*Journal of Ceramic Processing Research. Vol. 13, No. 2, pp. 97~100 (2012)*

JOURNAL OF
**Ceramic Processing Research**

# Properties of porous PSZ ceramics according to the curing behavior of the phenolic resin with varying relative humidity

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**The properties of partially stabilized zirconia (PSZ) as porous ceramics were investigated with various relative humidities (RH) in terms of the curing behavior of the phenolic resin (PR). The PSZ powders with 5 wt.% of PR as a binder were stored in a constant chamber condition at a temperature of 50 °C and different humidity levels (25, 50, 75, and 95%) for 1 h before compaction. The green and the sintered density were gradually decreased with an increase in the humidity level. The porosity of specimens increased and the Young's modulus was decreased in response to a decrease of the sintered density. As the RH level increases, a rough surface and an irregular microstructure of the green body were observed because of the agglomerated particles, and the degree of curing for the PR was improved from 10.1% to 59.7%. The agglomerates were sufficiently hard to endure a compaction pressure owing to the curing of the PR, so the green density was decreased by the large volume of voids and the internal spaces. The curing behavior of PR with various RH was proved by the decomposition of hexamine as a curing agent using FT-IR, which was similar to the effect of temperature on the curing of the PR. It could be concluded that the formation of hard agglomerated particles generate a reduction of green density, and it can affect the properties of porous PSZ.**

**Key words: Porous PSZ ceramics, Relative humidity (RH), Phenolic resin (PR), Curing behavior, Agglomerated particles.**

## Introduction

Porous ceramics have received considerable interest because of their excellent mechanical and thermal properties, so they have been widely used in various industries [1]. In the application of porous structural ceramics, calcia partially stabilized zirconia (CaO-PSZ) has been commonly used in submerged entry nozzles (SEN), and is one of the most important refractories for the continuous casting process in steel making [2]. In this process, an inert gas is injected through a SEN into the system to facilitate the prevention of clogging in the flow delivery system and to promote the collection of inclusions such as $Al_2O_3$ which are responsible for deterioration of steel quality [3].

In the processing of porous ceramics, organic binders, such as poly-vinyl alcohol (PVA), poly-acryl acid (PAA), and phenolic resin (PR), are used not only to provide the good flowability of particles but also to improve the strength of the green body [4]. It is important to select the appropriate organic additives, because the additives can enhance the strength of the green body without defects like the surface segregation of the binder and the agglomerated particles [5]. Among them, the PRs have been widely used in many industrial applications as thermosetting binders due to their excellent thermal and chemical resistance, dimensional stability, and low manufacturing cost [6-7].

The environmental conditions strongly influence the properties and performance of porous ceramics in the fabrication process [8]. When a change in the green density has occurred by an environmental condition in the manufacturing process of a SEN, it could affect the properties such as thermal shock resistance and permeability which might cause a cease in the operations. Because the deformation behavior of the binder is very dependent on moisture and temperature, so a variation of the green density is generated [8]. The PRs, used in a SEN as a binder, are also deformed by the environmental conditions, and it has been reported that the curing behavior of a PR is enhanced by an increase of the temperature [9]. Several studies of the variation of green density with various binders and environmental conditions have been performed. However, there are insufficient studies to elucidate the relation between the properties of porous ceramics containing PR and the relative humidity (RH). An investigation of the influence of the curing behavior of a PR on the properties was needed to prevent undesirable property variations of porous ceramics with RH.

In the present study, the properties of porous PSZ ceramics containing PR as a binder were evaluated with various RH. The thermodynamic behavior and intermolecular interactions of the PR were investigated to verify the relation between the properties of a porous PSZ and the curing behavior of PR with atmospheres of different humidity levels.

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## Experimental procedure

Partially stabilized zirconia (below 10 μm) with a 4 wt.% CaO addition and phenolic resin (Kangnam Chemical Co., Novolac) as a binder were used to prepare the porous specimens. They were mixed using a ball mill with zirconia balls for 24 h. The mixture, containing 5 wt.% of the binder, was exposed at different RHs 25, 50, 75, and 95% for 1 h, and maintained by using a constant temperature & humidity chamber (Aero Tech, TATC-150). The mixture was pressed into a cylindrical steel die of 25 mm diameter under a uniaxial pressure of 20 MPa, and then the green density was measured. The green bodies were kept in a humidity-controlled desiccator so as to avoid any dimensional changes due to the effects of the ambient humidity.

The microstructures of the fracture surfaces for the green bodies were observed by using a scanning electron microscope (SEM, Hitachi, S-4700). The green bodies were fired at 1000 °C for 1 h, and the apparent density and the porosity of specimens were determined via water immersion based on the Archimedes method [10]. The elastic property of the specimens was evaluated from a pulse velocity method using an ultrasonic tester at 50 kHz (Marui & Co., Ltd, MIN-020-1-00). Differential scanning calorimetry (DSC, TA Instruments Ltd, Q200) was used to analyze the exothermic peak related curing of PR. The thermograms were obtained over a temperature range of 90-200 °C at a heating rate of 10 $K \cdot min^{-1}$ in an inert atmosphere. The area under the exothermic peak enclosed by a baseline is associated with the amount of the heat reaction for the curing of PR. The degree of curing for PR was defined by the equation [11], $\alpha = (Q_T - Q_R)/Q_T$, where $Q_T$ was the reference value for the total heat of curing for the PR without exposure to a humid atmosphere, $Q_R$ was the residual heat of curing for the PR exposed to a humid atmosphere, and α was converted into the percentage of curing. The curing behavior of PR was established by the analysis of the inter-molecular interactions of the binder using a Fourier transform-infrared spectroscopy (FT-IR, Thermo Scientific, Nicolet 6700). Infrared spectra on KBr pellets were averaged over 20 scans taken at 4 $cm^{-1}$ resolution and recorded from 4000 to 400 $cm^{-1}$.

## Results and Discussion

The PSZ powders containing 5 wt.% of PR were exposed in the humidity range from 25 to 95% RH for 1 h before compaction to confirm the effects of RH on the properties of porous PSZ ceramics. Fig. 1 shows the variation of green and sintered density of the porous specimens. The green density was gradually decreased with increasing RH level, and the sintered density was dropped from 3.85 $g/cm^3$ to 3.61 $g/cm^3$ in response to the change in green density. Also, the width of the density distribution was relatively extended at higher RH levels, so this variation may cause the large deviation in properties of the sintered body. It was anticipated that the moisture in the humid atmosphere influenced the deformation characteristics of the PR molecules as a binder.

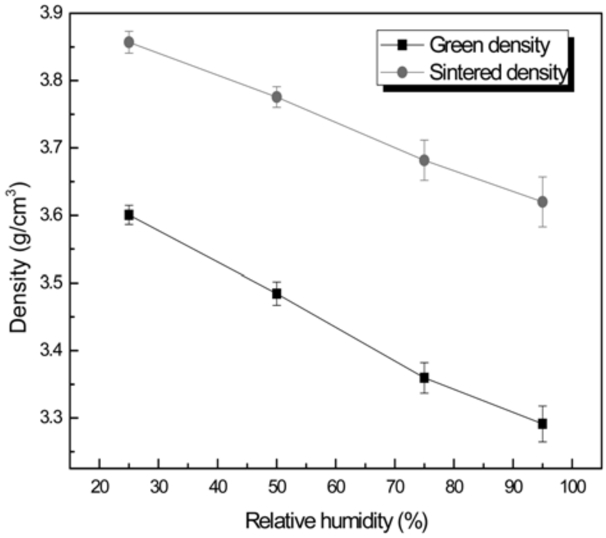


**Fig. 1.** Green and sintered density of the PSZ as a function of RH.

The porosity and the Young's modulus of specimens were measured and are shown in Fig. 2 to prove the relation between the properties of porous PSZ specimens and the RH. The Young's modulus of specimens was reduced from 2.34 GPa to 2.21 GPa and the porosity rose from 35.7% to 38.1% with increasing RH levels, respectively. The properties were linearly transformed corresponding to the changes in green and sintered density as shown in Fig. 1. Also, the specimens exposed to 75% and 95% RH show a wider scatter of data than the other specimens. It seems that the relatively larger moisture contents in the humid atmosphere generate a large scatter of porosity and Young's modulus. From these results, it is suggested

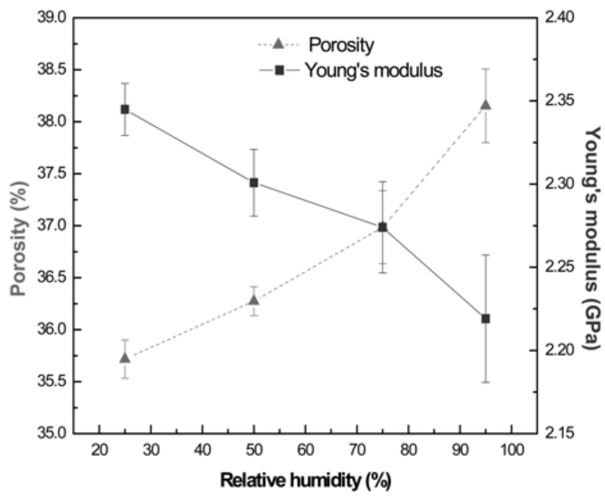


**Fig. 2.** Porosity and dynamic Young's modulus of porous PSZ specimens as a function of RH.

that an exposure to the humid atmosphere beyond 75% RH can cause poor durability and a lack of reproducibility of porous PSZ.

Fig. 3 shows SEM images of the fracture surfaces of green bodies exposed at 25% and 95% RH. The microstructure of the specimen exposed at 25% RH (Fig. 3(a)) exhibited a uniform and dense microstructure, whereas the micrograph of the specimen exposed at 95% RH (Fig. 3(c)) showed an irregular microstructure with a rough surface. Compared at a higher magnification, the specimen at 25% RH (Fig. 3(b)) appeared with a relatively homogeneous particle size ranging from 1 to 5 μm, while the specimen at 95% RH (Fig. 3(d)) had some agglomerated particles above 10 μm. The agglomerated particles were formed by the increase of the moisture content in the humid atmosphere, which led to a large volume of voids and internal spaces. It seems that these agglomerates were sufficiently hard to endure at a pressure of 20 MPa, so the green density was decreased by the large volume of voids and the internal spaces.

From DSC curves in Fig. 4(a), the curing behavior of PR with at different RH levels was determined. The PRs exhibited a broad exothermic peak (120-160 °C), and the peak was attributed to a condensation reaction of the methylol groups which leads to an insoluble and infusible network [12]. As the RH level increases, the exothermic peaks became smaller, and this result indicates that when PRs were exposed to a humid atmosphere, the moisture in the air could enhance the curing rate and the degree of curing.

The areas under the exothermic peaks enclosed by a baseline were calculated to determine the degree of cure for the PR, and an illustrated in Fig. 4(b). The degree of cure for the PR was improved with an increase in the RH level. In particular, the slope relatively rapidly increased between 50% and 75% RH from 22.2% to 46.1% cure. It is proposed that the curing reaction of PR may be prominent above 50% RH. Upon elevation of the RH levels, the curing of the PR made the agglomerated particles harder, so it was difficult to deform at a given compaction pressure.

FT-IR spectra of the PRs exposed at 25% and 95%

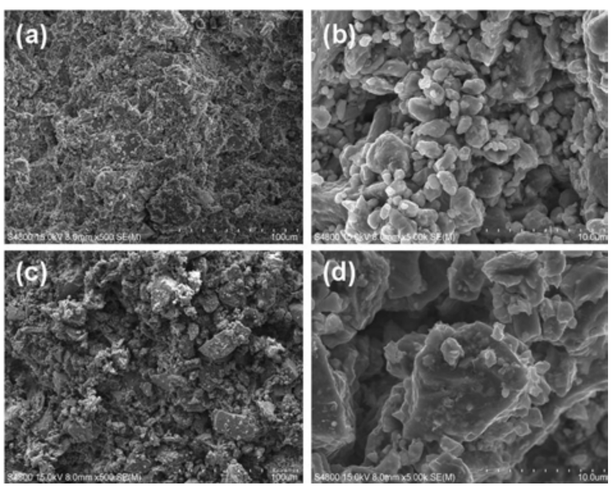


**Fig. 3.** SEM images of fracture surfaces of green bodies : (a) exposed at 25% RH, (b) higher magnification, (c) exposed at 95% RH, and (d) higher magnification.

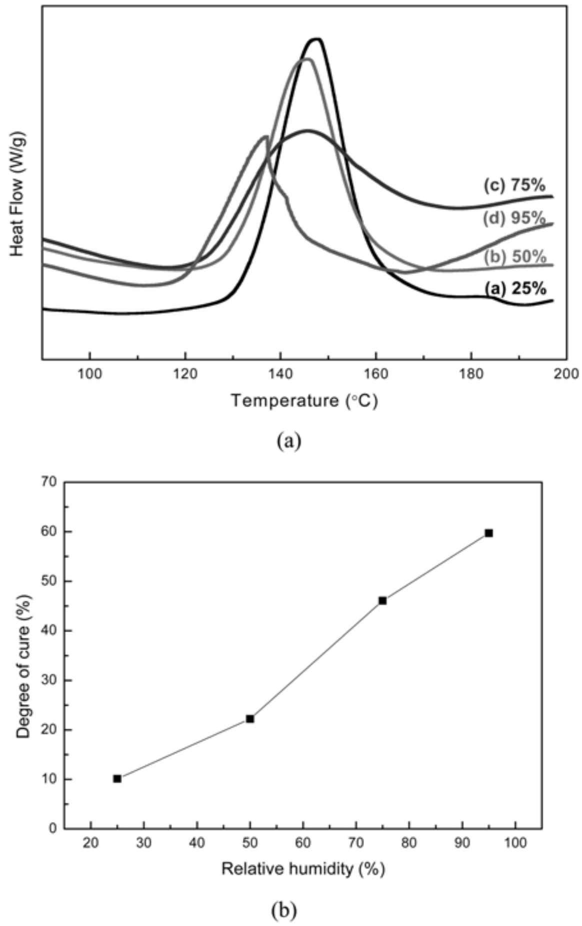


**Fig. 4.** (a) DSC thermogram curves of PR and (b) degree of curing for PR as a function of RH.

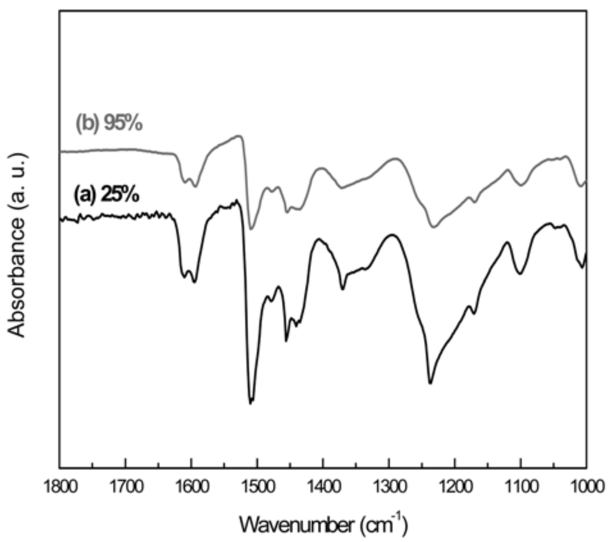


**Fig. 5.** FT-IR spectra recorded in the 1800-1000 cm$^{-1}$ region of the PR (a) exposed at 25% RH and (b) exposed at 95% RH.

RH are presented in Fig. 5. The bands corresponding to the ether groups (1200-1300 $cm^{-1}$) and the phenolic ring substituted at the *ortho* or *para* positions (1500 $cm^{-1}$) distinctly appeared in the PR sample stored at 25% RH (Fig. 5(a)), while the bands were diminished in the PR sample stored at 95% RH (Fig. 5(b)) [13]. These results were interpreted in that the ether groups were attributed to the interaction with the phenolic-OH group and the hexamethylenetetramine (hexamine). The reduction of ether groups was associated with the decomposition of hexamine as a curing agent, because the moisture in the humid atmosphere acted as a catalyst for the decomposition of hexamine. Choi *et al*. demonstrated the curing behavior of PR with an increase in the temperature from 25 °C to 240 °C using FT-IR [9]. They reported that the intensity of the band at 1500 $cm^{-1}$ started to decrease at 90 °C, and the intensity abruptly decreased at 140-150 °C. In this study, the experiment was carried out under a constant temperature of 50 °C and different RH levels (25, 50, 75, and 95%) to establish the curing behavior of PR. The degree of curing was prominent beyond 50% RH, and it was improved with an increase in the RH despite the temperature being lower than 90 °C. A reduction of the band at 1500 $cm^{-1}$ was observed as shown in Fig. 5, and these results correspond with the study for the effect of temperature on the curing behavior. As a result, this suggests that temperature and RH affect the curing of PR with a catalytic role. Therefore, the properties of porous PSZ are varied with a reduction of the green density because of the formation of hard agglomerated particles. The hardened agglomerates arose from the curing of the PR which is enhanced by an increase in the temperature and/or the RH.

## Conclusions

The effects of the curing behavior of PR on the properties of porous PSZ sample with different RH levels were investigated. As the RH level increases, a lower green density and a more irregular microstructure were observed because of the agglomerated particles. The variation of density, porosity, and Young's modulus of specimens after firing were also correlated with the decrease of green density. The density and the Young's modulus of specimens were gradually reduced, whereas the porosity was increased. These results were explained by the curing of the PR which made the agglomerated particles harder, so it was difficult to deform samples at a given compaction pressure. The curing behavior of PR with different RH levels has been confirmed as due to the decomposition of hexamine as a curing agent. This suggests that the curing of PR occurred by an increase of the temperature and/or the RH, because they affect the curing of PR with a catalytic role. Consequently, the changes in the properties of porous PSZ can originate from the formation of agglomerated particles with a rise in the degree of curing for PR due to an increase of the moisture content.

## Acknowledgement

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy (M-2009-01-0028) and partially supported by grants-in-aid for the National Core Research Center Program from MEST/KOSEF (No. R15-2006-022-01001-0), Republic of Korea.

## References

1. G.J. Zhang, J.F. Yang and T. Ohji, J. Am. Ceram. Soc. 84 (2001) 1395-1397.
2. M.O. Suk and J.H. Park, J. Am. Ceram. Soc. 92 (2009) 717-723.
3. G.M. Evans, G.D. Rigby, T.A. Honeyands and Q.L. He, Chem. Eng. Sci. 54 (1999) 4861-4867.
4. S. Baklouti, J. Bouaziz, T. Chartier and J.F. Baumard, J. Eur. Ceram. Soc. 21 (2001) 1087-1092.
5. S. Tanaka, C.C. Pin and K. Uematsu, J. Am. Ceram. Soc. 89 (2006) 1903-1907.
6. X.M. Wang, B. Riedl, A.W. Christiansen and R.L. Geimer, Wood Sci. Technol. 29 (1995) 253-266.
7. M.O. Abdalla, A. Ludwick and T. Mitchell, Polymer 44 (2003) 7353-7359.
8. Y. Saito, J. Nyumura, Y. Zhang, S. Tanaka, N. Uchida and K. Uematsu, J. Eur. Ceram. Soc. 22 (2002) 2835-2840.
9. M.H. Choi, I.J. Chung and J.D. Lee, Chem. Mater. 12 (2000) 2977-2983.
10. M. Chen, C. Lu and J. Yu, J. Eur. Ceram. Soc. 27 (2007) 4633-4638.
11. X.M. Wang, B. Riedl, A.W. Christiansen and R.L. Geimer, Polymer 35 (1994) 5685-5692.
12. A.W. Christiansen and L. Gollob, J. Appl. Polym. Sci. 30 (1985) 2279-2289.
13. M.P.S. Aan, M. Krishna, H.N.N. Murthy and S. K. Rai, Fiber. Polym. 11 (2010) 1083-1087.