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Tensile strength of aqueous-based alumina tapes using a PVP–PVA–gelatin cobinder

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Abstract

A cobinder, consisting of polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA) and gelatin, was used to prepare aqueous-based alumina tapes for three-dimensional forming. The tensile strength, humidity dependent strength degradation, and drying rate of the tapes were investigated by varying the amounts of PVA and gelatin. Gelatin was beneficial for increasing the tape strength and the drying rate, and the addition of PVA alleviated the humidity sensitive strength degradation. The overall performance of the alumina tape was optimized with the use of a cobinder containing 89.5 wt.% PVP, 10 wt.% PVA, and 0.5 wt.% gelatin.

Keywords: A. Tape casting; C. Strength; D. Al_2O_3

1. Introduction

Ceramic tapes are mainly manufactured using non-aqueous-based solvents such as alcohol and ketone or hydrocarbons to ensure the dispersion of ceramic powder and the dissolution of organic components such as dispersant, binder and plasticizer. The organic solvents are widely used because of the easy availability of binders soluble in the solvents as well as the lower sensitivity of the non-aqueous-based slurries to process perturbations. However, the volatility, the toxicity, and the cost of the organic solvents lead to increasing interest in tape casting using water-based solvents [1–6]. Although the use of water-based solvents in the tape casting can eliminate these problems, there are difficulties arising in the process such as low strength of water-soluble binders, the slow drying rate of cast tapes, and the agglomeration of powders due to hydrogen bonding [2,7]. This requires a careful selection of the slurry additives together with an accurate control of many tape processing parameters.

The three types of water-soluble binders that have been frequently utilized in the aqueous-based tape casting are cellulose [1,8], acrylate [1,2], and vinyl [1,9]. The viscosity of the slurries containing cellulose, which has a hydrocarbon backbone structure, is usually high so that the tape cast using cellulose as a single binder possesses low flexibility, which leads to difficulties either in laminations or in three-dimensional shaping. Accordingly, cellulose is often used as a cobinder, mixed with another water-soluble binder, especially to control the thickness of aqueous-based tapes [10]. On the other hand, the acrylic binders render high flexibility and adhesiveness to the tapes because of the low glass transition temperature [1]. In addition, such tape properties as the tensile strength, flexibility, and adhesiveness are not affected by relative humidity since polyacrylic emulsions consist of dispersions of hydrophobic polymer particles [11]. However, ceramic tapes containing acrylic binders have a disadvantage in the recycling of the tapes due to their insolubility in water and their frequent contamination by alkali ions and impurities [1,2]. The vinyl-type

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binders have a low viscosity, which allows for the uniform casting of ceramic tapes and the mixing of various plasticizers with the binders to manipulate tape properties [12].

Polyvinyl alcohol (PVA) has been most widely used as a water-soluble organic binder whose properties depend on molecular weight and the level of hydrolysis [9]. A fully hydrolyzed PVA with a high molecular weight possesses high water resistance and high tensile strength. However, due their low adhesiveness, alumina tapes prepared using the PVA binder showed limitations in applications requiring three-dimensional shaping, such as all-ceramic dental crowns [13]. On the other hand, aqueous-based alumina tapes using polyvinyl pyrrolidone (PVP) as a binder have shown high flexibility and high adhesiveness [14]. However, the critical drawback of the PVP binder in this application was a degradation of the tape strength at a high relative humidity. In the present study PVA and gelatin were added to the PVP binder in an effort to alleviate the relative humidity dependent strength degradation of the aqueous-based alumina tapes for such three-dimensional forming applications as all-ceramic dental crowns and asymmetric ceramic membranes.

2. Experimental procedure

Alumina powder of 3 μm particle size (AL-M43, Sumitomo, Japan) was used for the tape casting. The tapes were prepared using five different binder combinations: PVP (MW: 1,300,000, Aldrich, U.S.A.), PVA (MW: 124,000–186,000, Aldrich, U.S.A.), PVP + PVA, PVP + gelatin (calf skin, Aldrich, U.S.A.), and PVP + PVA + gelatin. The compositions of the slurries are listed in Table 1. Prior to the preparation of the slurries, PVP and PVA were dissolved in distilled water to form 25 and 10 wt.% solutions, respectively, at 80 °C, and a 10 wt.% gelatin solution was obtained by dissolving in the water at 40 °C. For slurries with vinyl-type binders, 19 cm^3 of distilled water was mixed with 100 g of the alumina powder. For slurries containing gelatin, 45 cm^3 of distilled water was added to compensate for water evaporation during de-airing at 80 °C. 0.25 g of ammonium polyacrylate salt dispersant (D-3005, Rohm & Hass, Philadelphia, PA) was added to the powder and ball milled for 4 h. After ball milling triethylene glycol (TEG) (MW: 150, Yakuri, Japan), as the plasticizer, was poured and ball milled for 1 h, and then the vinyl-type binders were added and ball milled additionally for 18 h. The compositions of the binders and the plasticizer are summarized in Table 1. It was desirable to add about 0.75 wt.% of a wetting agent to the slurry to prevent the tape from shrinking while drying [15]. About 0.2 g of a defoamer (SN-Defoamer 483, SanNopco Korea Ltd., Korea) was added to the ball milled slurry and stirred at 250 rpm in a vacuum to remove bubbles and to adjust the viscosity of the slurry to about 2000 cP s for an optimal casting performance. The de-aired slurries were cast on a moving Mylar film at a speed of 30 cm/min beneath a doctor blade height of 0.8 mm. For the tape casting containing gelatin, a gelatin solution was added to the de-aired slurry while being stirred at 80 °C for 5 min, and then the slurry was cast beneath a blade heated to 50 °C in order to prevent gelation during casting.

The tensile strength of the dog bone shaped tape specimens was measured using a test machine (Instron 4465, Instron, UK) with a loading rate of 50 mm/min according to the ASTM standard D-638 IV. Five specimens were used for each measurement. The influence of relative humidity on the strength was determined by performing a tensile strength test while locating the specimens inside a temperature/humidity controlled chamber that was annexed to the test machine. The drying rate of the tapes was determined at room temperature by weight change of specimens using an electronic balance (AB204-S, Mettler Toledo, Switzerland) with an accuracy of 10^{-4} g.

3. Results and discussion

PVP, a water-soluble polymer with amide groups, is thermally cross-linked into a three-dimensional molecular network and becomes thermally stable after cross-linking [12,16]. The PVP of relatively low molecular weights has been used as a dispersant for the production of Al_2O_3 hollow fiber membrane [17] and hydroxyapatite tapes [18] because of its nature of a plasticizer, especially at high humidity [19]. This property provided the alumina tapes prepared with the PVP with even higher molecular weight as a binder with high flexibility and high adhesiveness [15]. Accordingly, the alumina tape containing the PVP (PVP-tape) showed the low tensile strength of 0.3 MPa, as exhibited in Fig. 1. By comparison, the strength of the tape containing the same amount of PVA was 2.6 MPa. The difference is due to the fact that PVA has a strong binding force associated with the interaction of hydroxyl groups pendant from the carbon

Table 1
Compositions of aqueous-based alumina tapes having various binders in terms of weight ratios of alumina powder, binder, and plasticizer

Binders	Alumina/(alumina + binder + plasticizer)	Binder/(binder + plasticizer)
PVA	0.87	0.7
PVP	0.87	0.65
PVP (90 wt.%) + PVA (10 wt.%)	0.87	0.7
PVP (99.5 wt.%) + gelatin (0.5 wt.%)	0.84	0.7
PVP (89.5 wt.%) + PVA (10 wt.%) + gelatin (0.5 wt.%)	0.84	0.7

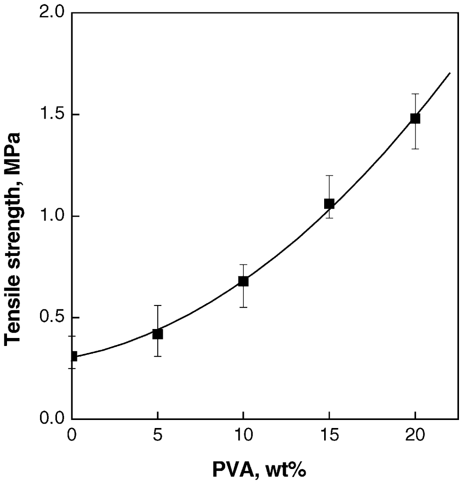

Fig. 1. Influence of the addition of PVA on tensile strength of aqueous-based alumina tapes containing PVP as a binder, determined at 25 °C and 60% relative humidity.

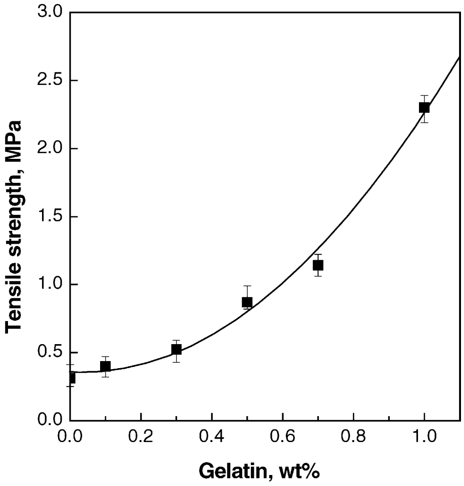

Fig. 2. Influence of the addition of gelatin on tensile strength of aqueous-based alumina tapes containing PVP as a binder, determined at 25 °C and 60% of relative humidity.

backbone of the PVA [9]. Thus, the addition of the PVA binder enhanced the tensile strength of the PVP-tape, as shown in Fig. 1. As the addition was higher than 10 wt.%, however, the flexibility and the adhesiveness decreased because of its high hydrolysis level and high molecular weight, and so the tapes were not adequate for three-dimensional forming applications.

Gelatins are water-soluble, high molecular weight polypeptides derived from collagen, the primary protein component of such animal connective tissues as skin and tendons [20,21]. The gelatin has been used as an additive for gelcasting of alumina powder because of the ability of a cross-linking into a three-dimensional network at a relatively high viscosity [22]. The gelatin was added in an effort to increase the tensile strength of the PVP-tape. In the PVP-tape containing the gelatin, the weight ratio of alumina/(alumina + binder + plasticizer) was 0.84, which was lower than the ratio for the PVP-tape and the PVP-tape containing PVA, as shown in Table 1. When the ratio was higher than 0.84, the slurry viscosity was too high to cast the tape. Fig. 2 shows the influence of the addition of gelatin on the tensile strength of the PVP-tape. The tape strength was improved to 2.3 MPa with the addition of 1.0 wt.% gelatin. The increase in the strength was due to the increased rigidity of the binder as a result of the formation of a three-dimensional network of gelatin in the tape below the gelation temperature of about 40 °C [20]. Accompanying the increase in strength, flexibility and adhesiveness were decreased so that the PVP-tapes having gelatin contents higher than 0.5 wt.% could not be used for three-dimensional forming applications. By comparing the results shown in Figs. 1 and 2, it is obvious that the gelatin is more effective than the PVA for the enhancing the strength of the PVP-tape.

Fig. 3 illustrates the dependence on the relative humidity of the tensile strength of PVP-tape and the tapes containing the optimum amounts of PVA and gelatin, respectively. As the humidity was raised from 30 to 80%, the strength of the PVP-tape dropped more than three times. This is because the flexibility of the tape was increased as a result of the decrease in the glass transition temperature of PVP when increasing the humidity [19]. For the PVP-tape containing 0.5 wt.% gelatin, the trend of descending strength was almost identical even though the strength was higher than the PVP-tape over the entire humidity range. As 10 wt.% PVA was added, the strength was also improved, but the degradation was minimal. The alleviation of the strength degradation was achieved due to the fact that the water-resistance of the PVA caused the strength to become less sensitive to the humidity.

Besides the strength degradation, the slow drying rate has been one of the problems of the PVP-tapes. The drying rates

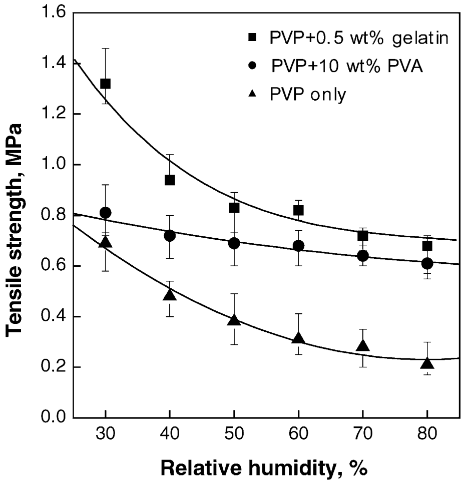

Fig. 3. Variation of tensile strength of aqueous-based alumina tapes containing PVP only, PVP + 0.5 wt.% gelatin, and PVP + 10 wt.% PVA as a function of relative humidity, determined at 25 °C.

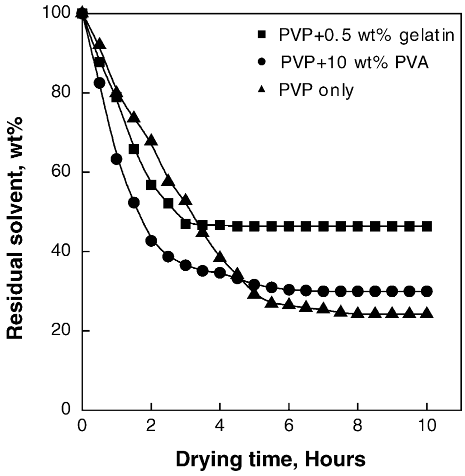

Fig. 4. Effect of additions of 0.5 wt.% gelatin and 10 wt.% PVA on drying rate of alumina tapes having PVP binder at room temperature.

of the alumina tapes prepared using three different binder compositions are compared in Fig. 4. The drying of the PVP-tape was completed after 8 h and the drying of the PVP-tape containing 10 wt.% PVA was done in 7 h, indicating that the addition of the vinyl-type binder does not significantly change the drying rate of the PVP-tape. However, the drying time was remarkably reduced to 3 h by the addition of 0.5 wt.% gelatin. The shortened drying time was attributed to the fact that the water solvent in the tapes was used up to form a three-dimensional network of gelatin corresponding to a viscoelastic gel [20]. After the completion of drying, thus, the PVP-tape having the gelatin was about 24 wt.% heavier than the PVP-tape.

In order to obtain a PVP-tape with a humidity insensitive strength and a high drying rate, both 10 wt.% PVA and 0.5 wt.% gelatin were added, and the result is shown in Fig. 5. The humidity dependence of the strength was almost identical to the result for the PVP-tape having only the PVA in Fig. 3 and the addition of gelatin was beneficial to the drying rate of the PVP-tape. The alumina tape prepared using the ternary cobinder was acceptable for forming all-ceramic crowns not only because of the relatively high tape strength, flexibility, and adhesiveness but also because of the high drying rate and the low strength degradation under high humidity.

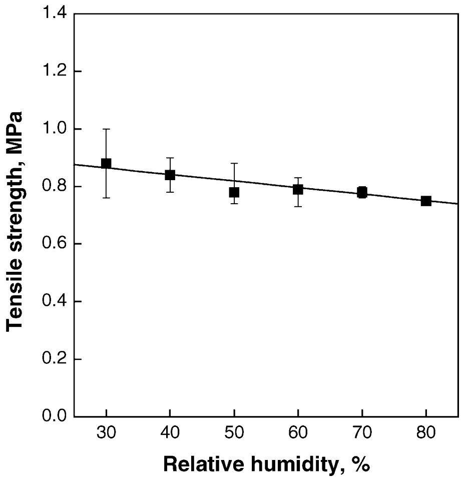

Fig. 5. Relative humidity dependence of tensile strength of aqueous-based alumina tapes containing ternary binder of 89.5 wt.% PVP + 10 wt.% PVA + 0.5 wt.% gelatin at 25 °C.

4. Conclusions

The drawbacks of the aqueous-based alumina tapes using the PVP as a binder for the applications of three-dimensional forming were eliminated by the addition of PVA and gelatin. The PVA alleviated the relative humidity sensitive strength degradation of the PVP-tape due to the high hydrolysis level and the high molecular weight of the PVA. On the other hand, the gelatin increased the tensile strength and the drying rate of the alumina tapes containing the PVP binder as a result of gelation while drying. The strength, flexibility, and adhesiveness of the aqueous-based alumina tape were optimized by using a cobinder whose composition was 89.5 wt.% PVP, 10 wt.% PVA, and 0.5 wt.% gelatin.

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