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Polymer Effects on the Chemorheological and Drying Behavior of Alumina–Poly(vinyl alcohol) Gelcasting Suspensions

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A new gelcasting system based on aqueous alumina (Al_2O_3)–poly(vinyl alcohol) (PVA) suspensions cross-linked via titanium ion complexation has been developed as a feedstock for bulk casting and solid freeform fabrication (SFF) routes. Its chemorheological properties, as measured by stress viscometry and oscillatory techniques, exhibited a strong dependence upon polymer hydrolysis and molecular weight. The gelation time of systems of constant PVA volume fraction (ϕ_{PVA}^{soln}) and cross-linker concentration decreased with increasing degree of hydrolysis and molecular weight, whereas their steady-state elastic modulus (G') exhibited the opposite dependence. Stress evolution during drying of gelcast layers was measured *in situ* using a controlled-environment, cantilever deflection apparatus. Both the maximum and residual drying stresses increased with increasing degree of hydrolysis, with only a modest molecular weight effect observed.

I. Introduction

GELCASTING, a bulk forming technique developed by Janney and co-workers,[1] employs a highly loaded ceramic slurry suspended in a monomeric solution, which is gelled by *in situ* polymerization. The as-formed organic network encapsulates the ceramic particles imparting high green strength. Recently, Morissette and Lewis[2] developed an alternative gelcasting approach based on cross-linking of a ceramic-filled poly(vinyl alcohol) (PVA) solution via metal ion complexation. They have demonstrated that this system is suitable for both bulk casting and solid freeform fabrication (SFF),[2–4] and have shown that its chemorheological behavior can be tailored through changes in cross-linker, polymer, and ceramic filler volume fraction as well as processing temperature.

PVA, which is synthesized via hydrolysis of poly(vinyl acetate), is a copolymer containing both vinyl alcohol and residual vinyl acetate groups, as shown in Fig. 1(a).[5] The degree of hydrolysis describes the mole percent of hydroxyl groups (x) relative to the residual acetate groups ($1 - x$) along the PVA chain. The presence of bulky acetate groups weakens both intra- and intermolecular hydrogen bonding interactions between nearby hydroxyl groups.[6] In solution, the PVA interchain separation distance decreases with increasing degree of hydrolysis causing a competition between polymer–solvent and polymer–polymer interactions. It has been shown that the degree of hydrolysis, as well as the molecular weight, strongly influences the properties of both pure PVA solutions and gels;[7–9] however, scant attention has been given to their effects on ceramic-filled PVA solutions and gels.

Here, we study the influence of polymer chemistry and molecular weight on the chemorheological behavior and drying stress development of alumina (Al_2O_3)–PVA gelcasting suspensions. Stress viscometry and oscillatory measurements were carried out to investigate the gelation behavior of PVA solutions and gelcasting suspensions. As the degree of polymer hydrolysis and molecular weight increased, the gel time decreased accompanied by an increase in the equilibrium elastic modulus (G') of the gelled system. The drying behavior of gelcast films was studied using a controlled-environment, cantilever deflection device, in which the stress evolution and weight loss were measured *in situ* during drying. We have shown that both the maximum and residual drying stresses increase with increasing degree of hydrolysis, with only a modest dependence on initial PVA molecular weight.

II. Experimental Procedure

(1) Materials System

Al_2O_3 powder (AKP-30, Lot No. 8111, Sumitomo Chemical Co., Japan), with an average particle size of 0.4 μm and a specific surface area of 7.3 m^2/g, as measured by nitrogen gas adsorption (ASAP Model 2400, Micromeritics, Norcross, GA) served as the ceramic phase. The alumina was dispersed in deionized water using Darvan C (R. T. Vanderbilt Co., Norwalk, CT) which contained 25 wt% solids of ammonium polymethacrylate (APMA, weight average molecular weight of 15 000 g/mol). Poly(vinyl alcohol)–acetate copolymers (Kuraray America, Inc., New York, NY) of varying degree of hydrolysis (80.8%–98%) and molecular weight (17 000–86 000 g/mol) served as the binder phase. Their properties are provided in Table I. PVA was cross-linked with an organotitanate additive (Tyzor TE, Lot No. 519, DuPont Chemical, Wilmington, DE) which contained 8.73% Ti solids by weight. The critical concentration of titanium ($[Ti]_c$) needed to induce PVA gelation in solution ($\phi_{PVA}^{soln} = 0.05$) and gelcasting suspensions ($\phi_{Al_2O_3} = 0.45$, $\phi_{PVA}^{soln} = 0.05$) was 1.45 and 1.26 mg of Ti/mL, respectively, as determined previously.[2] A defoamer, DF-75 (Air Products and Chemicals, Inc., Allentown, PA), was added at 0.1 wt% to minimize the foam content of the system.[10]

(2) Sample Preparation

Polymer solutions (5 vol% unless otherwise noted) were prepared by fully dissolving the appropriate amount of PVA copolymer in deionized water, which required temperatures of 22°, 60°, and 80°C for PVA (80.8%), PVA (88%), and PVA (98%), respectively. Upon complete dissolution, each polymer solution was adjusted to a pH of 4 by HNO_3 or NH_4OH additions.

Gelcasting suspensions were prepared by adding the appropriate amount of Al_2O_3 (40–45 vol%) and dispersant (3 mg of APMA/(g of Al_2O_3)) to deionized water while magnetically stirring. To facilitate mixing, the Al_2O_3 powder was added in several parts. The suspensions were ultrasonicated for 2 min and 30 s using a sapphire-tipped ultrasonic horn (Fisher Scientific 550 Sonic Dismembrator, Fisher Scientific, Itasca, IL) in pulsed 1 s (on/off) intervals after each addition. The suspensions were then magnetically stirred for 12 h after the total amount of powder was incorporated. An appropriate amount of PVA stock solution (20

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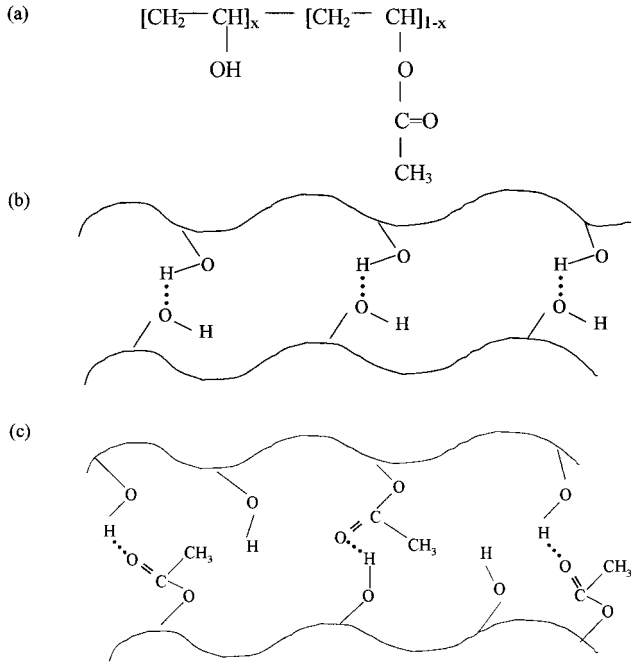

Fig. 1. (a) Schematic of the chemical structure of poly(vinyl alcohol) where *x* ranges between 79 and 99 mol%. Schematic of carbon backbone of PVA with (b) high hydrolysis (>98%) resulting in strong hydrogen bonding (···) between hydroxyl groups of neighboring chains and (c) low hydrolysis (<88%) showing larger chain separation distance due to bulky acetate groups (adapted from Ref. 5).

vol%) was then added to the as-mixed ceramic suspension such that the final concentration of PVA in solution was 5 vol%. This was followed by the addition of 0.1 wt% defoamer. A 1*M* solution of HNO_3 was used to adjust the pH of the suspensions to 8.5. Finally, the suspensions were mixed for a minimum of an additional hour to ensure their homogeneity.

(3) Rheological Measurements

Gelcasting suspensions and corresponding polymer solutions were characterized using a controlled-stress rheometer (Rheolgi CS-10, Bohlin Instruments, Cranbury, NJ) in either stress viscometry or oscillatory mode. Double-concentric (DG 40/50) or concentric cylinder (C25 or C14) geometries were utilized, with most of the measurements carried out using the C14 cup and bob (bob diameter of 14 mm and cup width of 0.7 mm), which yielded a stress of 0.14–1389 Pa. A specially designed solvent trap, filled with deionized water, was used to minimize evaporation during the measurements. An inert layer of silicone oil (η = 1000 cP, Brookfield Engineering Laboratory, Stoughton, MA) was syringed on the top of the solution or suspension to further minimize evaporation. All measurements were carried out at 22°C unless otherwise noted.

The apparent viscosity (η_{app}) as a function of shear stress of PVA (88%) solutions of varying molecular weight was measured to determine the critical overlap concentration (ϕ^*), which denotes the transition from dilute ($\phi < \phi^*$) to semidilute ($\phi > \phi^*$) behavior. The solution viscosity (η_{app}) is known to exhibit a power law concentration (ϕ) dependence:[11]

$$\eta_{app} \propto \phi^{1} \qquad (\phi < \phi^*) \tag{1}$$

$$\eta_{app} \propto \phi^{3,4} \qquad (\phi > \phi^*) \tag{2}$$

On the basis of these measurements, ϕ^* was found to be 0.0296, 0.025, and 0.0134 for respective molecular weights of 1.7×10^4, 2.8×10^4, and 8.6×10^4 g/mol.

The time-dependent evolution of the apparent viscosity (η_{app}) of polymer solutions and alumina suspensions was measured using stress viscometry at a constant shear rate of 0.1 s^{-1}. The titanium concentration [Ti] was held constant at 2.2 mg/(mL of PVA solution) while the polymer hydrolysis and molecular weight were varied. In addition, oscillatory measurements were carried out at a frequency of 0.1 Hz and a strain of 3.5% to determine the effects PVA hydrolysis and molecular weight on the steady-state modulus (G'_{equil}) of the as-gelled systems.

Table I. Properties of Poly(vinyl alcohol)

Kuraray product identification	Hydrolysis (mol%)	Viscosity average mol wt (g/mol)	Degree of polymerization
PVA 405	80.8	28 000	550
PVA 205	88	28 000	550
PVA 105	98	28 000	550
PVA 203	88	17 000	350
PVA 205	88	28 000	550
PVA 217	88	86 000	1700

(4) Stress Evolution During Drying

Stress evolution during drying of gelcast layers was characterized using a controlled-environment, cantilever beam deflection device.[12] This device monitors *in situ* stress development in cast films and coatings by relating the end deflection of the clamped substrate to the stress developed during drying in the attached film. A schematic of the stress device is shown in Fig. 2. The substrate deflection was measured with an optical level consisting of a helium–neon laser, an optical mirror, and a position-sensitive photodiode and recorded via a computerized data acquisition system. The underside of each stainless steel substrate was polished to a mirror finish to enhance its reflectivity. After cleaning, the substrate was securely clamped at one end in a movable sample holder. Once calibrated, the substrate was maneuvered into casting position beneath a doctor blade. Gelcasting suspensions were chilled to 5°C, then mixed with an appropriate amount of the cross-linking agent, and finally syringed onto the substrate. The layer was generated by moving the substrate beneath the doctor blade at a casting speed of 1 cm/s. All films in this study were cast at an initial height of 300 μm and dried at 25°C (±1°C) in 33% relative humidity (±2% rh). The chamber temperature was maintained by two heating elements and a thermocouple feedback control unit.

The end deflection (*d*) is related to the in-plane stress in the film by the Corcoran equation:[13]

$$\sigma = \frac{dEt^3}{3cL^2(t+c)(1-\nu)} \tag{3}$$

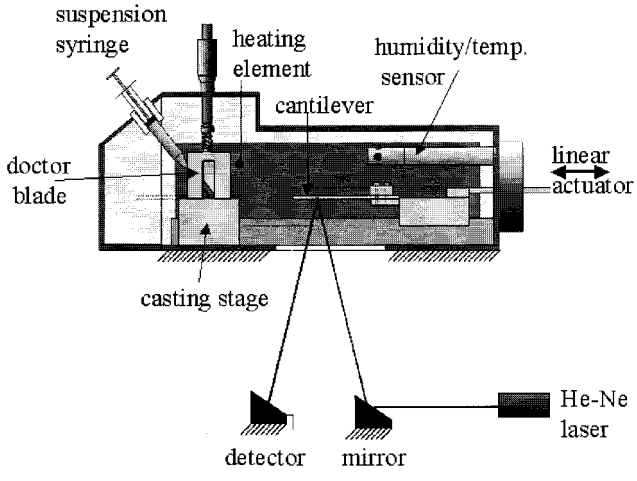

Fig. 2. Schematic illustration of the controlled environment, cantilever beam deflection device.

where E is the elastic modulus of the substrate, ν is Poisson's ratio of the substrate, t is the thickness of the substrate, L is the length of the cantilever substrate, and c is the coating thickness. This equation is valid when the elastic modulus of the coating is much smaller than E, as is the present case. The substrates used were stainless steel cut to the dimensions of 76.2 mm × 6.35 mm, whose properties were E = 190 GPa, ν = 0.29, t = 210 μm, and L = 5.08 mm. Note that the coating thickness used in Eq. (1) is the average thickness of the dried film, which leads to an overestimation of the drying stress initially, but has little effect on the maximum and residual drying stress values reported here. Simultaneous weight-loss measurements were carried out in the same device by suspending an analogously prepared film from a balance (Model A160, Mettler Instruments Corp., Heightstown, NJ).

III. Experimental Results

(1) Polymer Hydrolysis Effects on Gelation Behavior

The apparent viscosity (η_{app}) as a function of gelation time for PVA solutions (ϕ_{PVA}^{soln} = 0.05) and Al_2O_3–PVA suspensions ($\phi_{Al_2O_3}$ = 0.45, ϕ_{PVA}^{soln} = 0.05) of varying degree of hydrolysis (MW = 28000 g/mol) is shown in Figs. 3(a) and (b), respectively. In both cases, the gelation time strongly decreased with increasing PVA hydrolysis. This effect was more pronounced for PVA solutions. For example, the gelation time decreased from roughly 50 min to 1 min with an increase from 80.8% to 98% hydrolysis. The gel times were defined from the x-axis intercept of the tangent to each viscosity curve at η_{app} = 1000 Pa·s. The addition of ceramic particles ($\phi_{Al_2O_3}$ = 0.45) led to a significant increase in apparent viscosity. For example, the initial suspension viscosity exceeded 1000 Pa·s for all systems studied, and increased to values approaching 10^6 Pa·s (the detection limit of the rheometer) as gelation proceeded.

The time-dependent evolution of the elastic modulus (G') for PVA solutions ($\phi_{PVA}^{soln} = 0.05 \approx 2\phi^*$) and Al_2O_3–PVA suspensions ($\phi_{Al_2O_3}$ = 0.45, ϕ_{PVA}^{soln} = 0.05) at varying degrees of hydrolysis (MW = 28000 g/mol) is shown in Figs. 4(a) and (b), respectively. In both cases, the equilibrium elastic modulus (G'_{equil}) increased with increasing PVA hydrolysis. For example, G'_{equil} increased from approximately 40 Pa to 300 Pa for PVA solutions and 3000 Pa to 7000 Pa for gelcasting suspensions when the degree of hydrolysis increased from 80.8% to 98%. The incorporation of the ceramic phase led to a substantial rise in G'_{equil} independent of polymer chemistry.

(2) Polymer Molecular Weight Effects on Gelation Behavior

The apparent viscosity (η_{app}) as a function of gelation time for PVA solutions (ϕ_{PVA}^{soln} = 0.05) and Al_2O_3–PVA ($\phi_{Al_2O_3}$ = 0.45, ϕ_{PVA}^{soln} = 0.05) suspensions of varying molecular weight (88% hydrolysis) is shown in Figs. 5(a) and (b), respectively. In both cases, the gel times were found to decrease with increasing polymer molecular weight. This trend was most pronounced for PVA solutions, where no gelation was observed for the lowest

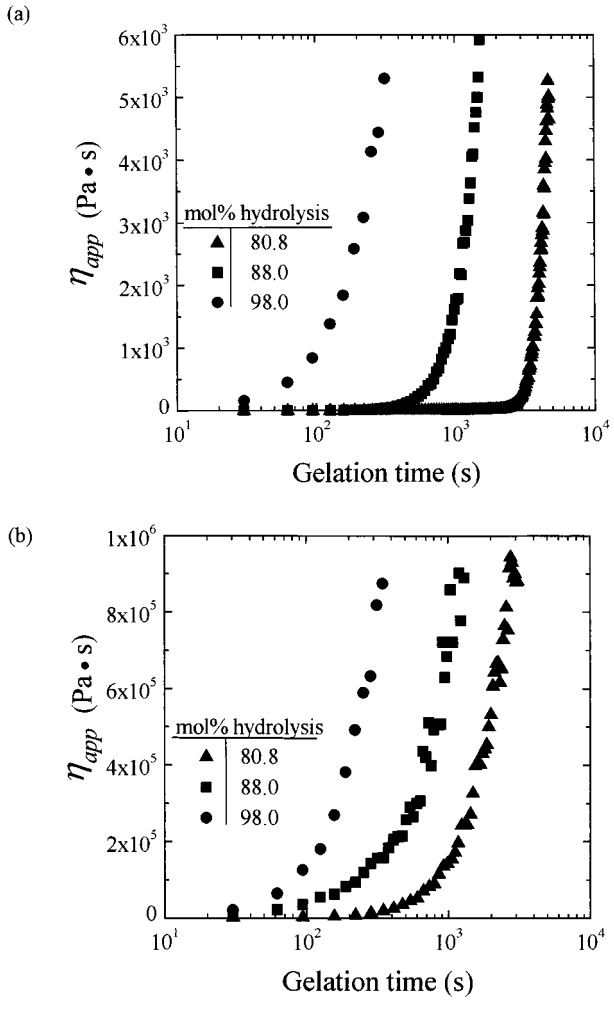

Fig. 3. Semilog plots of apparent viscosity (η_{app}) as a function of gelation time for (a) PVA solutions (ϕ_{PVA}^{soln} = 0.05) and (b) Al_2O_3–PVA suspensions ($\phi_{Al_2O_3}$ = 0.45, ϕ_{PVA}^{soln} = 0.05) at varying degree of hydrolysis (MW = 28000 g/mol) and [Ti] = 2.2 mg of Ti/mL.

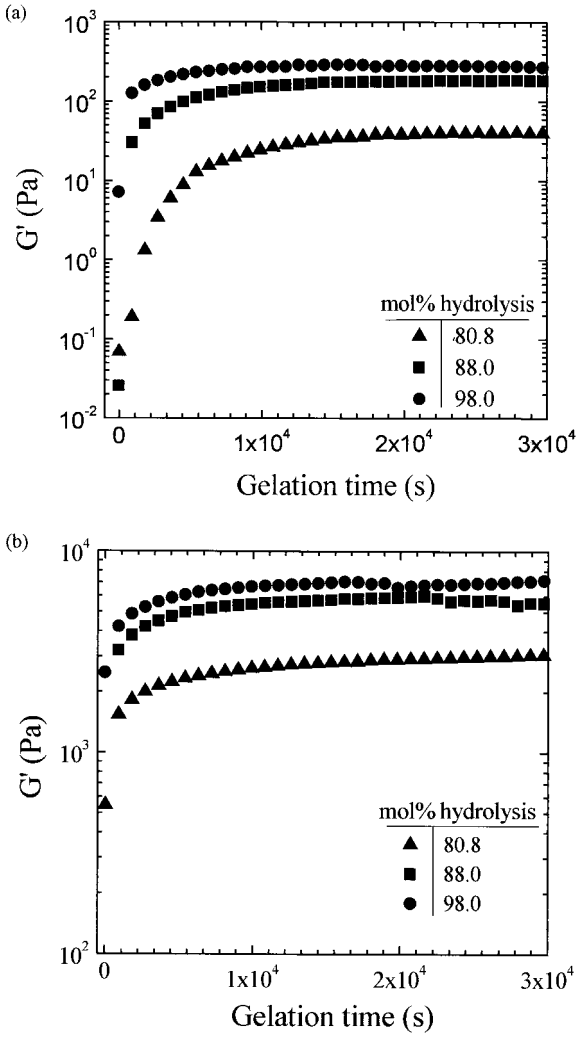

Fig. 4. Semilog plots of elastic modulus (G') as a function of gelation time for (a) PVA solutions (ϕ_{PVA}^{soln} = 0.05) and (b) Al_2O_3–PVA suspensions ($\phi_{Al_2O_3}$ = 0.45, ϕ_{PVA}^{soln} = 0.05) at varying degree of hydrolysis (MW = 28000 g/mol) and constant [Ti] = 2.2 mg of Ti/mL.

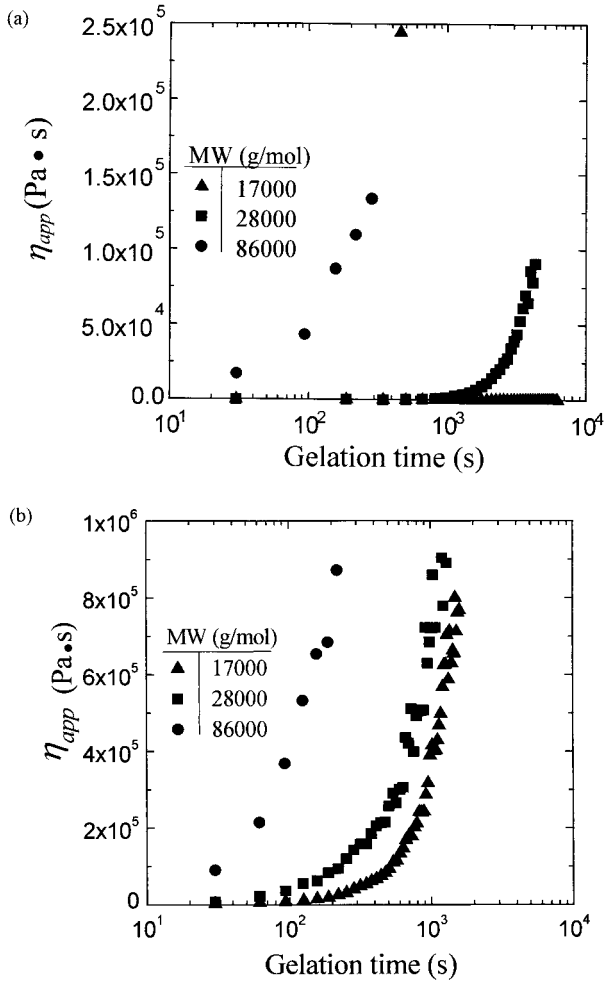

Fig. 5. Semilog plots of apparent viscosity (η_{app}) as a function of gelation time for (a) PVA solutions ($\phi^{soln}_{PVA} = 0.05$) and (b) Al_2O_3–PVA suspensions ($\phi_{Al_2O_3} = 0.45$, $\phi^{soln}_{PVA} = 0.05$) of varying molecular weight (88% hydrolysis) at constant [Ti] = 2.2 mg of Ti/mL.

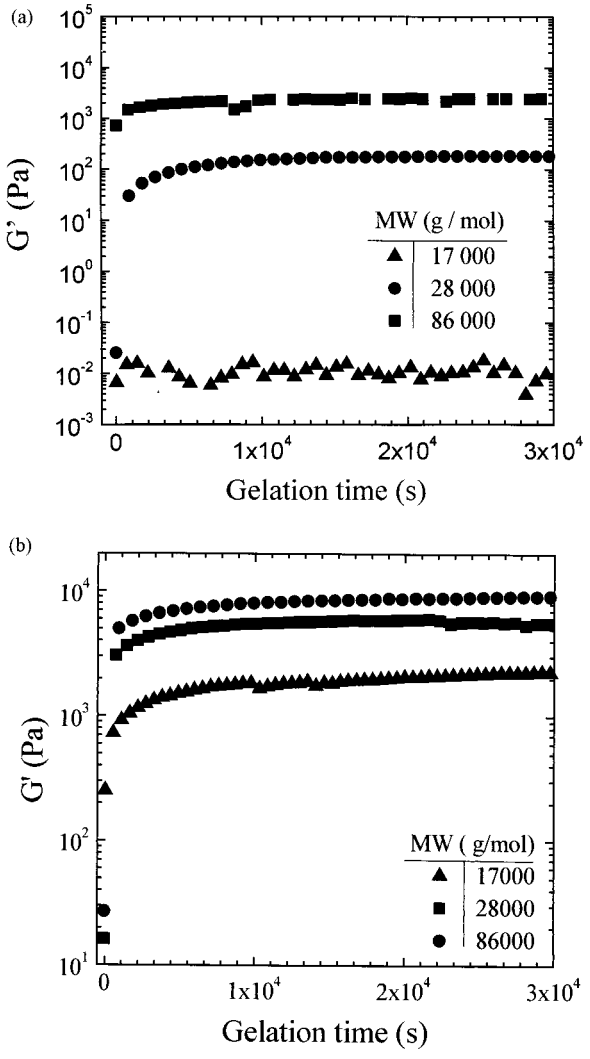

Fig. 6. Semilog plots of elastic modulus (G') as a function of gelation time for (a) PVA solutions ($\phi^{soln}_{PVA} = 0.05$) and (b) Al_2O_3–PVA suspensions ($\phi_{Al_2O_3} = 0.45$, $\phi^{soln}_{PVA} = 0.05$) of varying molecular weight (88% hydrolysis) at constant [Ti] = 2.2 mg of Ti/mL.

molecular weight studied (MW = 17 000 g/mol) over the experimental times probed (~24 h). Note that an excess cross-linker addition of 4.35 Ti/mL corresponding to roughly $3[Ti]_c$ was required to induce gelation in this sample. The presence of ceramic particles enhanced the gelation kinetics of each system, such that gelation was observed even for the lowest molecular weight PVA studied (MW = 17 000 g/mol).

The influence of PVA molecular weight on the time-dependent elastic modulus (G') for PVA solutions ($\phi^{soln}_{PVA} = 0.05$) and Al_2O_3–PVA suspensions ($\phi_{Al_2O_3} = 0.45$, $\phi^{soln}_{PVA} = 0.05$) of varying molecular weight (88% hydrolysis) is shown in Figs. 6(a) and (b), respectively. The equilibrium elastic modulus increased with increasing PVA molecular weight, in both cases. Because of the absence of gelation, G'_{equil} of the lowest molecular weight PVA solution (MW = 17000 g/mol) was several orders of magnitude lower than that observed for the higher molecular weight PVA solutions (MW = 28000 and 86000 g/mol), which exhibited values of approximately 200 and 2700 Pa, respectively. The addition of ceramic particles significantly enhanced the mechanical properties of these gels, as illustrated by the lowest molecular weight suspension (MW = 17000 g/mol) whose $G'_{equil} \sim 2500$ Pa. Note that this value is roughly equivalent to G'_{equil} of an Al_2O_3–PVA suspension ($\phi_{Al_2O_3} = 0.45$, $\phi^{soln}_{PVA} = 0.05$) incorporating PVA (80.8% hydrolysis, MW = 28000 g/mol) which was successfully deposited via SFF fabrication in earlier work.[3,4] This similarity highlights our ability to tailor gel properties simply by altering polymer chemistry and/or molecular weight.

(3) Stress Development in Gelcast Layers

Stress development as a function of drying time for a pure Al_2O_3 film ($\phi_{Al_2O_3} = 0.40$) and an Al_2O_3–PVA layer ($\phi_{Al_2O_3} = 0.40$, $\phi^{soln}_{PVA} = 0.05$) in the absence of cross-linker additions is shown in Figs. 7(a) and (b), respectively. These data serve as benchmarks for understanding the more complicated behavior exhibited by gelcast films, in which gelation and drying occur simultaneously. The binder-free, Al_2O_3 film exhibited a stress history characteristic of ceramic layers,[14] where the drying stress rises slowly to a maximum value of 0.64 MPa followed by a decrease to a negligible residual stress. The peak stress coincided with approximately 60% solvent loss, where the film underwent a transition from a supersaturated to a saturated state (i.e., solid network contraction ceases). In contrast, the Al_2O_3–PVA layer exhibited a similar initial rise in stress, with the first peak observed at roughly 50% solvent loss (again coincident with the onset of the saturated state) followed by a second rise to a maximum stress of 0.69 MPa at ~90% solvent loss. Beyond this second peak stress, the stress relaxed slowly, yielding a residual stress which exceeded 0.4 MPa in the dried film.

The effects of PVA hydrolysis and molecular weight on the stress development in gelcast films ($\phi_{Al_2O_3} = 0.40$, $\phi^{soln}_{PVA} = 0.05$) are shown in Figs. 8(a) and (b), respectively. The initial peak stress of such films coincided with the onset of the saturated state. Beyond this point, the drying stress relaxed slightly prior to increasing to its maximum values. This intermediate transition

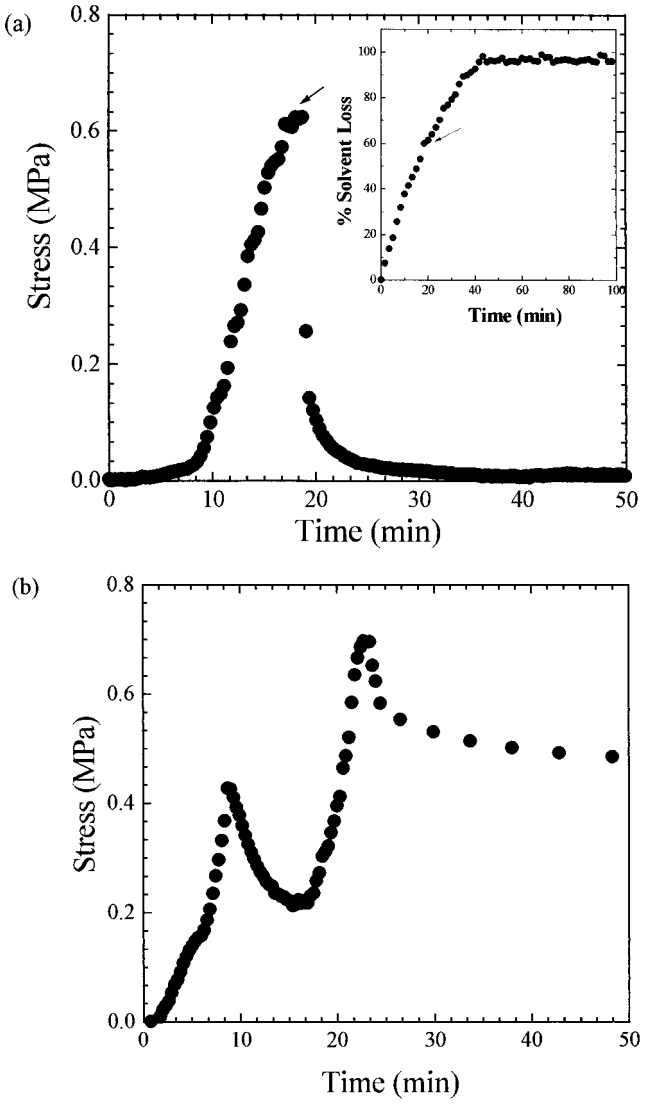

Fig. 7. Stress development as a function of time for (a) a pure Al_2O_3 suspension ($\phi_{Al_2O_3} = 0.40$) and (b) an Al_2O_3–PVA suspension ($\phi_{Al_2O_3} = 0.40$, $\phi_{PVA}^{soln} = 0.05$ (80.8% hydrolysis, MW = 28000 g/mol)) in the absence of cross-linking additions. (Inset plot shows simultaneous weight loss curve with arrows indicating time at which peak stress occurs.)

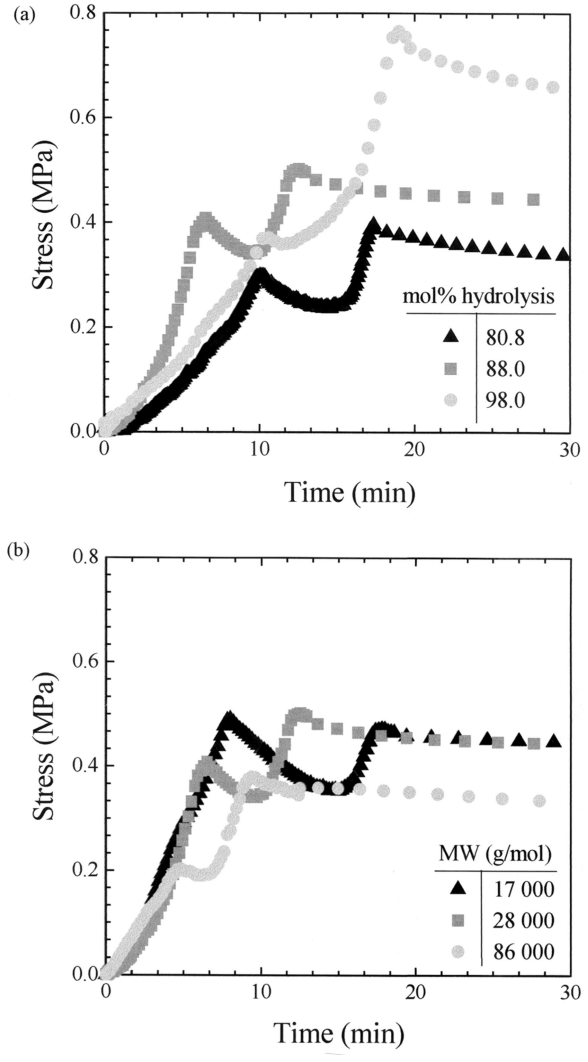

Fig. 8. Stress development as a function of time for gelcast films ($\phi_{Al_2O_3} = 0.40$, $\phi_{PVA}^{soln} = 0.05$, [Ti] = 2.2 mg of Ti/mL) of varying (a) degree of hydrolysis (MW = 28000) and (b) molecular weight (88% hydrolysis).

from stress relaxation to stress generation occurred at varying PVA volume fractions in solution of 0.143, 0.087, and 0.078 for 80.8%, 88%, and 98% hydrolysis, respectively, and 0.145, 0.087, and 0.082 for 1.7×10^4, 2.8×10^4, and 8.6×10^4 g/mol, respectively. Following the second stress peak, a modest stress relaxation was observed for all films. Both the maximum and residual stresses increased with increasing degree of PVA hydrolysis, with only a modest, molecular weight dependence observed. Stress relaxation in Al_2O_3–PVA layers was suppressed as the degree of hydrolysis and molecular weight increased, with the most profound example occurring in the gelcast layering containing the 98% hydrolysis PVA. It should be noted that this film also exhibited the highest maximum stress of 0.76 MPa.

IV. Discussion

The experimental results clearly demonstrate that polymer chemistry and molecular weight strongly influence the chemorheological properties and drying stress evolution of the Al_2O_3–PVA gelcasting system. To understand such effects, we first discuss the influence of PVA hydrolysis and molecular weight on solution properties. Next, we relate this to the observed gelation phenomena presented above. We then discuss the drying behavior of gelcast films within this framework. Finally, the impact of our observations on fabrication of gelcast components is presented.

(1) Polymer Effects on Gelation Behavior

The degree of hydrolysis is a key parameter for PVA, affecting its water solubility, degree of crystallinity, chain mobility, and, ultimately, its tensile film strength.[5,6] As the degree of hydrolysis increases, the mole fraction of hydroxyl side groups along the PVA backbone approaches unity. This change in molecular architecture results in a significant rise in intra- and interchain bond strength due to hydrogen bonding, which initially inhibits the solubility of PVA in water under ambient conditions and subsequently affects its coil configuration in solution.[6,9,15] For example, because of the difficulty of disrupting strong hydrogen bonding between chains, a dissolution temperature of 95°C is required to completely solubilize fully hydrolyzed PVA in water, whereas partially hydrolyzed PVA readily dissolves under ambient conditions.[5,6] Once such species are dissolved, however, it is expected that both the coil dimensions ($\phi < \phi^*$) as well as the interchain separation distance ($\phi > \phi^*$) would decrease with increasing degree of hydrolysis due to a reduction of bulky acetate side groups.[6,15–17] Hence, enhanced gelation kinetics are expected for PVA solutions and gelcasting suspensions with increasing degree of hydrolysis, since it should be easier to form cross-links between chains due to their closer proximity. Such trends are clearly reflected by both gelling PVA

solutions and Al_2O_3–PVA suspensions, which exhibited significantly shorter gel times with increasing degree of hydrolysis. In addition, the equilibrium elastic modulus of both systems also increased with increasing degree of hydrolysis. This observation likely reflects either a decrease in the distance between cross-links or an increase in the relative ratio of inter- to intrachain cross-links formed during gelation.

Molecular weight is another key parameter for PVA, affecting its solution viscosity, degree of crystallinity, chain mobility, and tensile film strength.[5,6,18] As the molecular weight increases, the critical concentration (ϕ^*) required to promote the transition from dilute to semidilute solution behavior decreases significantly. For example, there was more than a twofold decrease in ϕ^*, as the molecular weight increased from 17000 to 86000 g/mol at a constant degree of hydrolysis. In our experiments, the volume fraction of PVA in solution was held constant at 0.05, so differences in the extent of chain overlap are expected between systems of varying molecular weight. As the volume fraction of PVA in solution approaches ϕ^*, i.e., as the MW decreases, it becomes increasingly difficult to induce gelation. We observed such difficulties for the lowest molecular weight PVA solution (MW = 17000 g/mol) studied here, which did not gel in the absence of ceramic filler additions. For higher molecular weight PVA solutions and Al_2O_3–PVA suspensions, gelation kinetics increased with increasing molecular weight. We attribute such observations to the increased ease with which cross-links form as well as increased physical entanglements between overlapping chains, as the extent of coil overlap increases. The increased equilibrium elastic modulus also observed with increasing polymer molecular weight likely stems from similar origins. For example, Kjøniksen and Nyström[19] reported that the gel strength of cross-linked PVA solutions depended more on physical entanglements than cross-link density at high polymer concentrations.

(2) Drying Behavior of Gelcast Films

Stress develops during drying of constrained ceramic layers due to the volume shrinkage associated with solvent loss. Capillary forces, which drive consolidation, induce a compressive stress on the solid network of equal magnitude to the tension in the liquid phase.[20–23] Previous work on binder-free ceramic layers has shown that the maximum drying stress is coincident with the transition to the saturated state, i.e., where the resulting solid network resists further shrinkage.[14,24] We observed analogous behavior during drying of pure Al_2O_3 films studied here. Recently, Lewis and co-workers[25] have shown that tapecast ceramic layers, which contain a significant amount of organic binder, exhibited more complicated stress histories. They studied both plasticized and nonplasticized Al_2O_3–poly(vinyl butyral) (PVB) layers and found that the binder phase strongly influenced their stress histories. For plasticized layers, a distinct stress maximum was observed, followed by a reduction of stress as the liquid–vapor interface advanced into the interior of the film. In contrast, substantial stresses continued to build in the nonplasticized layers long after this advancement occurred. Two opposing processes influence stress development during drying: one generating stress due to volume shrinkage, and the other diminishing stress due to relaxation.[25] The presence of the plasticizing species, dibutyl phthalate, mitigates PVB chain interactions, thereby reducing characteristic relaxation time(s). The Al_2O_3–PVA layers studied here exhibited drying behavior that was intermediate relative to the results of the tapecast layers. We attribute such differences to the transient nature of the plasticizer species (i.e., water) in the present system.[26] Immediately following the first stress peak, the Al_2O_3–PVA layers underwent stress relaxation. In this regime, the pore solution within the films contains less than 10 vol% PVA. As the drying proceeds, the pore solution becomes increasingly enriched in polymer, thus inhibiting polymer relaxation processes. Stephans and Foster[7] have shown that polymer–polymer interactions stemming from hydrogen bonding lead to network formation (in PVA solutions ~10 vol% or higher). As this value was approached, we observed a transition from stress relaxation to stress development, which led to the development of a second stress peak at roughly 90% solvent loss. Finally, beyond this maximum stress, the stress relaxed slowly yielding a residual stress, which exceeded 0.4 MPa.

The drying behavior of Al_2O_3–PVA layers with cross-linker additions is further complicated by gelation phenomena, which occur simultaneously and lead to dramatic changes in the viscoelastic properties of the film (refer to Figs. 4(b) and 6(b)). A key difference between the stress histories of the Al_2O_3–PVA layers in the presence and absence of the cross-linker is the extent of stress relaxation observed between the first and second stress peaks. Not surprisingly, the addition of cross-links to the PVA network reduces its ability to relax stress during the initial stage of drying. The influence of the polymer properties on the stress histories of Al_2O_3–PVA gelcast layers is attributed mainly to the extent to which polymer–polymer interactions dominate, leading to the formation of crystalline domains within the dried films. The density of crystallites in PVA has been reported to increase with increasing degree of hydrolysis or decreasing molecular weight.[5,27] We observed that gelcast layers containing PVA species with higher degree of hydrolysis or lower molecular weight exhibited both higher maximum and residual stresses as a result of additional shrinkage associated with crystalline domain formation. The most pronounced example of such behavior was observed for gelcast layers containing PVA (98% hydrolysis) in which hydrogen bonding effects were expected to play the greatest role. In this case, minimal stress relaxation occurred following the first peak stress, leading to significant stress generation prior to the second stress peak.

(3) Impact of Gel-Derived Ceramic Components

Recently, we have demonstrated that the Al_2O_3–PVA gelcasting system serves as an excellent feedstock material for solid freeform fabrication of complex ceramic components.[3,4] The combination of gel-based formulations and SFF yields green machinable components with significantly enhanced handling strength. Our results show that the mechanical properties of gelcast layers can be readily tailored through compositional changes. Both the degree of hydrolysis and molecular weight of PVA can be altered, resulting in widely varying gelation times, equilibrium elastic moduli, and stress history behavior. In the latter case, gelcast layers were shown to retain stresses generated during the initial stage of drying. While such stresses could likely be mitigated with the addition of a nontransient plasticizer species (e.g., poly(ethylene glycol)), this approach would simultaneously lower the handling strength of the as-formed component. It is unclear whether these residual stress levels will have a deleterious affect on the dimensional stability of SFF-derived gelcast components. This is a subject of further investigation.

V. Conclusion

The effects of PVA hydrolysis and molecular weight on chemorheological and drying behavior of an Al_2O_3–PVA gelcasting system have been studied for the first time. Increasing the polymer hydrolysis or molecular weight increased the equilibrium elastic modulus (G'_{equil}) while simultaneously reducing gelation time. Al_2O_3 filler additions into the polymer matrix led to significantly enhanced gelation kinetics as well as increased equilibrium elastic moduli. We showed that the drying behavior of Al_2O_3–PVA films in the absence of cross-linker species was intermediate to that observed previously for plasticized and nonplasticized tapecast layers. We attributed such differences to the transient nature of the plasticizer species (i.e., water) in the present case. Finally, we showed that the stress histories of gelling layers were affected by both simultaneous cross-linking reactions and polymer properties, which led to diminished stress relaxation processes associated with the organic phase. In summary, we have shown that the properties of Al_2O_3–PVA gelcast layers can readily be tailored via compositional variations within the organic phase.

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