Processing and Characterization of YSZ-PSS-DBS Composites

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ABSTRACT: PSS-PEGL and PSS-PEGL-DBS polymeric systems have been used in YSZ slurry formulation. These organic materials with different chemical structure and functional groups had great effect on the ceramic slurry formulation. Physical properties, such as viscosity of slurry, hardness and density for green and sintered bodies, and thermal decomposition, were studied as a function of the binder composition. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 502–509, 1999

Key words: YSZ; PSS-PEGL; PSS-PEGL-DBS; thermal and mechanical properties

INTRODUCTION

The performance of technical ceramics depends strongly on the size and frequency of voids along the pressed surface or within the body. The quality of the ceramic is highly dependent on the processes involved in its manufacture. Some work has been done to implement new binder systems. Binder is the most important additive for ceramics, and it has strong influence on the properties of granules, such as bulk density, flow rate, and compaction behavior. A good binder for ceramic applications should provide both high green strength and high green density at a low level of usage. Green strength is controlled by the polymer–polymer and polymer–ceramic powder interactions. Generally, green density will decrease with the addition of a binder. However, a high-performance binder will have a less negative impact on green density.

Poly (vinyl alcohol) (PVA) and poly (ethylene glycol) (PEG) are the two most popular binders for dry-pressing ceramics. PVA binders generally provide high green strength, but the binder does not press easily and results in many voids in green and fired bodies. Press capacity keeps the manufacturer from achieving the required green densities with larger parts that use the PVA binder system. PEG binders usually provide high green density.

The glass transition temperature (T_g) of polymeric binders is one of the key parameters controlling binder performance during dry pressing and strongly affects the quality of dry-pressed ceramic parts. It has been reported that binder T_g has effect on the green density and green strength of dry-pressed ceramic parts. Lower binder T_g gave higher density, presumably because the softer binder deforms more easily. But binders with higher T_g values showed higher strength than those with lower T_g values.

Production of dry-pressed technical ceramics requires a series of processing steps, including powder milling and slip dispersion, spray drying, pressing, green machining, sintering, and fired-body machining. As a result, process step changes in manufacturing must be examined with respect to their effects on the entire program. There are two ways to improve the present system: a more pressable binder and an improved granulate quality. Both of them have important effects on green-body density, surface quality, and micro-

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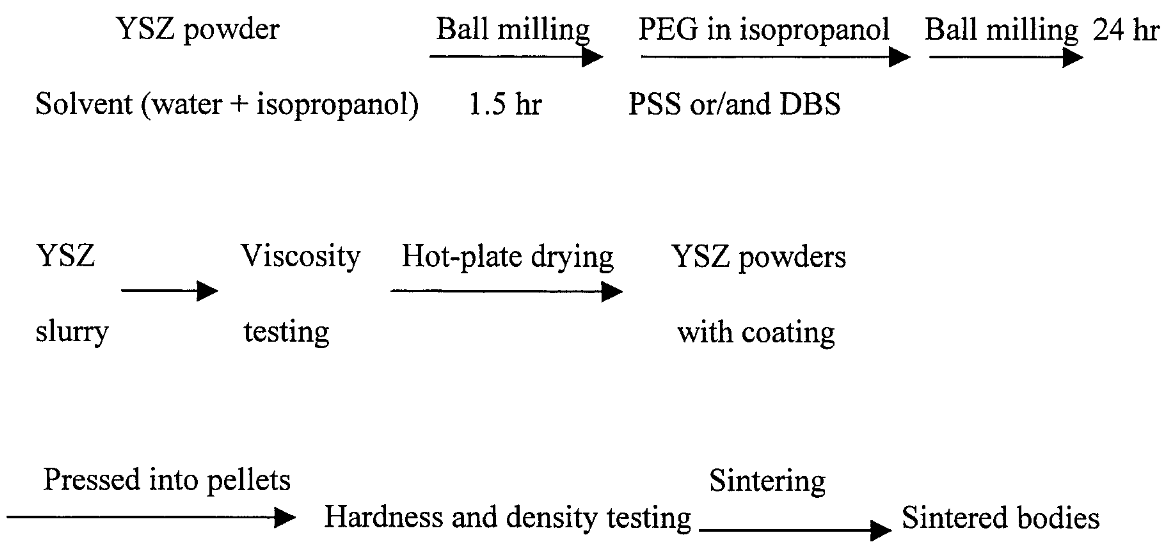


Figure 1 Slurry formulation.

structure. A more pressable binder allows granules to deform more easily during pressing. This reduces void space between granules in the pressed green body and produces a smoother pressed surface. Granule quality can also have a large effect on the properties of a pressed green body. Granules from the dryer should be solid, dense, and spherical to allow good compaction during pressing. Granule defects, such as hollows, dimples, donuts, or satellites, often result in large voids in pressed bodies, even if a highly pressable binder is used.

In this work, we used two kinds of binder systems to study the effect of binders on processing. Two or three kinds of organic materials were used, and they had different properties, for example, they had different T_g. Some ceramic properties were studied, such as viscosity of slurry, hardness and density for green and sintered samples, thermal properties for binders, and the morphology for sintered samples.

EXPERIMENTAL

Materials

YSZ, obtained from NexTech Materials, Ltd., are hydrothermal yttria-stabilized zirconia powders. They are very fine white powders and have very high surface areas (60 to 150 m^2/gram). Poly (styrenesulfonate) (PSS) was obtained from Aldrich Chemical Company, Inc.; PSS has average molecular weight (M_w) about 70,000. Polyether glycol (PEGL) was obtained from Aldrich Chemical Company, Inc.; average molecular weight M_n is approximately 2,000. Dodecylbenzenesulfonate (DBS) was obtained from Aldrich Chemical Company, Inc. All organic materials were used without further purification. 2–propanol obtained from Fisher Scientific and distilled water were used as solvents.

Processing

One part PEGL was dissolved in two parts isopropyl alcohol. The clear solution was obtained. Figure 1 shows the YSZ slurry formulation. YSZ powder (40 g) was added into the mixed solvent (160 g) of water and isopropanol (1:1 weight ratio), and the mixture was ball-milled for 1.5 h. Then, PEG in isopropanol, PSS, and/or DBS were added into the mixture, which was then ball-milled for an additional 24 h. The YSZ slurry was hot-plated dried and then dried until constant weight at 100°C in a vacuum oven. The samples were ground into fine powders and pressed into pellets. The green pellets were made from YSZ dried granules compressed using a 0.5-inch hard steel die at a pressure of 2500 pounds at room temperature. The pellets were sintered in air in an electric high-temperature furnace at 1450°C for 2 h.

Characterization

Density was calculated from the weight and dimensions of a pellet for both green and sintered

Table I The Compositions for YSZ Slurry Processing

Sample	YSZ (g)	PSS (g)	PEG (g)	DBS (g)	Water (g)	Isopropanol (g)
C-929	40	1.72	0.373	0	80	80
C-1021	40	1.72	1.043	0	80	80
C-1030	40	1.72	2.0	0	80	80
C-1113	40	2.2	0	2.0	80	80
C-1125	40	0	2.2	2.0	80	80
C-1201	40	2.2	2.2	2.0	80	80
C-1208	40	2.2	2.2	4.18	80	80
C-1211	40	2.2	2.2	1.0	80	80

samples. The following equation was used to calculate the density (ρ):

$$\rho = 4m/(\pi d^2 h) \quad (1)$$

Pellet weight (m) was accurate to ± 0.0001 g. Pellet dimensions—diameter (d) and height (h)—were measured with a digital caliper accurate to ± 0.01 mm.

The burnout profile was obtained by standard thermal gravimetric analysis (TGA). TGA, as the name implies, monitors weight loss as temperature is increased. Weight losses occur as the result of driving off volatile and, at higher temperatures, degradation products. Thus this technique can be used both to examine the state of a material and to investigate the process of degradation. It can provide information about the thermal stability of a material. The TGA measurements were carried out in oxygen at the heating rate of 20°C/min.

Hardness was measured by a Leco M-400-Hi hardness testing machine, and the sample was dyed before testing because all of the samples had light color. The viscosities of the slurries were measured by a Brookfield digital viscometer Model DV-I with a #1 spindle at different speeds.

Scanning electron microscopy (SEM) provides unique information about the surface of materials and is outstanding for topographic examination. Its basic principle is to scan a specimen with a finely focused electron beam of kilovolt energy. An image is built up point by point; it shows the variations in the generation and collection efficiency of the beam-excited signals at different points on the specimen. It has the advantage of a large depth of focus, examining rough, solid specimens with a minimum of specimen preparation. In this work, a Hitachi S-4000 scanning electron microscope was used to study the morphologies of sintered samples.

RESULTS AND DISCUSSION

As listed in Table I, samples with different compositions were prepared. Water and isopropanol were used as the cosolvents, the ratio was kept constant (1 : 1 by weight), and the total weight of solvent was kept constant. The relationship between ceramic properties (viscosity, hardness, and density) and binder compositions (PSS, PEGL, and DBS) were studied and are discussed as follows.

Viscosity

We first studied the effect of PSS-PEGL binder system on the properties of YSZ powders. The weight of PSS was kept constant, and the weight of PEGL was increased from 0.373 g to 2.0 g (from 4.97 wt % to 8.51 wt %). We also studied the effect of DBS on the ceramic slurry properties.

Factors influencing slurry viscosity include ceramic loading level, powder morphology, powder surface chemistry, use level, and properties of the dispersant and binder. We found that the amount of both PEGL-PSS and PSS-PEGL-DBS binder systems had great effect on the slurry viscosity. The viscosity decreased sharply with increased amount of binders (as shown in Figs. 2 and 3). For example, for PSS-PEGL system, the viscosity of sample C-929 (binder level 4.97 wt %) is 59.5 cP, and that of sample C-1021 (binder level 6.46 wt %) decreased sharply to 10.0 cP. For PSS-PEGL-DBS system, the viscosity of sample C-1211 with binder level of 11.89 wt % is 38.6 cP, and that of sample C-1201 with binder level of 13.79 wt %

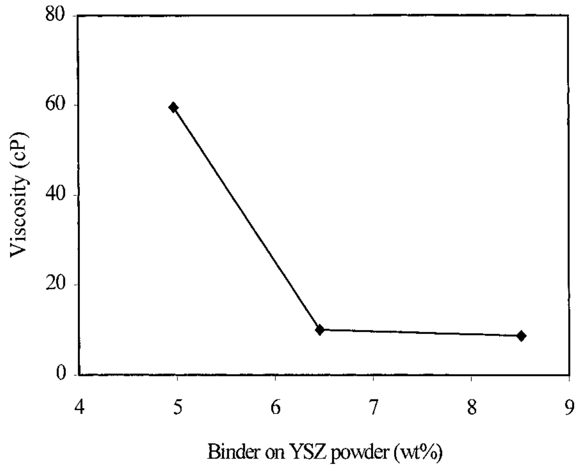


Figure 2 Dependence of viscosity on PSS and PECL composition.

Table II Density of the Green and Sintered Samples (g/cm^3)

Sample	Green Density	Sintered Density	Relative Density (%)
C-929	2.40	5.01	89.5
C-1021	2.29	4.78	85.4
C-1030	2.18	4.88	87.1
C-1113	2.47	4.73	84.5
C-1125	2.61	5.07	90.5
C-1201	2.34	5.12	91.4
C-1208	2.53	5.07	90.5
C-1211	2.23	5.09	90.9

Note: relative density (%) = sintered density/ideal density of YSZ*100

decreased sharply to 17.3 cP. Increasing the concentration of PEGL decreases the viscosity and improves the processibility of the slurry. Generally, the dependence of the viscosity of the slurries on the type and amount of binders used can be explained in two ways. The binders act as plasticizers; they insert themselves between the ceramic units, thereby reducing the physical attraction between the ceramic units. Also the binders coat the ceramic particles, increasing their effective size and reducing the electrostatic interaction in the system. The interaction of the binders with the slurries is believed to occur via the sulfonate —SO3— and the ester carbonyl —O–C = O— units, respectively.

Density

Green density is one of the most important parameters in the forming of ceramic articles. For a given ceramic powder, higher green density indicates better packing and results in less shrinkage during firing. Green densities and densities of sintered samples were listed in Table II and shown in Figures 4 and 5.

For the PSS-PEGL system, the green density decreased with increasing amounts of PEGL. It can be explained as that the volume occupied by the binder phase causes separation of ceramic particles, leading to the observed density decrease with added binder. But it is very interesting and unusual for the PSS-PEGL-DBS system, and the green density increased with the increasing amounts of DBS when two other organic materials were kept constant. The reason for this trend is not clear. Our result showed that the presence of the binder made the ceramic powder easier to press and resulted in a reduction in the

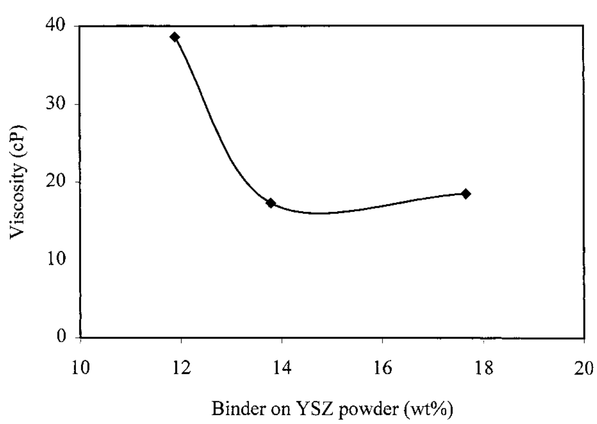


Figure 3 Dependence of viscosity on PSS-PEGL-DBS composition.

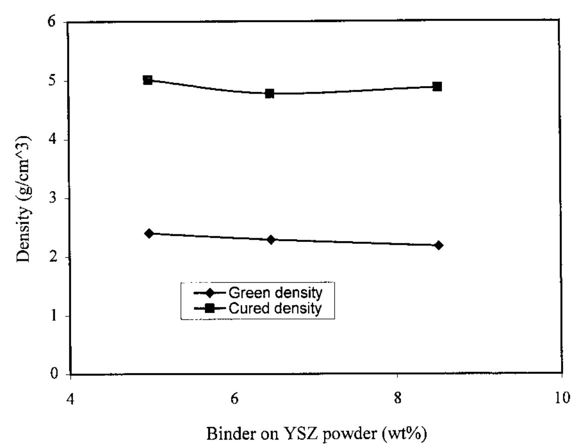


Figure 4 Dependence of density on PSS and PEGL composition.

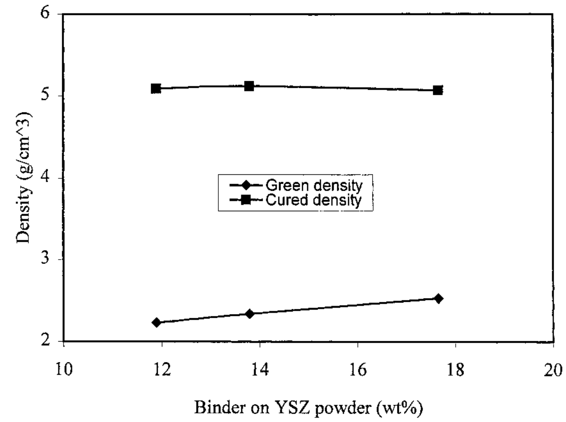


Figure 5 Dependence of density on PSS-PECL-DBS composition.

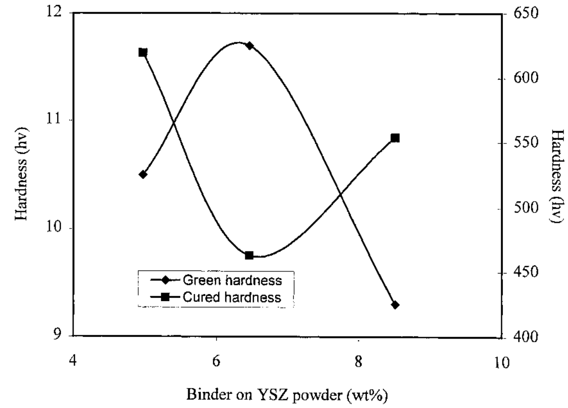


Figure 6 Dependence of hardness on PSS and PECL composition.

amount of voids in ceramic blocks. The higher the amount of binder present, the easier the samples were to pressed into pellets, and the higher their density. Because an ideal binder should provide both high green strength and high green density, it will be a very useful system to be used and studied in ceramic processing.

The densities of sintered samples were also studied. Our results showed that the sintered bodies have much higher densities of about twice those of the green bodies. For the PSS-PEGL system, sintered density of a sample containing lower binder content is a little higher than that of a sample with a higher binder content. However, the PSS-PEGL-DBS system has higher densities than the PSS-PEGL system. For the PSS-PEGL-DBS system, sintered density did not change significantly with increased binder content and the real sintered density is about 5.1 g/cm^3. It was reported that YSZ ideal density is 5.60 g/cm^3. Our results were lower than that of a single crystal because the YSZ crystal samples were multicrystal and not perfect. Also, the presence of voids in the system may lead to reduction in density. The PSS-PEGL-DBS system was more effective in increasing both the green and sintered densities, and they should have good mechanical properties.

Table III Vickers Hardness Results of the Green and Sintered Samples (HV Number)

Sample	Green Hardness	Sintered Hardness
C-929	10.5	619.3
C-1021	11.7	462.8
C-1030	9.3	553.7
C-1113	12.9	678.4
C-1125	14.3	626.4
C-1201	8.9	803.9
C-1208	10.4	730.7
C-1211	10.6	718.4

Hardness

We also studied the Vickers hardness of green and sintered samples; the results are listed in Table III and showed in Figures 6 and 7.

The HV number for green density was around 10. It is well known that the bonds between ceramic powders in green samples are mostly physical bonds. The green hardness results are related to the size of powder, the amount of binder, the T_g of binders, and the load used to press samples. Green hardness decreased slightly with the increase of binders due to the lower hardness of the

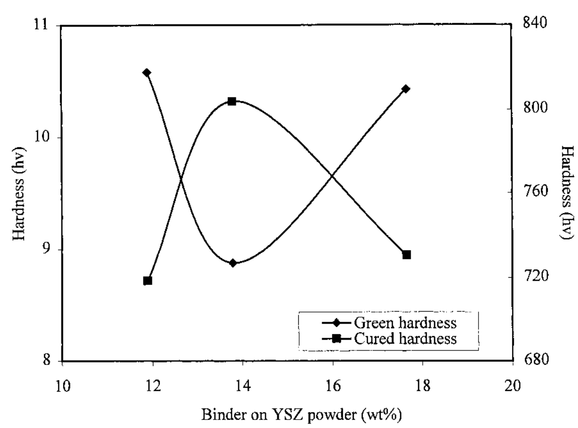


Figure 7 Dependence of hardness on PSS-PECL-DBS composition.

Table IV The Thermal Properties of YSZ Slurry Systems

Sample	T_{d1} (°C)	T_{d2} (°C) at 5 Wt % Loss	Weight Loss in Theory (%)	Weight Loss at 900°C (%)
PSS	50	400(step2)	—	60
DBS	300	630(step2)	—	70
PEGL	—	310	100	100
YSZ	75	360	0	7.5
C-929	75	395	4.97	8.0
C-1021	75	340	6.46	10
C-1030	—	250	8.51	14.0
C-1104	—	190	8.51	18.0
C-1113	—	350	9.5	11.0
C-1125	—	250	9.5	12.0
C-1201	—	280	13.79	17.0
C-1208	—	295	17.66	17.0
C-1211	—	295	11.89	13.0

binders (especially PEGL and DBS, which have long and flexible aliphatic units) compared to ceramic materials.

All the sintered samples have very high hardness numbers, 50 to 100 times higher than green. For each binder system, the sintering hardness did not vary linearly with an increased amount of binder. For example, sample C-929 (with lower PEGL content) had a very high sintered hardness number, up to 620, for the PSS-PEGL system; sample C-1201 (with higher DBS content) had a very high sintered hardness number, up to 800, for the PSS-PEGL-DBS system. These results show that PSS-PEGL-DBS system, especially DBS, had more effect on mechanical property, and it is compatible with the density results.

Comparison between PSS and PEGL

Samples C-1113 and C-1125 show the effect of PSS and PEGL with DBS as cobinder. PSS gave higher hardness, lower density, and lower viscosity. PEGL gave higher viscosity and density, but slightly lower sintered hardness. This probably is due to the differences between the T_g of the two polymers. PEGL has lower T_g; this low-T_g binder is therefore tackier than the higher T_g polymer under the experimental conditions, and it is much easier to be pressed into pellets. This resulted in higher viscosity and density, and lower hardness.

Thermal Properties

TGA was performed on all of the samples, including the polymer binders. The thermal decomposition of the samples is listed in Table 4. Figures 8 and 9 show TGA traces obtained at a heating rate of 20°C/min for the three organic materials and the YSZ coated with the organic binders in air. The samples show different burnout profiles. DBS and PSS gave somewhat more gradual burnout than PEGL. The decomposition temperature of PEGL is the lowest, around 310 °C; this is due to its low molecular weight and chemical structure. Because PSS and DBS are sodium salts, they showed higher decomposition temperature, and the residue is high owning to the salt product in the ash.

Pure YSZ powders have two decomposition steps in TGA plot (as shown in Fig. 9); one is at around 100°C and weight loss of about 3%, and the other is at around 300°C and weight loss around 7.5%. It suggests that there are some low molecular weight molecules and organic components in the YSZ powder. As the polymer binders caused the decomposition temperature shift to the low temperature, the temperature scale became narrow. The temperatures at weight loss of 5% were recorded as decomposition temperatures (T_d). For example, T_d of sample C-929 is around 360°C (starting from 50°C and ending at 450°C), and T_d of sample C-1030 is around 250°C (starting from 50°C and ending at 300°C). The weight loss at 900°C was compared with the theoretical calculated weight loss, and they were in a good agreement.

From the TGA results, it can be seen that the binder system with PSS, PEGL, and DBS has better thermal properties in the ceramic slurry system because of their lower decomposition tem-

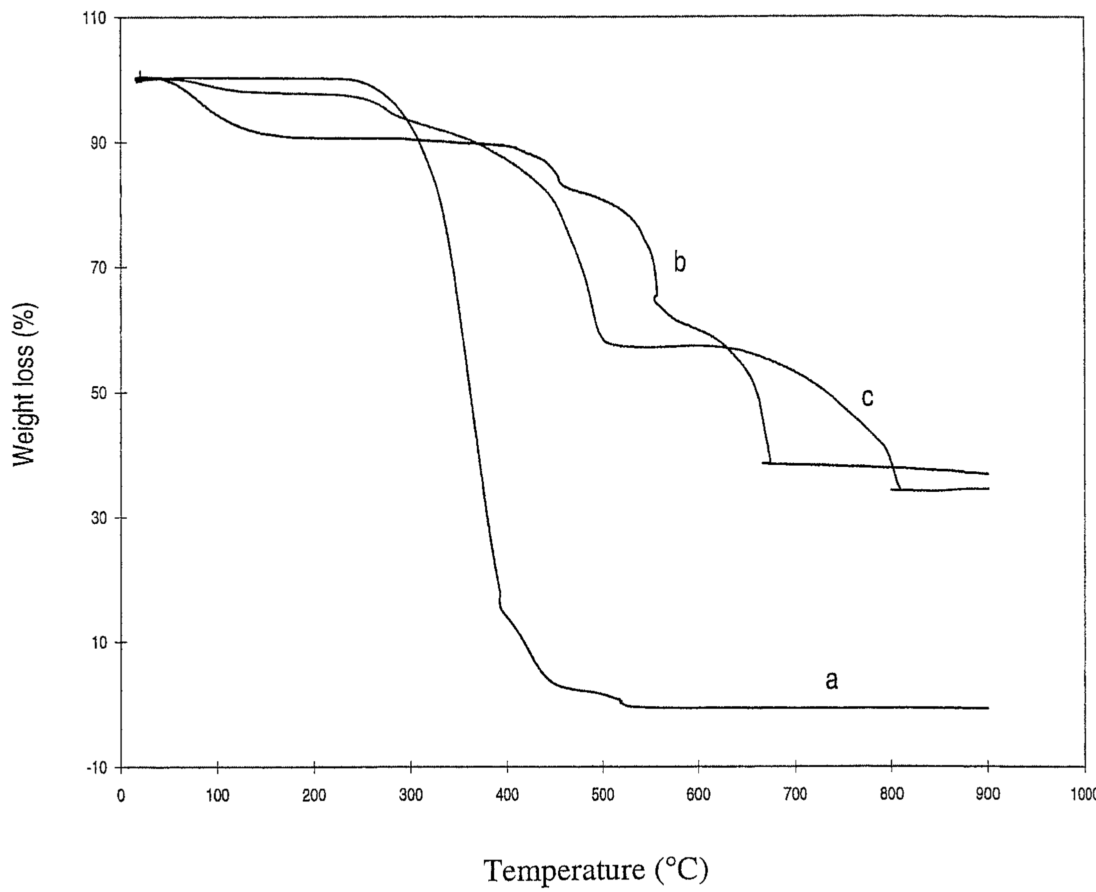


Figure 8 TGA traces for PEGL (a), DBS (b), and PSS (c).

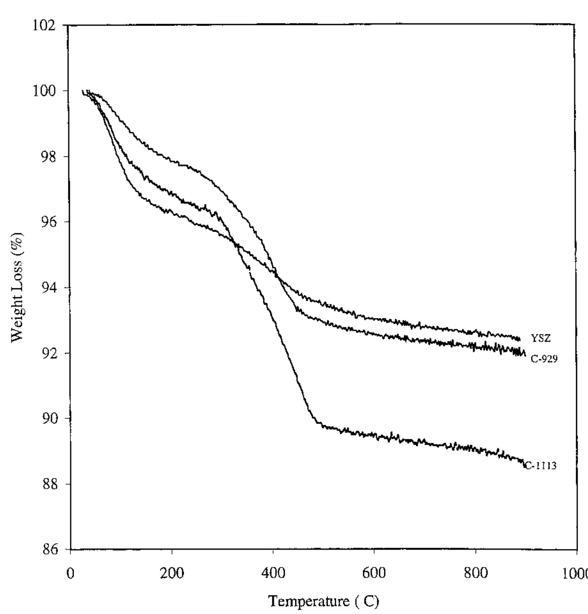


Figure 9 TGA traces for YSZ, C-929, and C-1113.

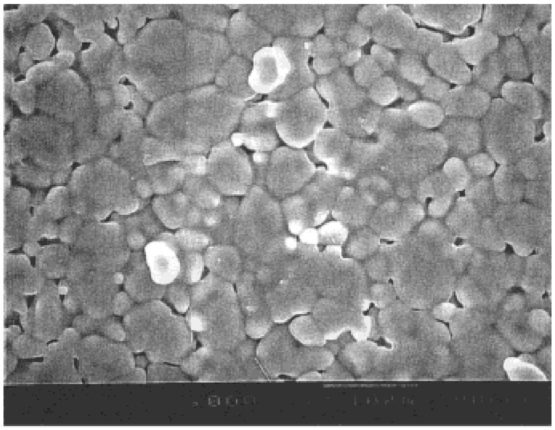
perature and lower polymer residue after burnout. It is good for the sintering process later. And TGA results are helpful and important to sintering program for decomposition of binders.

Morphology

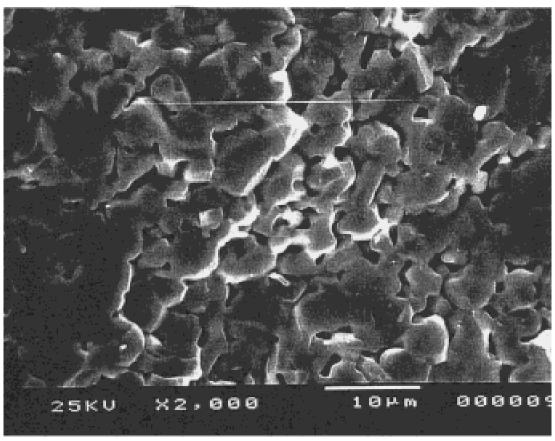
SEM was used to study the morphology of sintering sample. Figure 10 shows the surface and fracture surface pictures of YSZ pellets. The surface picture shows a dense and relatively uniform sample. The average diameter of grains was 3.3 μm. The pellets had lower porosity and higher density, as mentioned earlier. Some liquid phase was seen, and it may have been caused by a glassy phase with lower T_g.

CONCLUSION

Two binder systems, PSS-PEGL and PSS-PEGL-DBS, have been used in YSZ slurry formulation.



(a)



(b)

Figure 10 SEM pictures of sintered YSZ pellets showing (a) surface structure and (b) fracture surface.

These organic materials with different chemical structure and functional groups had great effect on the ceramic slurry formulation. Some ceramic properties were studied, such as viscosity of slurry, hardness and density for green and sintered samples, thermal properties for binders and slurry systems, and the morphology for sintered samples.

The amount of binder had great effect on the slurry viscosity. The slurry viscosity decreased sharply with an increased amount of binders. The amount and types of binder system also had effect on the green and sintered densities; especially for the PSS-PEGL-DBS system, higher green density can be obtained. All the sintered samples had higher density, and the relative density was about 91%. The hardness of the sintered bodies was 50 to 100 times higher than the green and was dependent on the type of binder used. Thermal behavior of binders and slurry was studied. The decomposition temperature and decomposition rate were affected by the presence of the binders. SEM pictures showed dense and relatively uniform sintered bodies.

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