquid desiccant method, the critical stage of drying process of gelcast parts could be carried out safely, (i.e. no cracks, warpage or uncontrolled shrinkage) and the part safely continues its drying in air at room conditions or in an oven.

## Acknowledgements

The authors wish to thank Tarbiat Modarres University (TMU) for the financial support of this work. Also, thank co-workers and technical staff in the Department of Polymer Engineering of the TMU for their help during various stages of the work.

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