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# DEHYDRATION OF POLYMERIC HYDROGELS DESIGNED FOR GELCASTING METHOD IN CERAMICS

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Key issue in the gelcasting method is the way water is released from the ceramic–hydrogel system. It is the first step to the formation of ceramic materials called green body.

The purpose of the presented investigations is to establish the range of temperatures in which dehydration of the various hydrogels takes place, and at what temperatures the eight prepared hydrogels are disintegrated.

The set of hydrogels polymers was obtained by radical polymerization from ionic and non-ionic monomers. The polymers were solved in water causing formation of clear gels. The dehydration and thermal decomposition of the obtained hydrogel samples was studied using thermal analysis techniques. The amount of water contained in hydrogels was determined as well as the temperature and products of polymer disintegration. Enthalpies of dewatering were also determined.

***Keywords:*** *dehydration, DSC, gelcasting, hydrogel, TG*

## Introduction

Gelcasting is a new ceramic process [1–3] of fabricating high-quality, complexed–shaped parts without using clay minerals. Instead of them the ceramic powders are prepared from $Al_2O_3$, $ZrO_2$, SiC, etc., and dispersed in an aqueous polymer solution containing a cross-linker, free radical initiator and most often a catalyst for breaking the initiator. The slurry with such ingredients is poured into an appropriately designed mould and polymerized in situ to form a polymer–water gel that immobilizes the dispersed particles in the defined shape. Then the gelled part is removed from the mould while still wet and dried to the green body which finally is fired. The gelled part is sufficiently strong and open to be machined to form features that otherwise would be difficult to mould.

The content of water in the polymer gel ranges between 80–85 mass%. The rest is provided by the polymer. In the drying step the water (eventually other liquid) has to be removed without defecting the green body. Its structure should be somewhat porous to allow the exit of gases during the firing step preventing the development of inner pressure.

The drying process is one of the keys to using gelcasting effectively. The second key is to choose an appropriate monomer/cross-linker combination. As polymeric chain formers most common are used acrylamide (AAm), methacrylamide (MAAm), hydroxy-methacrylamide, N-vinylpirolydon, etc. The cross-linker most often used is methylene-bisacrylamide (NMBA). Among factors which are affected by the choice of the monomer and initiator system are reactivity, gel toughness, wet and dry strength, green machinability. The price plays also an important role. To get the best effects sometimes the monomers are used in combination with one another which combination must be established experimentally. The same concerns the monomer concentration in solution and the cross-linker/monomer ratio. The water-solubility of the monomers should also be taken into account. All the above mentioned factors are additionally influenced by the particular ceramic powder being used.

Despite the many applications the gelcasting procedure has found in manufacturing of specific ceramic materials, still many problems are to be solved by scientific investigations aimed at making this method even more versatile.

In the present paper a set of hydrogel-polymers was obtained by radical polymerization from ionic and non-ionic monomers (i.e. acrylamide and methacrylamide, ammonium acrylate and methacrylate). The polymers were solved in water (~85 mass%) causing formation of clear gels. The dehydration and thermal decomposition of the obtained hydrogel

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samples was studied using thermal analysis techniques (DSC, EGA-TG/DTG/SDTA) in the argon atmosphere. The water contained in the hydrogels was determined as well as the temperature and the products of polymer disintegration.

The structure of respective hydrogels, which were either ionic or non-ionic, has affected the results obtained.

## Experimental

Monomers used for the synthesis of hydrogels were: for non-ionic – acrylamide, (AAm, 97%); methacrylamide, (MAAm, 98%); for ionic – acrylic acid, (AAc, 99%); methacrylic acid, (MAAc, 99%); cross-linker agents: N, N'-methylenebis(acrylamide), (NMBA, 99%) or 3-(acryloyloxy)-2-hydroxypropyl methacrylate, (3A2H). All monomers were purchased from Sigma-Aldrich and used as received without further treatment. As initiators ammonium persulfate (APS, 98%) and tetramethylenoethylenodiamina (TMEDA, 97%) were used.

For the synthesis of hydrogels aqueous solutions of monomers were prepared at concentrations ranging between 15–18 mass/mass%. Aliquot samples (50.00 g) of the stock solution were taken and supplemented by the following weighings NMBA (0.75 g), or 3A2H (1.00 g) respectively. To each mixture a solution of APS (10 mass/mass%), 4 droplets of aqueous TMDEA (10 mass/mass%) were added. The mixture was supplemented with distilled water, so that the final concentration of monomers was about 15 mass/mass%. Finally it was flushed with argon for 15 min. The flasks were placed in a thermostatically chamber at 55°C for 3 h. Acrylic and methacrylic acids were employed in form of ammonia salts obtained by neutralization. Concentrations of both the monomers were determined by bromination. The composition of monomers used in the present research as well as their acronyms are shown in Table 1. Examples of hydrogel structures are depicted in Fig. 1.

**Table 1** Chemical constitution of hydrogels

| No. | Composition | Character | Acronym |
|---|---|---|---|
| 1 | AAm+NMBA | non-ionic | Hydrogel-1 |
| 2 | MAAm+NMBA | non-ionic | Hydrogel-2 |
| 3 | 0.5AAm+0.5MAAm+NMBA | non-ionic | Hydrogel-3 |
| 4 | AANH$_4$+NMBA | ionic | Hydrogel-6 |
| 5 | AANH$_4$+3A2H | ionic | Hydrogel-7 |
| 6 | MANH$_4$+NMBA | ionic | Hydrogel-9 |
| 7 | MANH$_4$+3A2H | ionic | Hydrogel-10 |
| 8 | 0.3AANH$_4$+0.7AAm+NMBA | ionic | Hydrogel-11 |

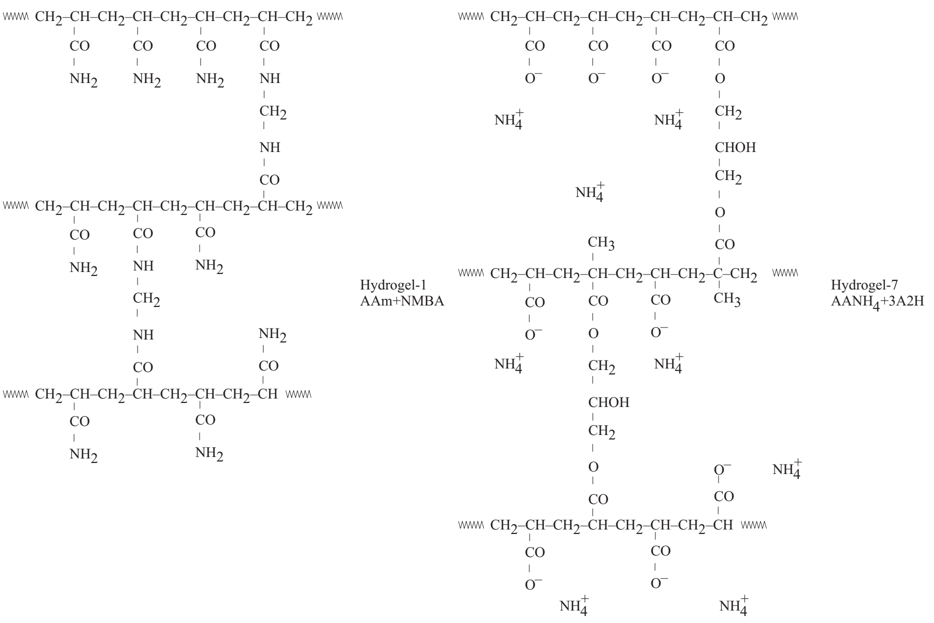

**Fig. 1** Structural formulas of the non-ionic (Hydrogel-1) and ionic (Hydrogel-7) polymer networks

Thermogravimetry (TG) coupled with mass spectrometry analysis (MS-TG/DTG) experiments were performed using Mettler-Toledo 851$^e$ apparatus in 40 μL closed aluminum crucibles with a microhole [4, 5] under flow of argon (80 mL min$^{-1}$), within temperature range 25–600°C with heating rate of 5°C min$^{-1}$. The simultaneous evolved gas analysis (EGA) was performed during the experiments by joined on-line quadruple mass spectrometer (QMS) (Thermostar-Balzers).

Differential scanning calorimetry (DSC) experiments were performed using Mettler-Toledo 821$^e$ calorimeter equipped with intracooler Haake in 40 μL closed aluminum crucibles with a microhole [5] under constant flow of argon (80 mL min$^{-1}$) within temperature range 25–600°C with the same heating rate of 5°C min$^{-1}$ as TG experiments.

## Results and discussion

As can be seen from the figures in the range between 90–105°C the only event which takes place is the evaporation of water from the polymer. For non-ionic hydrogels the temperature range in which water is evolving appears to be less narrow (Figs 2 and 4). Hydrogels synthesized from ammonium acrylate and/or methacrylate displays a much broader range of temperatures for the loss of water while the DTG peaks are asymmetric (Figs 3 and 5). At temperatures between 180–230°C the polymer is eliminated and/or is burned. Broader ranges of temperature are favourable from the production point of view of the green bodies for the gelcasting. The reason is to get a uniform gel-structure at the first stage of green body formation.

From the DSC measurements enthalpies of water evaporation (Δ*H*) have been calculated (Table 2). The results were compared to the respective enthalpy for

**Table 2** The average values of Δ*H* (enthalpy of water evaporation) and determination the content of water in hydrogels

| Sample | Water content/% | | $-\Delta H$/kJ g$^{-1}$ |
|---|---|---|---|
| | TG | DSC | |
| Hydrogel-1 | 85.40 | 87.43 | 2.25809 |
| Hydrogel-2 | 85.70 | 85.57 | 2.20214 |
| Hydrogel-3 | 85.60 | 86.62 | 2.23178 |
| Hydrogel-6 | 80.60 | 79.61 | 2.17861 |
| Hydrogel-7 | 81.80 | 75.74 | 2.04218 |
| Hydrogel-9 | 74.00 | 66.40 | 1.97903 |
| Hydrogel-10 | 71.80 | 72.76 | 2.23524 |
| Hydrogel-11 | 72.40 | 70.37 | 2.14373 |
| $H_2O$ | – | – | 2.20560 |

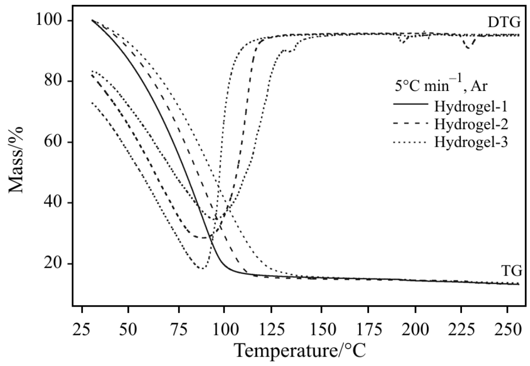

**Fig. 2** TG/DTG analysis of dehydration of the non-ionic hydrogels

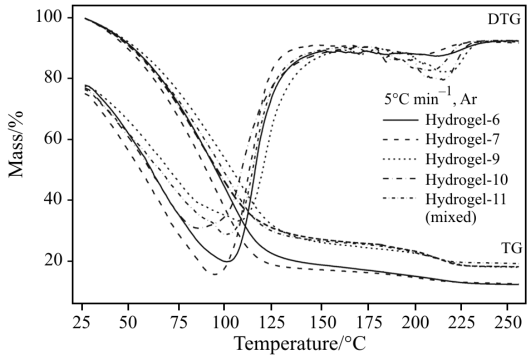

**Fig. 3** TG/DTG analysis of dehydration of the ionic hydrogels

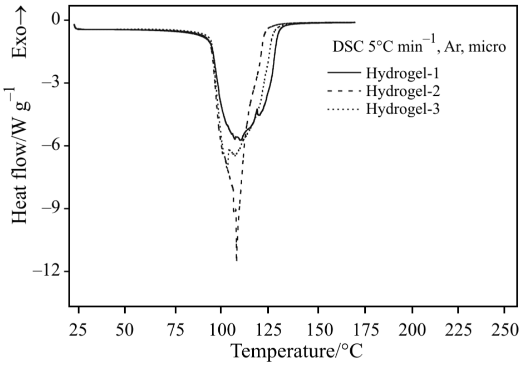

**Fig. 4** DSC curves of dehydration of the non-ionic hydrogels

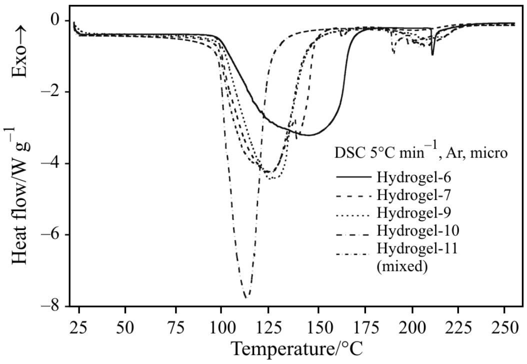

**Fig. 5** DSC curves of dehydration of the ionic hydrogels

evaporation of pure water. Differences in $\Delta H$ may result from various kinds of the chemical networks and of their not a like hydrophilic character.

## Conclusions

The key to produce green bodies effectively is to prepare hydrogels which release water on drying in the same way as if no polymer-networks were present. That condition is providing by those hydrogels which have been synthesized from non-ionic monomers cross-linked by NMBA (Table 2 and Figs 2 and 4).

In case of ionic networks the results are less favourable due to stronger association effect which hamper the release of water during the drying operation. These findings are in harmony with statements issued in literature [6] on drying of gel-parts contaminated with ionic ingredients. Respective conclusions are yielded from data in Table 2 and the patterns shown in Figs 3 and 5.

Results obtained in investigations in the present paper will be utilized in further researches on the formation of the green bodies based on $ZrO_2$ ceramic powders.

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