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Rheological property and drying mechanism of thermoresponsive gelcasting of ZnO

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Abstract: To solve the problem of drying gelcast green body, the thermoresponsive gel system which contains macromonomer graft chains was used in gelcasting of ZnO. The effects of the amount and length of graft chains macromonomer PIPAAm, the total amount of organic matters, and the solid loading on the rheological properties of suspensions were investigated, and the drying mechanism of gelcast green body was analyzed. The results show that ZnO suspensions with the gel system still display shear-thinning rheological behavior, but its viscosity increases with increasing the addition amount and relative molecular mass of PIPAAm graft chain, and the total organic matter content. The PIPAAm graft chains inhibit or even eliminate the formation of the "dense layer" on the surface of gelcast ZnO green bodies, and accelerate the drying of green bodies. The introduction of PIPAAm graft chains facilitates the shrinkage of the gelcast ZnO green bodies, which is a feasible method to increase the relative density of green bodies.
Key words: ZnO; gelcasting; thermoresponse; rheological property; drying mechanism; *N*-isopropylacrylamide

1 Introduction

Gelcasting is a near-net-shape forming technique for making high-quality complex-shaped ceramic parts [1−3]. The advantages of this technique over conventional forming techniques are that, green bodies formed by this technique have high strength, high density and excellent machinability, and can be used to prepare large-sized complex-shaped parts at low cost [3,4]. However, despite these advantages, gelcasting has disadvantages, among which low drying efficiency is the most obvious one that has become the bottleneck restricting the development of gelcasting [4−6]. To solve this problem, JANNEY et al [7,8] proposed a liquid desiccant method that relies on the chemical potential difference to release the water inside the green bodies immersed in the liquid desiccant. This method increases the drying rate to a certain extent, but the drying efficiency is still fairly low. In fact, whether a green body is dried in air [6,9] or in liquid [8−10], the water on the surface of green body in direct contact with the atmosphere can be easily released. However, as drying proceeds, an increasingly thick and dense layer forms on the surface of green body, which makes it more and more difficult to remove the interior water and finally leads to a very low drying rate of the green body.

Recently, a thermoresponsive gelcasting technique by incorporating a thermoresponsive gel system into gelcasting has been proposed to effectively solve the problem of green body drying [5]. The wet alumina ceramic parts prepared by this technique are almost completely dried at 50 °C for 70 min. This technique considerably shortens the drying time of gelcast green bodies. In this work, this gel system was used in gelcasting of ZnO nanopowders. The effects of the addition amount and length of macromonomer graft chain, the total amount of organic matters, and the solid loading on the rheological properties of suspensions were investigated, and the drying mechanism of thermoresponsive gelcasting was analyzed.

2 Experimental

2.1 Synthesis of macromonomer graft chain poly (*N*-isopropylacrylamide) (PIPAAm)

The macromonomer graft chains PIPAAm were synthesized by the same procedure as reported in the

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previous work [11]. *N*-isopropylacrylamide (IPAAm, Aladdin Regent Co., Shanghai, China), 2-aminoethanethiol (AESH, Tokyo Chemical Industry Co., Japan) and *N*,*N*′-azobisisobutyronitrile (AIBN, Shanghai Chemical Reagent Co., China) were dissolved in *N*,*N*-dimethylformamide (DMF, Shanghai Chemical Reagent Co., China). The solution was bubbled with dried nitrogen gas for 10 min to remove the dissolved oxygen and then polymerized at 75 °C for 12 h. The reactant was poured into a large amount of diethyl ether to precipitate the semitelechelic PIPAAm. The polymer product was collected over a filter and purified by repeated precipitation in diethyl ether from DMF. The relative molecular mass of the graft chain was controlled to be 550, 1100, 4400, and 8800 by tailoring the monomer content. In order to introduce a polymerizable end group, the amino semitelechelic PIPAAm was reacted with *N*-acryloxysuccinimide (NAS, Tokyo Chemical Industry Co., Japan) in DMF at 4 °C. The reactant and product were also treated by repeated precipitation in diethyl ether [12].

2.2 Gelcasting

The gelcast ZnO green bodies were fabricated by typical gelcasting processing [5]. ZnO powders (d_{50}= 100 nm, Jiangxi Huarun Co., China) were added to a pre-mixed aqueous solution containing monomer *N*-isopropylacrylamide (IPAAm, Shanghai Chemical Reagent Co., China), cross-linker *N*,*N*′-methylenebisacrylamide (MBAM, Shanghai Chemical Reagent Co., China), macromomomer graft chain PIPAAm (30%, 40% and 50% in mass fraction of total organic matter) and dispersant ammonium polyacrylate (NH_4PAA). After ball milling for 24 h (mass ratio of ball to materials 1:1), ZnO suspensions with different solid loadings (10%, 20% and 30% in volume fraction) were obtained. The suspensions were degassed under vacuum, and initiator ammonium persulfate (APS, Shanghai Chemical Reagent Co., China) and catalyst *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, Shanghai Chemical Reagent Co., China) were added at room temperature (25 °C). The solution was then poured into a mold. After curing reaction within the suspensions, the green bodies were removed from the molds.

2.3 Characterization

The rheological behavior of the suspensions was investigated using a stress-controlled rheometer (AR2000, TA, USA) with a parallel plate of 40 mm in diameter. The viscosity measurements were performed in steady flow mode with a steady-state of shear rate ranging from 0.1 to 500 s^{-1}.

The bodies were dried in an oven at 50 °C according to the previous work [5]. The body was taken out every 10 min from the oven, and the residual liquid at the surface was absorbed by cotton, after which the mass and size of the bodies were measured. An electronic balance (Mettler−Toledo Co., Ltd., China) with an accuracy of 0.001 g was used to measure the mass and a vernier caliper (Harbin Measuring and Cutting Tool Group Co., Ltd., China) with an accuracy of 0.001 mm was used to measure the size [11].

3 Results

3.1 Rheological behavior of ZnO suspensions

Figure 1 shows the effect of the amount of macromonomer PIPAAm (the mass fraction of PIPAAm to IPAAm) on the rheological properties of ZnO suspensions. It is shown that the addition of PIPAAm does not change the rheological behavior of the suspensions, which still displays shear-thinning behavior. However, the viscosity of the suspensions increases with increasing the PIPAAm content. At a shear rate of 150 s^{-1}, the suspension without PIPAAm has a viscosity of 0.07 Pa·s whereas its viscosity increases to 0.2 Pa·s when the macromonomer content increases to 50%.

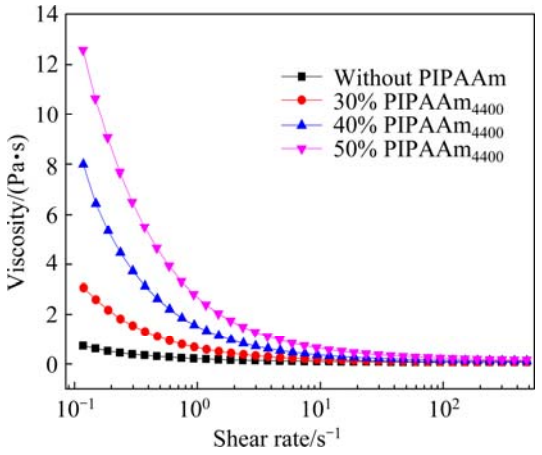

Fig. 1 Effect of PIPAAm content on viscosity of ZnO suspensions (Relative molecular mass of PIPAAm is 4400)

Figure 2 shows the effect of the relative molecular mass of PIPAAm on the rheological properties of suspensions. At a shear rate of 150 s^{-1}, the addition of PIPAAm graft chains with relative molecular mass of 550 and 1100 do not lead to any increase of suspension viscosity, which still remains at 0.07 Pa·s. When the relative molecular mass of the macromonomer graft chains is 4400 and 8800, the suspension viscosities increase slightly to 0.09 and 0.13 Pa·s, respectively, at the shear rate of 150 s^{-1}. This indicates that the relative molecular mass of PIPAAm has a certain effect on the suspension viscosity.

Figure 3 displays the effect of the total organic matter content (IPAAm+MBAM+PIPAAm) (the mass

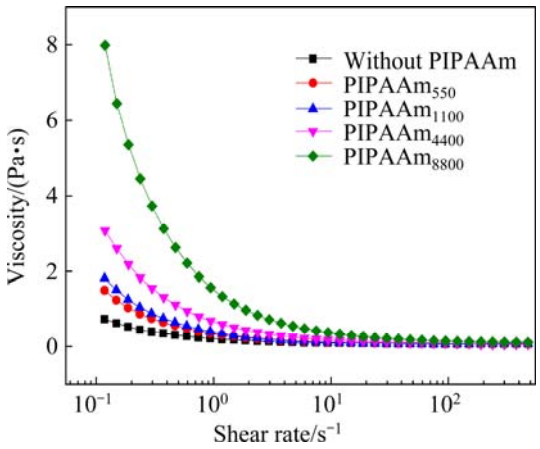

Fig. 2 Effect of relative molecular mass of PIPAAm on viscosity of ZnO suspensions (Solid loading of bodies is 30% in volume fraction)

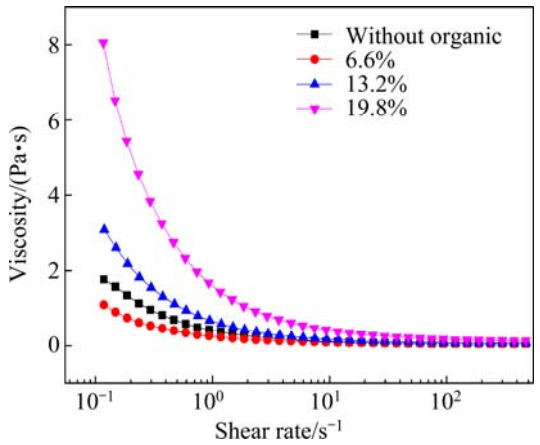

Fig. 3 Effect of total organic content on viscosity of ZnO suspensions (Solid loading of bodies is 30% in volume fraction)

fraction of organic matters relative to water) on the rheological properties of suspensions. When the total organic matter content is 6.6%, the viscosity of the suspension is slightly lower than that of the suspension containing no organic matters. When the organic matter contents increase to 13.2% and 19.8%, the suspension viscosity increases to 0.09 and 0.16 Pa·s, respectively, at the shear rate of 150 s^{-1}. It can be concluded that the addition of organic matters results in increased suspension viscosity, and the higher the organic matter content, the greater its effect on the viscosity.

Figure 4 shows the effect of the solid loading on the rheological properties of ZnO suspensions. As shown in Fig. 4, the suspension viscosity increases with increasing the solid loading. At a shear rate of 150 s^{-1}, the suspension viscosity increases from 0.07 to 0.09 Pa·s when the volume fraction of the solid increases from 20% to 30%.

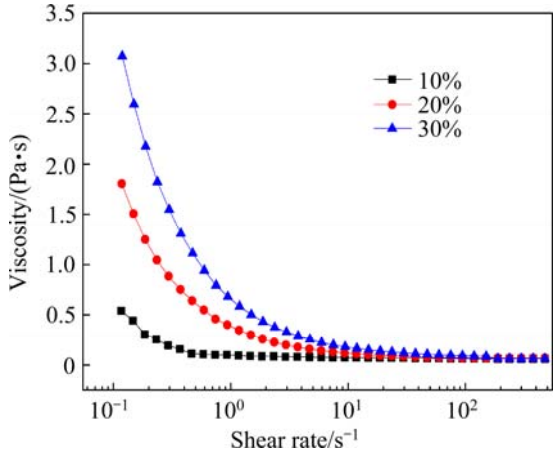

Fig. 4 Effect of solid loading on viscosity of ZnO suspensions (Relative molecular mass of PIPAAm is 4400)

3.2 Drying behaviors of ZnO thermoresponsive gelcasting green bodies

Figure 5 shows the effects of the amount of macromonomer PIPAAm on the mass fraction and length fraction of ZnO green body with 30% solid loading dried at 50°C. After 30 min drying, the ZnO green bodies

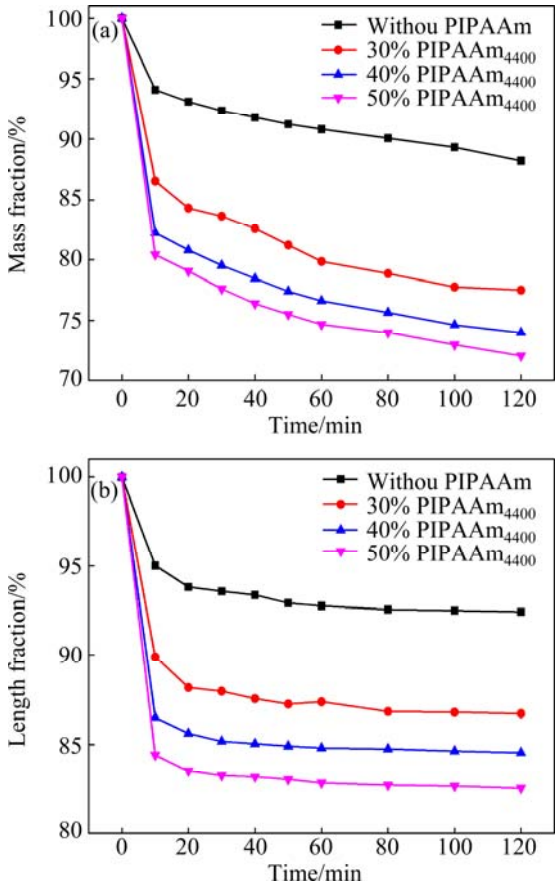

Fig. 5 Drying behaviors of ZnO thermoresponsive gelcasting green bodies with different PIPAAm contents: (a) Mass fraction; (b) Length fraction (Relative molecular mass of PIPAAm is 4400, and drying temperature is 50 °C)

containing no PIPAAm display only 6% mass loss and 6% linear shrinkage, whereas both the mass loss and linear shrinkage of green bodies containing PIPAAm are above 10%. When the amount of PIPAAm is 50%, the green body exhibits 23% mass loss and 17% linear shrinkage. It can be seen that as drying proceeds, the mass fraction and length fraction of the green body first decrease rapidly and then followed by a slow downward trend.

Figure 6 displays the effects of the PIPAAm graft chain length on the mass fraction and length fraction of ZnO green body with 30% solid loading dried at 50 °C. As shown in Fig. 6, after the addition of PIPAAm with different chain lengths, the green bodies exhibit a trend of fast initial decrease followed by subsequent slow reduction in both mass fraction and length fraction. In addition, as the length of PIPAAm graft chain increases, the green bodies release water at a significantly fast rate, leading to shortened drying time. After drying 30 min, the green body containing macromonomer with a relative molecular mass of 8800 exhibits around 20% mass loss, whereas the additions of PIPAAm with relative molecular mass of 550, 1100 and 4400 cause mass loss of 13%, 15% and 16%, respectively.

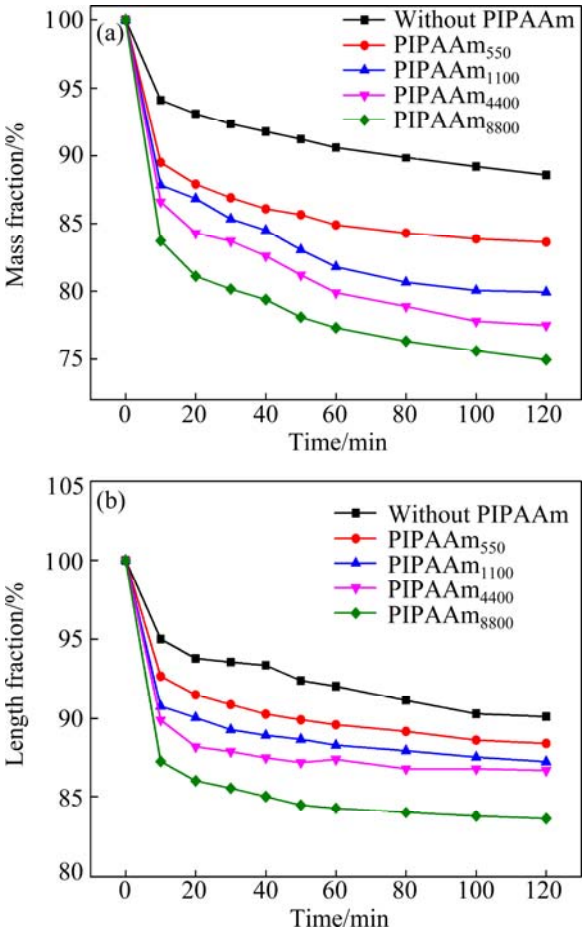

Fig. 6 Drying behavior of ZnO thermoresponsive gelcasting green bodies with different relative molecular mass of PIPAAm: (a) Mass fraction; (b) Length fraction (Solid loading of bodies is 30% in volume fraction, and drying temperature is 50 °C)

Figure 7 shows the effects of the organic matter content on the mass fraction and length fraction of ZnO green bodies with 30% solid loading dried at 50 °C. It is shown that both the mass fraction and length fraction of the green bodies exhibit a trend of fast initial decrease, followed by subsequent slow reduction. After drying for 30 min, the green body with 6.6% organic matters is found to have 14% mass loss and 10% linear shrinkage, whereas that with 19.8% organic matters is found to have 18% mass loss and 14% linear shrinkage. This indicates that the water release performance of the green bodies is improved as the organic matter content increases.

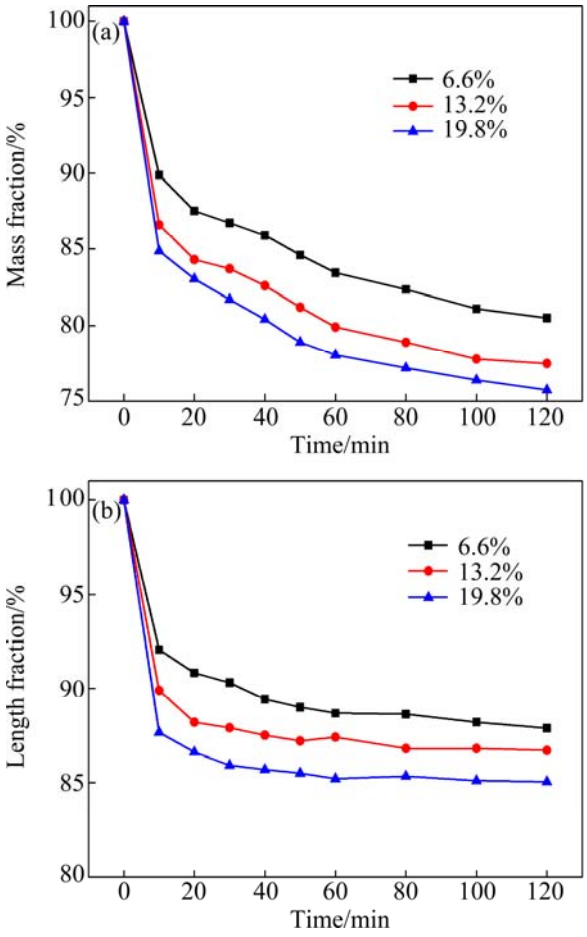

Fig. 7 Drying behavior of ZnO thermoresponsive gelcasting green bodies with different total organic contents: (a) Mass fraction; (b) Length fraction (Solid loading of bodies is 30% in volume fraction, and drying temperature is 50 °C)

Figure 8 displays the effects of solid loading on the mass fraction and length fraction of ZnO green bodies with the same PIPAAm content dried at 50 °C. As shown in Fig. 8, as the solid loading decreases, more and more significant changes in the mass fraction and length fraction of green bodies are observed. In addition, the

mass fraction and length fraction curves of the green bodies also exhibit a trend of fast initial decrease, followed by subsequent slow reduction over time. After drying for 30 min, the green body with 10% solid loading exhibits 35% mass loss and 30% linear shrinkage, whereas the green body with 30% solid loading displays 17% mass loss and 12% linear shrinkage. This indicates that the solid loading has a considerable effect on the dehydration of green bodies.

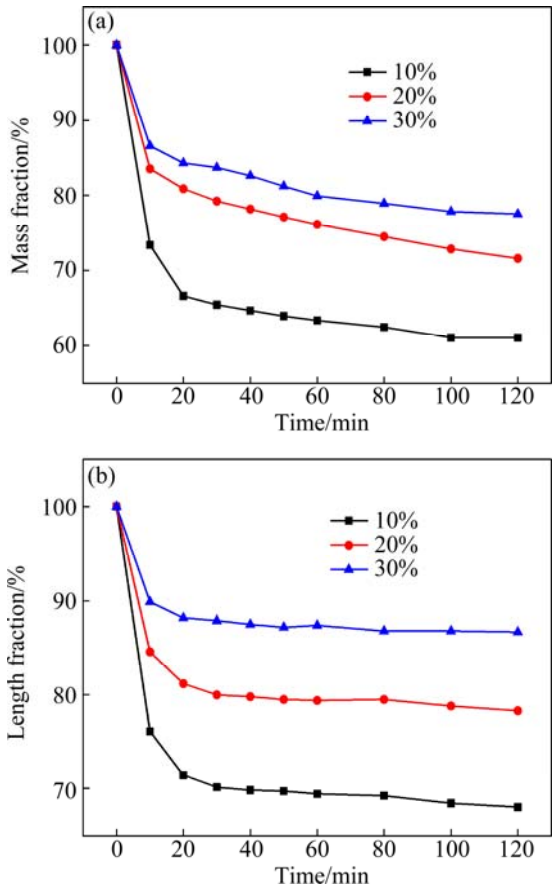

Fig. 8 Drying behavior of ZnO thermoresponsive gelcasting green bodies with different solid loadings: (a) Mass fraction; (b) Length fraction (Relative molecular mass of PIPAAm is 4400, and drying temperature is 50 °C)

4 Discussion

4.1 Factors affecting rheological properties of ZnO suspensions

In suspensions, the polymer molecules dissolved in solvent are either absorbed on the surfaces of powders, or in a free state. In the suspensions for gelcasting, stably dispersed powders absorb the dispersing agent, so organic matters such as polymer monomer and crosslinking agent mainly exist in a free state. On the one hand, these free polymer chains increase the viscosity of the solvent; on the other hand, they tend to cause bridging, depletion flocculation and other effects [13] that lead to increased viscosity and decreased stability of the suspensions, especially when there is excessive amount of free-state organic matters. Therefore, the tests show that the addition of organic matters, such as IPAAm, MBAM and PIPAAm, results in increased suspension viscosity (Fig. 3), which is in agreement with the results reported by YOUNG et al [2] and MAO et al [14].

As the amount of organic matters increases, the viscosity of the solvent increases, leading to increased suspension viscosity. Meanwhile, according to the polymer dissolution theory, when the solvency of a polymer exceeds a critical value (normally measured by Flory−Huggins constant, χ), sterically stabilized particles flocculate the so-called incipient flocculation [15], which also causes increased suspension viscosity. Therefore, increasing the amount of PIPAAm leads to increased suspension viscosity and the growth rate is high when the amount of PIPAAm is high (Fig. 1).

In fact, this change pattern with respect to the effect of free-state organic matters on suspension viscosity has been confirmed in other studies [13,15,16]. Similarly, increasing the relative molecular mass of polymer results in increased viscosity of the solvent and increased possibility of interlacing and bridging of molecular chains, finally leading to increased suspension viscosity. Therefore, increasing the relative molecular mass and length of macromonomer PIPAAm graft chain results in increased suspension viscosity (Fig. 2); the larger the relative molecular mass, the higher the extent of increase in suspension viscosity. The addition of $PIPAAm_{8800}$ graft chain results in a rapid increase of viscosity of the ZnO suspension, which complies with the change pattern with respect to the effect of the relative molecular mass of the dispersing agent on the suspension viscosity proposed by BARICK et al [17].

The suspension viscosity depends on the solid loading to a considerable extent. As the solid loading increases, the average distance between particles in the suspension decreases so as to increase the particle contact probability, which means increased chance of particle aggregation due to collision, leading to increased suspension viscosity [18]. Therefore, the viscosity of ZnO suspensions also increases with increasing the solid loading.

4.2 Drying mechanism of thermoresponsive gelcast green body

As a very important step in wet forming techniques, such as tap casting, the drying step determines the formation of defects in wet green bodies as well as the subsequent sintering step and directly affects the yield of finished products. Conventional gelcasting techniques possess very low drying efficiency of green bodies,

which seriously restricts the application of gelcasting techniques. In a conventional gelcasting process, an acrylamide gel system is introduced into the gelcasting process to obtain green bodies consisting of ceramic powders, water and organic matters with a three-dimensional network structure. In fact, according to the structural theory of organic chemistry, such green bodies are complexes of ceramic powders and aqueous acrylamide gel. Aqueous gel forms a "dense layer" inhibiting water diffusion from the inside to the outside on the surfaces of green bodies during the deswelling (i.e., drying) process and, as drying proceeds, such a "dense layer" becomes increasingly thick and imposes an increasingly strong inhibition effect on the water diffusion. Therefore, for conventional gelcasting procedures, the drying process of the green bodies is inevitably very slow with very low drying efficiency [5,19].

To solve this problem, thermoresponsive gelcasting is proposed, which uses a poly (*N*-isopropylacrylamide) gel system for gelcasting and relies on the hydrophilic−hydrophobic transition of the gel system to release water so as to dry green bodies. The previous study [5] showed that the wet ceramic parts with 50% solid loading formed by using this poly (*N*-isopropylacrylamide) gel system containing thermoresponsive graft chains were almost completely dried at 50 °C for 70 min. During the drying process, the thermoresponsive graft chains "connected" the gel system inside and outside of the green bodies to form channels for releasing the water, so the green bodies prepared using this gel system did not form a "dense layer". Therefore, the wet green bodies formed by thermoresponsive gelcasting can be quickly dried. Figures 9(a) and (b) show the schematic diagrams indicating the drying process of green bodies formed by thermoresponsive gelcasting and the conventional gelcasting procedure, respectively. For the green bodies formed by the conventional gelcasting procedure, during the initial stage, the water on the surface of wet green bodies can readily volatilize and the drying rate is high; as drying proceeds, an increasingly thick "dense layer" forms on the surfaces of the green bodies, leading to increasingly low drying rate; during the final drying stage, since there is a very thick "dense layer" on the surfaces of green bodies, it takes a very long time to completely dry the green bodies and the drying rate is very low. GHOSAL et al [9] investigated the drying process of green bodies formed by the conventional gelcasting procedure and confirmed that this drying process consists of three stages: fast drying stage, decelerating drying stage and slow drying stage. However, for the thermoresponsive gelcast green bodies, during the initial drying stage, the water on the surface of wet green bodies can readily volatilize and the drying rate is high; as drying proceeds, no "dense layer" forms on the surfaces of green bodies, but it takes some time for water inside the green bodies to diffuse to the surface, and the drying rate is a little lower than that of the initial stage. Overall, as drying proceeds, the drying rate of the green bodies is slowly decreased until the green body is completely dried, but the drying rate still remains at a high level. Therefore, the green bodies can be completely dried within a very short time. Accordingly, the drying process of the green bodies consists of two stages: fast drying stage and fairly fast drying stage (slower than the former), which was confirmed by the previous study [5].

As mentioned above, the gelcast green bodies are actually complexes of powders and water gel. Therefore, several factors, such as the amount and length of macromonomer graft chain, and total organic matter content, determine the structure of the aqueous gel so as to inevitably affect the drying of the green bodies. After the introduction of macromonomer graft chains, the

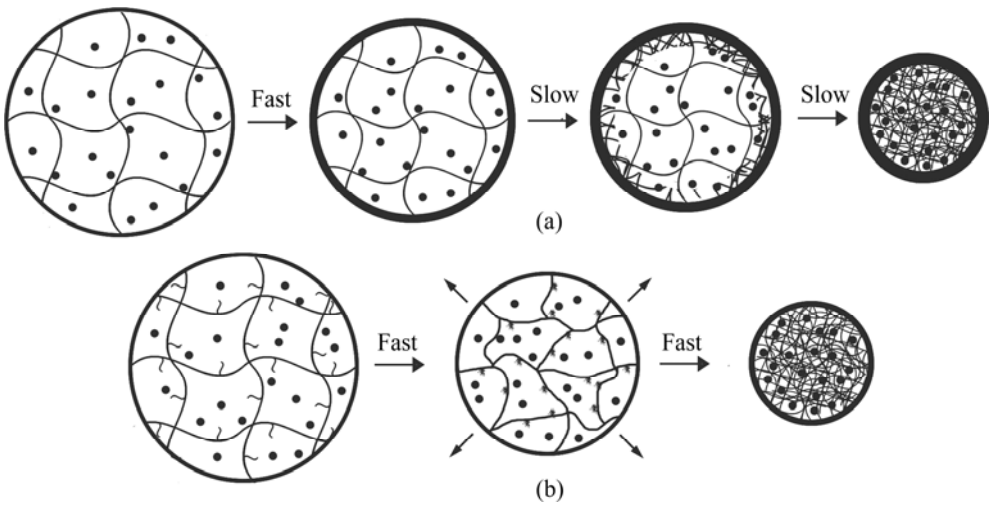

Fig. 9 Schematic diagram of drying mechanism of gelcasting green bodies: (a) Traditional gel system; (b) Thermoresponsive gel systems with grafted chain

freely mobile ends of these graft chains are added into the three-dimensional network structure of the gel. When the temperature is higher than the phase transition temperature, the freely mobile end changes from hydrophilic to hydrophobic to form an "aggregation force" among graft chains [20]. This facilitates three-dimensional network structure shrinkage, thereby releasing the water and drying the green bodies. The test results shown in Figs. 5−7 also confirm this mechanism. Obviously, as the amount of macromonomer graft chains increases, the content of the graft chains grafted into the three-dimensional network structure increases and the amount of the freely mobile end at the graft chain also increases. Therefore, during drying, a strong "aggregation force" is formed inside the green bodies to increase the hydrophobic action and shorten the drying time for the green bodies, as shown in Fig. 5.

KANEKO et al [20] indicated that the length of the macromonomer graft chain is another important factor. When the graft chains are short, the aggregation action among graft chains is relatively weak, resulting in decreased water release performance and increased tendency toward the formation of "dense layer" on the surfaces of green bodies. When the graft chains are long, the freely mobile ends at the graft chains are more mobile, leading to increased hydrophobic association effect and hydrophobic force. Therefore, during the drying process for the green body containing $PIPAAm_{8800}$, there is a stronger "aggregation force" among graft chains and such an "aggregation force" accelerates the aggregation of hydrophobic ends at the graft chains and increases the water repelling force so as to release the water from the inside of green bodies quickly, as shown in Fig. 6.

The total organic matter content directly determines the density of the three-dimensional periodic structure per unit volume of the green bodies. Therefore, during the drying process, as the total organic content in the green bodies increases, the density of three-dimensional network structure increases, the amount of freely mobile ends also increases, both the hydrophobic association effect and the aggregation force of the three-dimensional network structure are also strengthened, resulting in increased water repelling force inside the green bodies and accelerated water release, as shown in Fig. 7.

However, increasing the solid loading alleviates the drying effect on the gelcast green bodies, as shown in Fig. 8. This phenomenon has two main causes. On the one hand, increasing the solid loading results in a longer "diffusion path" that the water inside the green bodies has to pass through, which makes it more difficult to dry the green bodies; on the other hand, the green bodies with high solid loading exhibit stronger inhibition effect on the shrinkage of the three-dimensional network structure than those with low solid loading, and lead to reduced mobility of the freely mobile end at the graft chain. This finding is consistent with the result of the previous study [5].

In addition, Figs. 5−8 also show that the green bodies undergo not only mass loss but also linear (volumetric) shrinkage. If the extent of volume reduction of a green body is larger than the extent of mass loss, the relative density of green body will increase. In other words, it's possible to increase the relative density of a green body formed by thermoresponsive gelcasting through the post drying processing. In fact, this idea has been confirmed by another study [1], which revealed that optimizing the thermoresponsive PIPAAm graft chain and its amount can lead to increased shrinkage of green bodies so as to obtain smaller green bodies of the same mass. Therefore, this measure can also enable increased relative density of green bodies.

5 Conclusions

1) The ZnO suspensions with the thermoresponsive gel system still display shear-thinning rheological behavior, but its viscosity increases with increasing the amount and length of the macromonomer PIPAAm graft chain, and the total organic matter content. At a shear rate of 150 s^{-1}, when the amount and relative molecular mass of macromonomer, and the total organic matter content are 50%, 8800 and 19.8%, the maximum viscosities of suspensions are 0.2, 0.13 and 0.16 Pa·s, respectively.

2) The graft chains inhibit or even eliminate the formation of "dense layer" on the surface of thermoresponsive gelcast ZnO green bodies, and accelerate the drying. When the temperature is higher than the phase transition temperature, the freely mobile ends at the macromonomer graft chains change from hydrophilic to hydrophobic to form an "aggregation force" among graft chains, which facilitates the shrink of three-dimensional network structure so as to release the water from the green bodies. Accelerated drying is observed with increasing the addition amount and relative molecular mass of macromonomer graft chain and the total organic matter content. When the amount and relative molecular mass of macromonomer graft chain and the total organic matter content are 50%, 8800 and 19.8%, the maximum mass loss of various green bodies dried at 50 °C for 30 min is 23%, 20% and 18%, respectively.

3) The introduction of macromonomer graft chains facilitates the shrinkage of the thermoresponsive gelcast ZnO green bodies during drying. When the amount and relative molecular mass of macromonomer graft chain, and the total organic matter contents are 50%, 8800 and

19.8%, the maximum shrinkage of various green bodies dried at 50 ℃ for 30 min is 17%, 14% and 14%, respectively.

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ZnO 温度响应凝胶注模成型的流变性能和干燥机制

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摘　要：为解决坯体干燥问题，将含大单体支链的温度响应凝胶体系应用于 ZnO 的凝胶注模成型，研究大单体支链 PIPAAm 的加入量与支链长度、总有机物含量和固相体积分数对悬浮液流变性能的影响，并分析坯体的干燥机理。研究表明：添加该凝胶体系的 ZnO 悬浮液仍表现为剪切变稀流变行为，但其黏度随着 PIPAAm 支链的加入量与相对分子质量以及总有机物含量的增加而升高。大单体支链的引入抑制甚至消除 ZnO 温度响应凝胶注模坯体表面“密实层”的形成，加快坯体干燥，促进坯体收缩。

关键词：ZnO；凝胶注模；温度响应；流变性能；干燥机制；*N*-异丙基丙烯酰胺

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