ULTRASONIC CHARACTERIZATION OF GREEN AND SINTERED CERAMICS

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ABSTRACT

Ultrasonic velocity measurements of colloidally processed alumina ceramics were carried out using "dry" transducers. Ultrasonic velocities of green samples were found to be affected both by the density and the particle packing. Ultrasonic velocity paths depended on the initial green microstructure and were distinctly different upto a relative density of 70 %. The velocity showed a linear relation with density for higher density samples. Elastic moduli, calculated from ultrasonic velocities, were less sensitive to densification rates as compared to ultrasonic velocity measurements.

INTRODUCTION

In-situ quality control of ceramics bodies during various stages of manufacture is critical to meet quality specifications. Proper monitoring and understanding of the sintering process is generally necessary to obtain a desired ceramic microstructure. Microstructural and mechanical quantification of ceramics by conventional methods is mainly destructive and time consuming. In most cases attention is devoted towards characterization of fully densified structures, since partially sintered structures are difficult to handle due to their fragile nature. However, on-line process control will require an understanding of microstructural evolution from a porous to a fully densified state.   An alternative for porous material characterization is the use of non-destructive techniques such as ultrasonics.

Normal ultrasonic measurements carried out are those of velocity and attenuation. This

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paper focusses on ultrasonic velocity measurements to characterize porous, partially sintered and fully dense alumina bodies. Ultrasonic velocity is regarded as more of a macroscopic property and is mainly used for determination of elastic properties [1-3], although in many cases it may be used to determine microstructural changes[4]. Monitoring of ultrasonic velocity changes during sintering can serve as an indirect method of determining the densification rate. In case of green ceramics, it is necessary to use relatively low frequencies (5 MHz) for determining ultrasonic velocities on account of the high attenuation of ultrasound. Though it is generally expected that ultrasonic velocity of a green ceramic is a function of density [5], questions still remain, eg. will the velocity be similar for samples with same green densities but different particle packing. A continuous evaluation of velocity measurements at various stages of densification can provide significant information about the state of microstructural evolution.

EXPERIMENTAL PROCEDURES

The experimental details including materials and procedures are given below.

<u>Materials</u>

High purity alpha alumina powder[*] (AKP-30) of density 3.98 g/cc was used for this study. Reagent grade chemicals, including HNO_3, KOH and KNO_3, to adjust pH and ionic strength, were obtained from Fisher Scientific Co.

<u>Particle Characterization</u>

<u>Particle size</u>: Particle size distribution was measured using a light scattering technique[**]. The mean particle size measured was 0.49 microns.

<u>Surface Area</u>: The powder specific surface area[**] (multipoint BET) measured using nitrogen

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[*]   Sumitomo Chemical America, Inc., NY

[**]   Model CAPA-700, Horiba Instruments, Inc., Irvine, CA

[**]   Model OS-7, Quantachrome Corp., Syosett, NY

gas adsorption was 10 m^2/gm.

Surface charge: The surface charge of the alumina powder was measured by the ESA[*] (electrokinetic sonic amplitude) technique. In this technique, the ESA of a 2 vol.% suspension of alumina was measured at constant ionic strength (0.005 M KNO$_3$). The ESA measurements were then converted into the zeta potential (a standard measure of the surface charge) using the well known Smoluchowski equation, along with an additional inertial term [6,7].

Rheological measurements: The viscosity of the various suspensions was measured, as a function of shear rate, using a Brookfield splindle type digital viscometer.

Preparation of green samples

Various colloidal suspensions of alumina were prepared at different pH's (3.5 to 11.5). The solids loading of the suspensions was maintained at 40 vol%. The suspensions were sonicated to disintegrate the soft agglomerates and stirred with a high speed stirrer for adequate mixing. Green samples were prepared by slip casting. This was done by pouring the above suspensions into plastic rings set on absorbent plaster blocks. The cylindrical specimens thus prepared were approximately 26 mm in diameter and 6-8 mm in thickness.

Methods

Characterization of Green Samples

Mercury Porosimetry: Mercury Porosimetry[**] was used to measure the pore size distribution of green samples. The green density of the samples was then calculated from the total measured porosity.

Archimedes density: The green density, as well as the open and closed porosity of the samples was measured by the Archimedes technique. To impart sufficient strength for such

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[*] ESA-8000 System, Matec Applied Sciences, Hopkinton, MA

[**] Model SP-100, Quantachrome Corp., Syosett, NY

measurements, the green samples were heat treated at 700°C for 2 hrs. The green density was not expected to change due to this treatment, since the formation of interparticle contacts at 700°C during the initial stages of sintering would not cause densification.

Sintering: The green samples prepared above were sintered at temperatures of 1200, 1350 and 1500°C for times varying from 1 to 60 hrs. A wide range of samples with varying densities and microstructures were thus generated.

Characterization of sintered samples

Archimedes: The sintered samples were characterized for porosity and density by the Archimedes technique. The densities reported are expressed as percentages of the theoretical density of 3.98 g/cc.

SEM analysis: SEM* (scanning electron microscopy) was used to characterize the microstructure of the samples.

Ultrasonic Analysis: Ultrasonic analyses of both green and sintered samples was carried out at Ultran Labs., Boalsburg, PA. Pulsed ultrasound was employed to measure time of flights (TOF) by the dry coupling direct transmission method using 5 MHz dry transducers [8,9]. It was found, that at a frequency of 5 MHz, the ultrasonic attenuation was sufficiently low for efficient propagation of ultrasound. The ultrasonic velocity was determined by measuring the time of flight (TOF) between the top and bottom surfaces.

RESULTS AND DISCUSSION

In order to use Ultrasonics for the characterization of ceramics through all the stages of microstructural evolution, from the green to the sintered state, it was initially necessary to prepare green ceramics having controlled microstructures. In the present work, the variable used for controlling the green properties was the pH of the colloidal suspension. The pH in turn affects

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* JEOL 35 CF, JSM 6400

the surface charge or the zeta potential of the particles [6].

Rheology

The rheological properties of colloidal suspensions have a profound effect on the properties of the green ceramic [10]. These in turn depend on the zeta potential and the volume fraction of the particles, the shape, size and distribution of the particles, and a number of other factors. In the present investigation, the same powder (AKP-30) was used throughout. The volume fraction of the colloidal suspensions was always maintained at 0.4. Hence, the main variable that could affect the rheological properties of the suspensions was the zeta potential, which is dependent on the pH. Typically, colloidal suspensions having high zeta potential and low viscosities result in green bodies of high density and strength.

To assess the state of dispersion of various suspensions used for slip casting, the rheology of 40 vol% slurries prepared at various pH values was studied. The viscosity at a shear rate of 20 s^{-1}, and zeta potential as a function of pH are plotted in Figure 1. Dispersed suspensions having higher zeta potentials (pH 3, 4, 11.5) show much lower viscosities as compared to partially flocculated suspensions which have relatively lower zeta potentials (pH 5, 10.5). As one approaches the iep the viscosities increase dramatically.

Based on the above measurements, it was decided to slip cast suspensions prepared at pH 3.5, 4, 4.5, 5, 10.5, 11 and 11.5. The green bodies thus prepared would have a sufficiently broad range of densities and microstructures, which could then be characterized by conventional and ultrasonic techniques.

Green Sample Characterization

Characterization of green ceramic samples not only gives an indication of the properties of the final sintered product but also yields a great deal of information about the effects of the processing variables on the green body. The properties one normally assesses are the pore

size distribution and the green density, since these have a direct bearing on the quality of the final product.

Mercury Porosimetry of green samples: Figure 2 shows the pore size distributions of the partially flocculated and dispersed samples. As expected the well dispersed samples corresponding to pH 4, had a narrow pore size distribution with a low median radius of 30 ± 1 nm. The partially flocculated samples (pH 10.5) had a larger median radius 50 ± 1 nm and a broader pore size distribution. Pore size distributions of samples made from suspensions at other pH values were within those for the above two. Table 1 lists the median radii for various samples for the range of pH's used in this work.

Archimedes Density: The green samples were partially sintered at 700°C for 2 hours in order to impart sufficient strength for measuring the density by the Archimedes technique. It is seen from Table 2 that the well dispersed samples (pH 4) had a higher Archimedes green density of 63.4 % and negligible closed porosity (0.2 %), compared to the partially flocculated samples (pH 10.5) which had a green density of 54.6 % and a closed porosity of 3.2 %. This behavior is expected since the dispersed samples have better particle packing during the slip casting process as compared to the partially flocculated samples.

Ultrasonic Characterization of Green Samples: The ultrasonic longitudinal and shear velocities were measured using 5 MHz dry transducers. The velocities are plotted in Figure 3 for samples prepared at different pH values. The well dispersed samples (pH 3.5, 4) show higher velocities than the partially flocculated samples (pH 10.5). Thus the green ultrasonic velocity is sensitive to the processing parameter; in this case, the suspension pH. It has been demonstrated by many authors [11,12] that the density of sintered samples (> 90 %) has a very strong influence on the ultrasonic velocity. Similarly for green samples, it has been shown by Kupperman [5] that velocity and density are strongly related. Since the dispersed samples have much higher

densities than the partially flocculated samples, the observed behavior is expected.

The other important factor that could have an influence on the ultrasonic velocity is the velocity dispersion, which is a measure of the frequency dependence on ultrasonic velocity. Velocity dispersion in porous monolithic ceramics typically occurs due to the pores, their distribution and morphology within the samples, while for dense monolithic ceramics, it is mainly due to the grain boundaries. Velocity dispersion typically is a factor at higher frequencies (>50 MHz) for dense ceramics, where the attenuation of ultrasonic waves is significant. In case of green or porous ceramics, significant velocity dispersion can occur at much lower frequencies as compared to densified ceramics. In the present case, the velocity dispersion for a 5 MHz broadband dry transducer at a center frequency of 5 MHz was relatively low, since the attenuation of the ultrasonic wave at this frequency was minimum. Below this frequency, the attenuation increases on account of interference effects. However, even at this frequency, velocity dispersion can have an influence on the group velocity in a porous ceramic, although not of the same magnitude as the density of a sample. A sample having an inhomogeneous particle arrangement, as in the case of a partially flocculated sample, would in general experience greater velocity dispersion as compared to a sample with homogenous particle arrangement. Thus, if the effects of density and velocity dispersion are considered together, it would be expected that the dispersed samples would have higher ultrasonic velocities as compared to the partially flocculated samples. It should be noted, that in the case of green samples having minor density differences (3-4 %), the velocity dispersion may be the deciding factor in determining which among the samples would have a higher ultrasonic velocity. In other words inhomogeneities in particle packing would affect velocity measurements.

The partially flocculated and dispersed samples represent extreme cases for which the densities are significantly different. For samples inbetween, the velocity-density relationships

need not be straightforward. This is evident in Figure 4, where a graph of relative green density as a function of ultrasonic velocity is shown. The velocities are given along with the Mercury Porosimetry analysis in Table 3 for comparison purposes. There are two observations which are evident from Figure 4 and Table 3:

a. Samples at pH 4.5 and 11 show the same ultrasonic velocity (~ 1788 m/s), but have different green densities (61.7 % and 57.3 %).

b. Samples at pH 5 and 11.5 have similar green densities (58.7 %), but different ultrasonic velocities (1736 and 1850 m/s).

These two observations do not confirm to the normal linear behavior one associates between velocity and density. However, the samples considered here are porous and at a frequency of 5 MHz, velocity may be affected by inhomogeneities or particle structures within the samples.

The first observation has two samples (pH 4.5 and 11) with different densities (61.7 % and 57.3 %) showing similar ultrasonic velocities. Figure 5 shows the pore size distributions of these 2 samples. The median pore radius does not seem to be a factor, since although the sample with the higher density (pH 4.5) had a narrower distribution with a smaller median size, it still has a velocity quite similar to the lower density sample. However, Figure 5b does indicate the presence of a very small percentage of large sized pores for the pH 4.5 sample. As seen from Table 2, the Archimedes density technique reveals no significant differences in the amounts of open and closed porosity, when the samples were partially sintered (700°C-2 hrs.). Overall, it appears that the higher nonuniformity in the structure may have resulted in the lowering of velocity. Other factors related to the morphology of the pores, their connectivity, etc. may also be responsible for this behavior. Hence, although the densities differ by about 4 %, the difference is not significant enough to cause measurable changes in velocities.

The second observation has two samples (pH 5 and 11.5) with equal densities (58.7 %) but different velocities (1736 and 1850 m/s). One might expect that a difference in the pore size distribution might have contributed to the velocity differences. It is seen from Figure 6, that both samples have approximately similar pore size distributions and median pore sizes. However as in the earlier case, the lower velocity sample (pH 5) had a small fraction of larger pores present in the size range of 600 to 1300 nm (Figure 6b) and the closed porosities observed on partial sintering (700°C-2 hrs.) were different. The sample with the lower velocity (1736 m/s) had a higher closed porosity of 2.2 % as compared to a closed porosity of 1 % for the higher velocity sample (1850 m/s). These factors could have caused a reduction in the velocity. Other factors such as the morphology of the pores, the pore coordination number, formation of particle networks, connectivity between pores, etc. may also be responsible for the observed velocity difference.

Significance of Green Ultrasonic Velocity Measurement

In the present work, the main variable used to control the green body microstructure was the pH of the colloidal suspensions. It is seen from Figure 3 that the ultrasonic velocity is very sensitive to this processing parameter. A similar graph of green velocity against processing variables, used in other manufacturing processes, can serve as a simple method for assessing the effect of these variables on the green ceramic products. For example, the compaction pressure may be the major variable during dry pressing, while the binder content may be the significant variable during extrusion. A graph of longitudinal and shear ultrasonic velocities against these variables would be extremely valuable in controlling the process. In real scenarios however, a number of variables would be acting simultaneously and affecting the quality of the green product. Some variables may have dominant effects over others and their interactions may also be of significance. In such cases, use of experimental designs is recommended. The

ultrasonic velocities can serve as response variables for the necessary experimental design technique. An added advantage is that the ultrasonic velocities can be monitored in real time and can serve as an effective quality control tool during actual production [13].

Velocity dispersion studies can be very useful in understanding the internal structure of the green ceramic. These have however not been performed in the present work. For such studies the phase and group velocities in a specimen have to be determined. These can be determined by actual measurement or from the phase spectra of broad band pulses [14]. By accounting for phase velocity dispersion, measurement of subtle property variations can be made [15].

Sintering of Green Samples

The effect of different sintering treatments on green samples having varied microstructures is of interest to many researchers and quality control personnel, the major objective being the optimization of mechanical or other properties of interest. Ultrasonic measurements provide a convenient method of monitoring the changes occurring in a green ceramic upon sintering. In order to accomplish this, green samples were sintered in air at various temperatures and times so as to obtain a wide range of densities and microstructures. The sintered samples were characterized for density, open and closed porosity by the Archimedes technique and for the microstructure by SEM (scanning electron microscopy). Ultrasonic velocity and attenuation measurements were carried out to determine the acoustic properties of various samples.

Characterization of Sintered Samples

Archimedes: Green samples made from well dispersed suspensions (pH 4.0) have a higher densification rate and reach theoretical density at lower temperatures and times compared to samples made from partially flocculated suspensions (pH 10.5). The partially flocculated samples develop a higher fraction of closed pores at a much lower sintered density compared

to the dispersed samples.

<u>Ultrasonic Velocity of Sintered Samples</u>: The longitudinal ultrasonic velocities for the various samples as a function of density are shown in Figure 7 respectively. It is seen that after a relative density of about 70 %, the velocities for all the samples show a linear behavior and fall within a narrow band. The shear velocities show a similar behavior. The higher rate of velocity increase for the well dispersed samples is also evident from Table 4. This is consistent with the higher densification rate observed for these samples. The velocity paths of green and partially sintered samples below a relative density of about 70 % are different and are strongly dependent on the starting green microstructure. The longitudinal and shear velocities exhibit a similar pattern of behavior with the increase in densities of various samples. The longitudinal velocities are about 1.5-1.7 times the shear velocities, which is consistent with the fact that the longitudinal modulus of most ceramics are 1.5-2 times their shear modulus.

<u>Applications of velocity measurements of sintered ceramics</u>

Measurement of ultrasonic velocity of a partially sintered ceramic can give a reasonable indication regarding the elastic properties of the sample, its densification rate or path and its prior history. For example, in the present case for sintering treatments at 1200°C for 1, 3 and 12 hours, the dispersed samples had longitudinal velocities of 7846, 8312 and 9008 m/s while the partially flocculated samples had velocities of 6429, 6620 and 7102 m/s respectively (Table 4). The corresponding Archimedes densities for the dispersed samples were 76.1, 77.9 and 82.2 %, while for the partially flocculated samples they were 62, 63.9 and 66 % respectively. The velocity differences between the corresponding samples are significant. Even without a knowledge of the actual elastic properties of the samples or their prior history, it can be concluded that the dispersed samples had a higher densification rate (due to a superior green microstructure), since an increase in velocity is a strong indication of an increase in elastic properties which in turn is

related to the density.

<u>Elastic Moduli</u>

The greatest advantage of ultrasonic velocity measurements is the nondestructive determination of the elastic moduli. Assuming that the samples used in this analysis are isotropic, standard velocity-elasticity relations [1-3] can be used to calculate the various moduli. However, to make any inference about the mechanical strength of a ceramic, from the elastic moduli, a knowledge of the critical defects present is essential. In metals, this is more easily accomplished since the critical defects are generally quite large and these can be imaged using conventional ultrasonic C-scan imaging. The C-scan presentation gives a plan view indication of the material similar to an x-ray picture. Defects such as pores, inclusions, etc. can be seen on a C-scan provided they are sufficiently large. In ceramics, however, the defects (pores) are too small (<25 microns) to be reliably detected with the current state of ultrasonic technology. Nevetherless, in this work, since the prior history of the samples were known, it is expected that as compared to the dispersed samples the partially flocculated samples would have lower strengths due to the presence of larger defects (pores).

Figure 8 shows the variation of Young's modulus for dispersed and partially flocculated samples. It is observed that the Young's modulus follows a pattern quite similar to the velocities. However, the increase in modulus with densification is more gradual. The shear and bulk moduli also show a similar pattern. Figure 9 shows the variation of Poisson's ratio with density for samples having different green densities. The Poisson's ratio appears to fall within a band of 0.15 to 0.25 with a very gradual increase to the upper limit for higher density samples. As seen from the figure, the experimental error in determining the Poisson's ratio is relatively large, irrespective of the initial green microstructure. Green, et al. [16] have reported a similar result. This is not surprising, since it is a small quantity dependent on differences of the other elastic

properties and hence quite sensitive to errors in them [17].

CONCLUSIONS

Ultrasonic characterization of tailor made green and sintered ceramics of alpha alumina has been discussed. Prior to this investigation, the application of recently developed dry transducers for studying the velocity changes during the entire process of densification had not been demonstrated. This work establishes the potential of dry transducer technology for investigating the velocities of both green and sintered ceramics.

Green ceramics, made by controlling the pH of colloidal suspensions, showed high sensitivity to low frequency (5 MHz) ultrasound. Samples made from suspensions having high zeta potentials (dispersed) had higher green densities (62.2 %) and their green velocities were high (1881 m/s). Suspensions having low zeta potentials (partially flocculated) had low green densities (53.9 %) and their corresponding green velocities were the lowest (1689 m/s). However, for samples made from suspensions having zeta potentials inbetween the above two (acidic and basic pH values) and where the green density differences were less than 4 %, the green velocity did not show a linear correlation with the density. Rather, it seemed to be affected more by the particle packing of these samples. Upto a relative density of 70-75 %, the velocity paths for samples having different green densities were distinct. Beyond this, velocities for all samples showed a linear correlation with density and fell within a narrow band. The rate of velocity increase corresponded with the densification rate and the green density of samples. However, below a density of 70 % the velocity increase was magnified many times over.

Assuming conditions of isotropy, elastic moduli for various samples were calculated from their ultrasonic velocities. The Young's, shear and bulk modulus followed a pattern similar to the velocity. However, as compared to velocity increase, the increase in modulus was more gradual during the course of densification.

ACKNOWLEDGEMENTS

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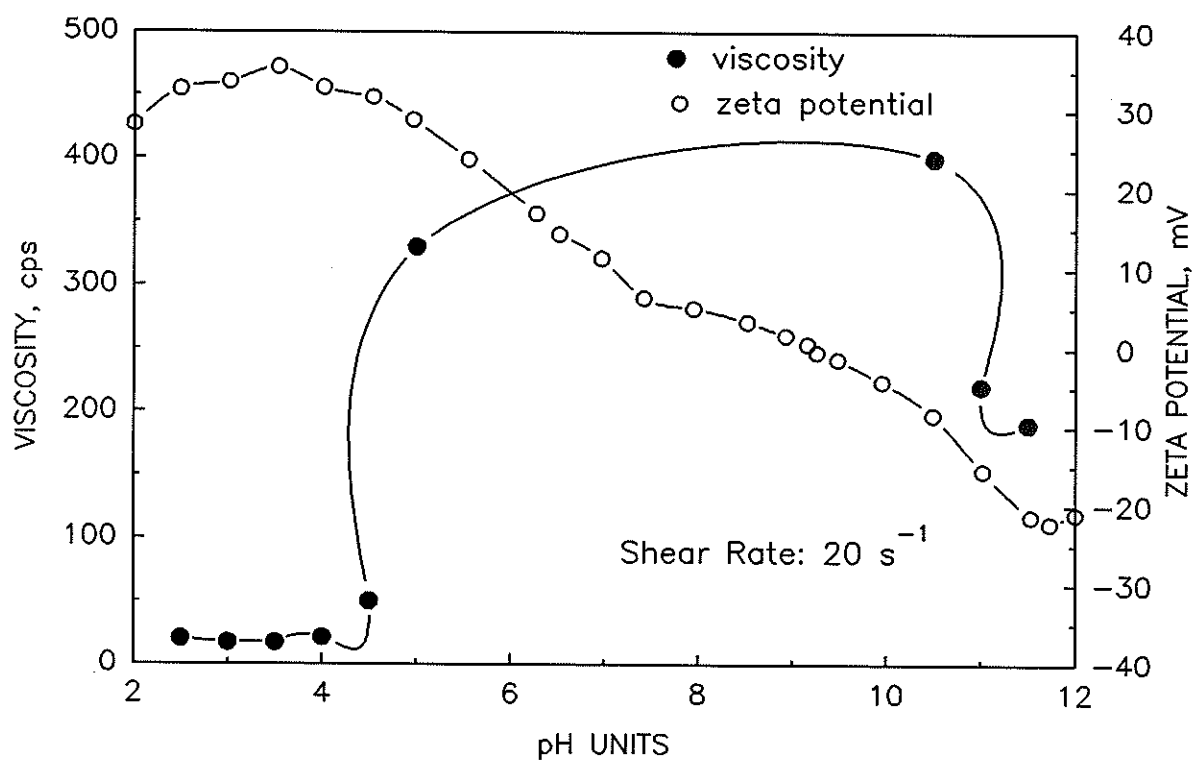Change Ref. to Paper in EPrs Japan

LIST OF FIGURES

Figure 1.   Viscosity (at 20 s^{-1}) and zeta potential of alumina suspensions as a function of pH.
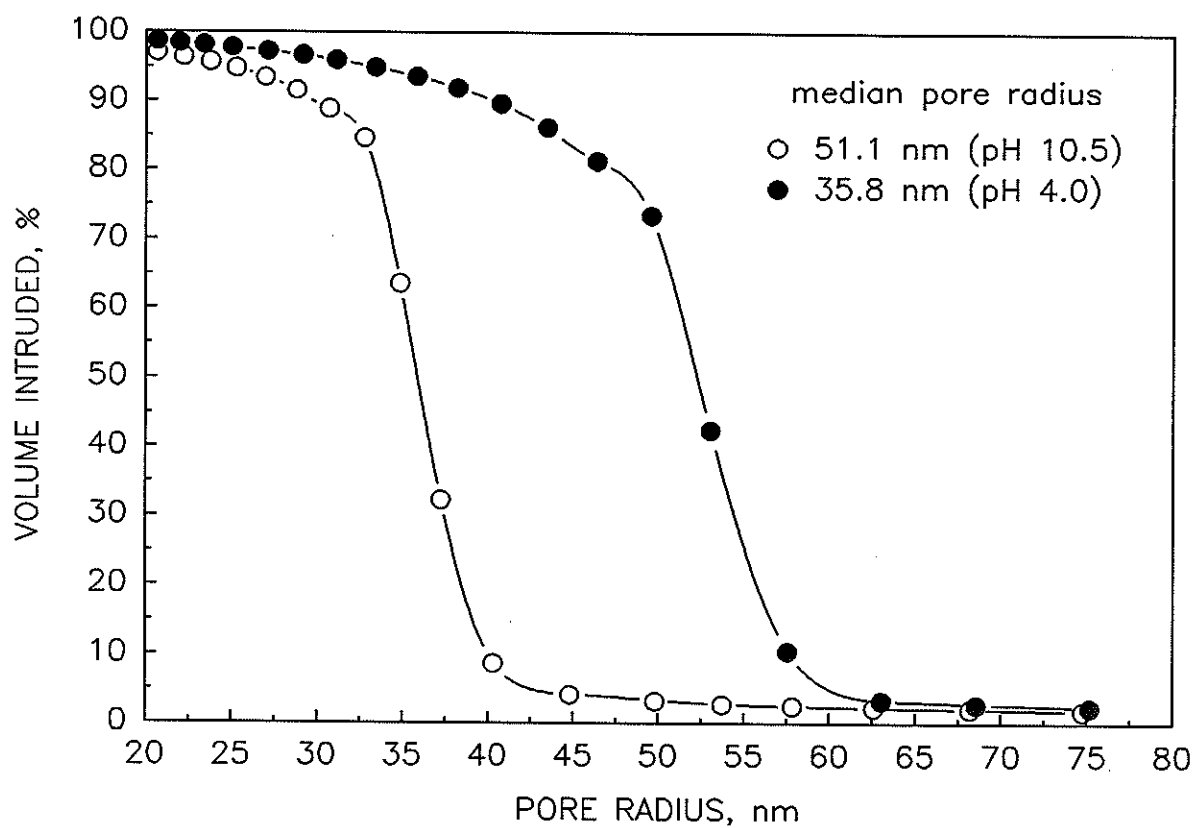
Figure 2. Pore size distributions of partially flocculated (pH 10.5) and dispersed (pH 4.0) green samples prepared by slip casting.
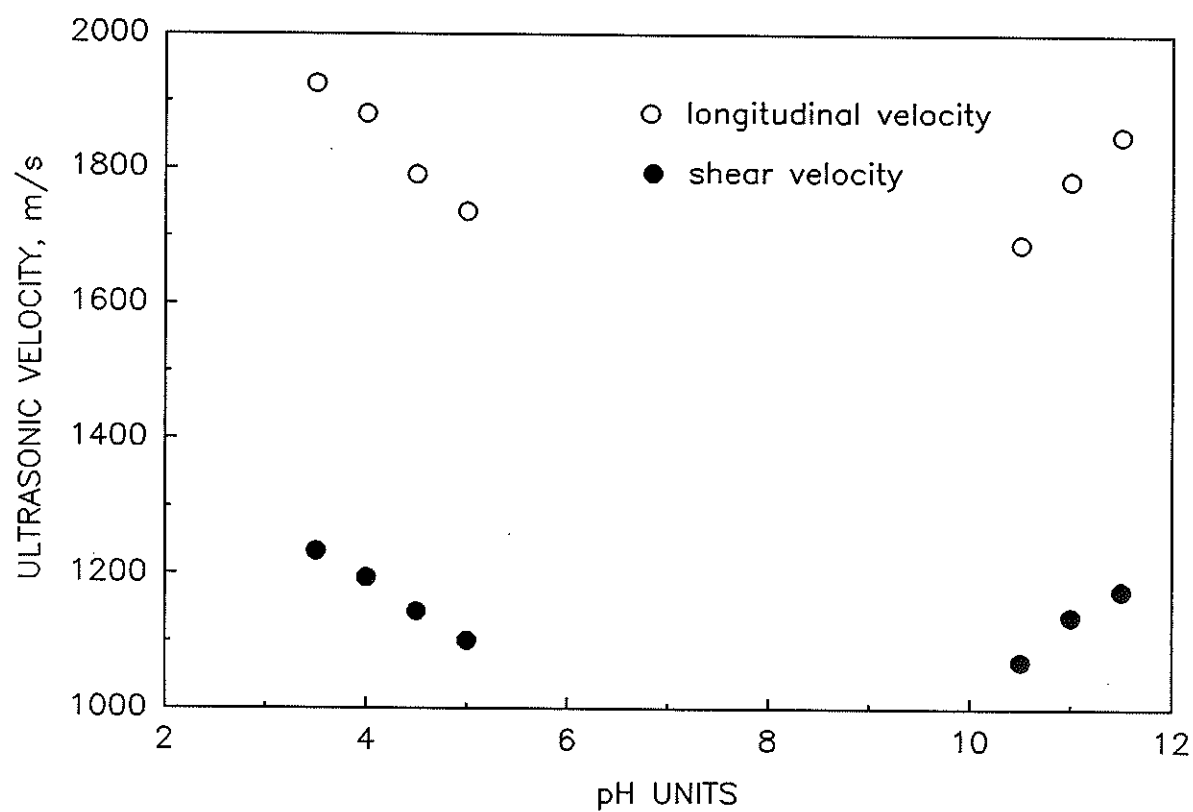
Figure 3.   Longitudinal and shear ultrasonic velocities for green samples prepared at various pH's.
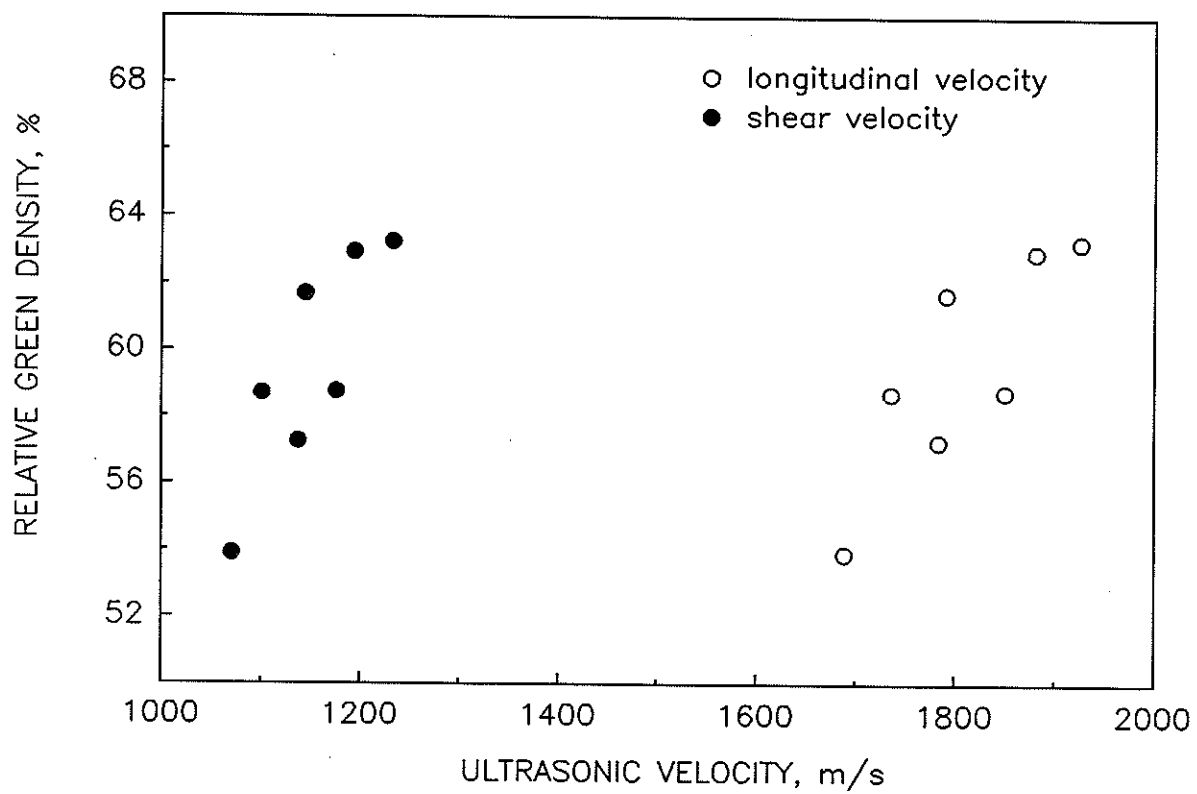
Figure 4.   Relative green density of samples against the longitudinal and shear ultrasonic velocities.
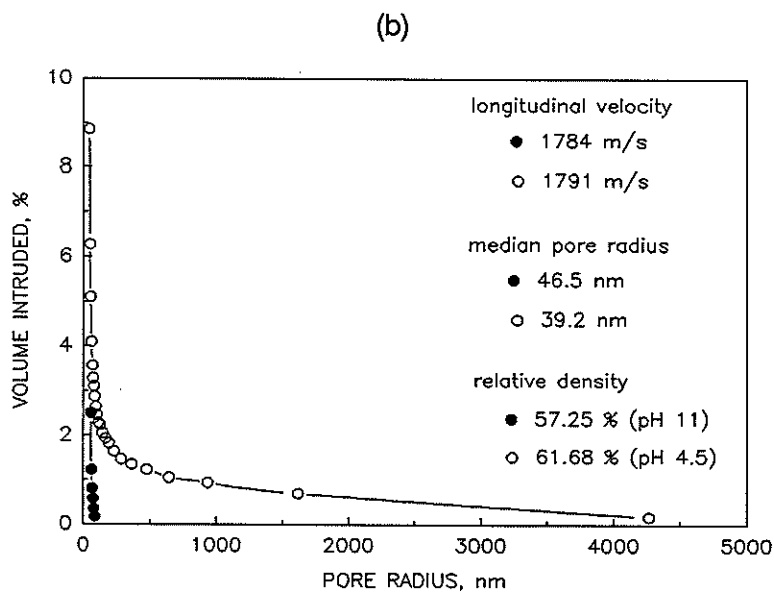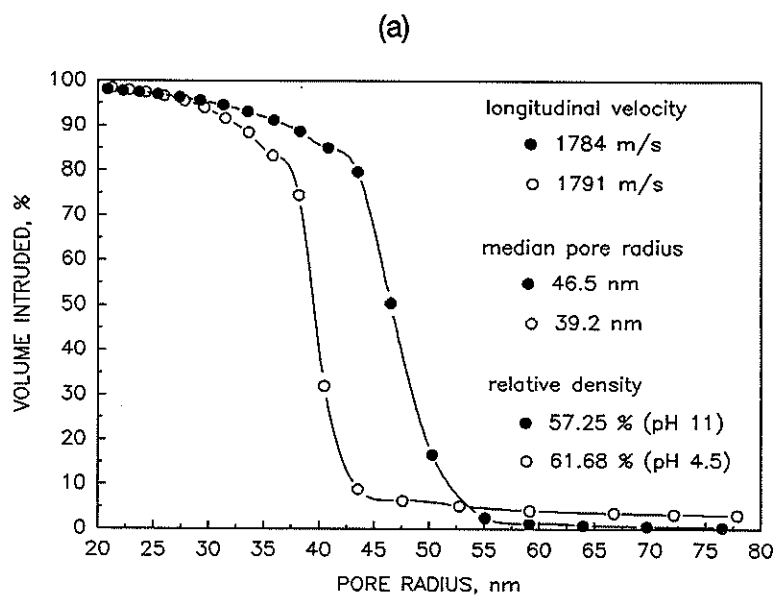
(a)

(b)

Figure 5.   Pore size distributions of samples having green densities 57.3 % and 61.7 %. (a) 100 % intrusion (b) 10 % intrusion.
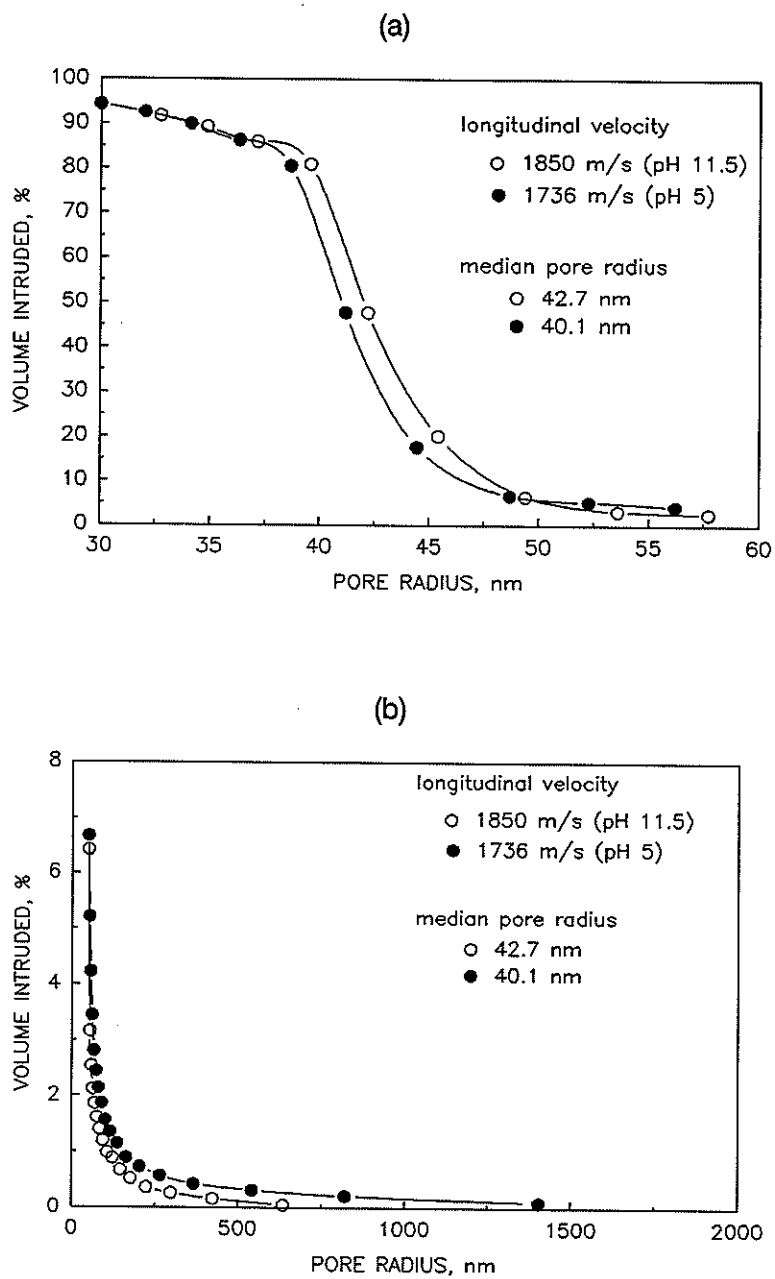
(a)

(b)

Figure 6.   Pore size distributions of green samples with similar densities (~58.7 %) but different ultrasonic velocities. (a) 100 % intrusion (b) 8 % intrusion.
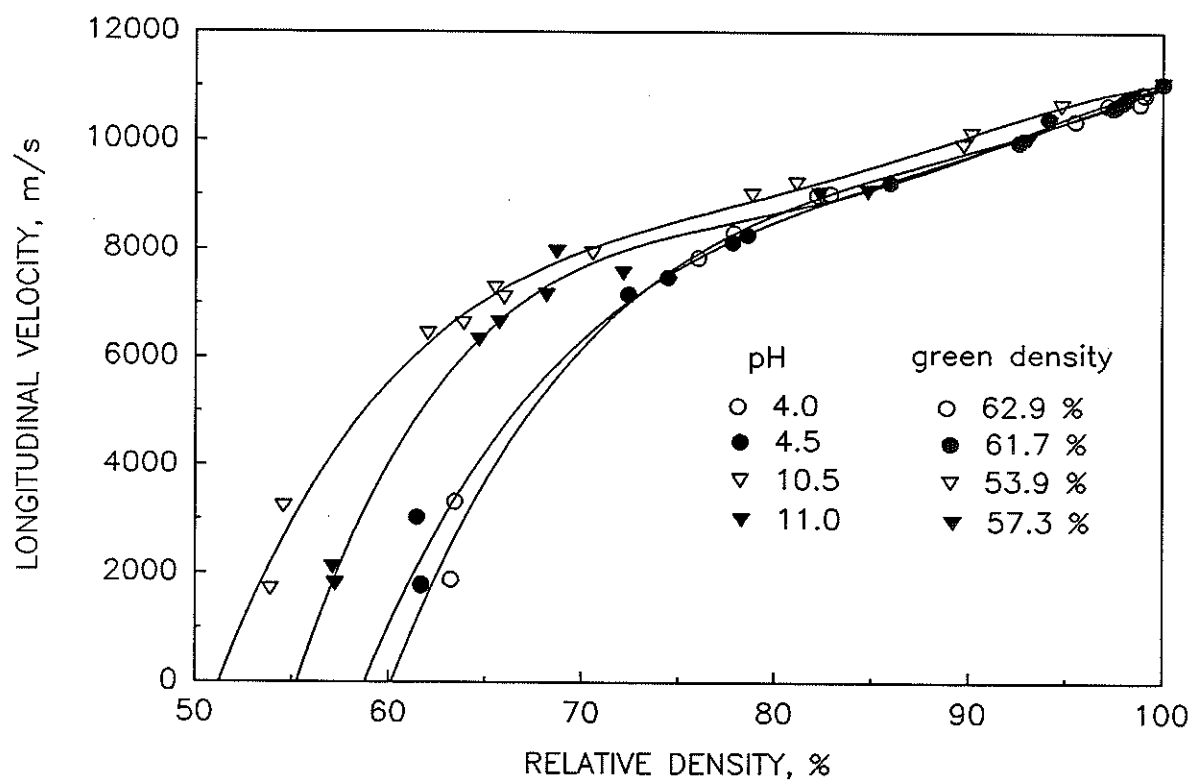
Figure 7.   Variation of longitudinal velocity with percentage relative density for samples having different green densities.
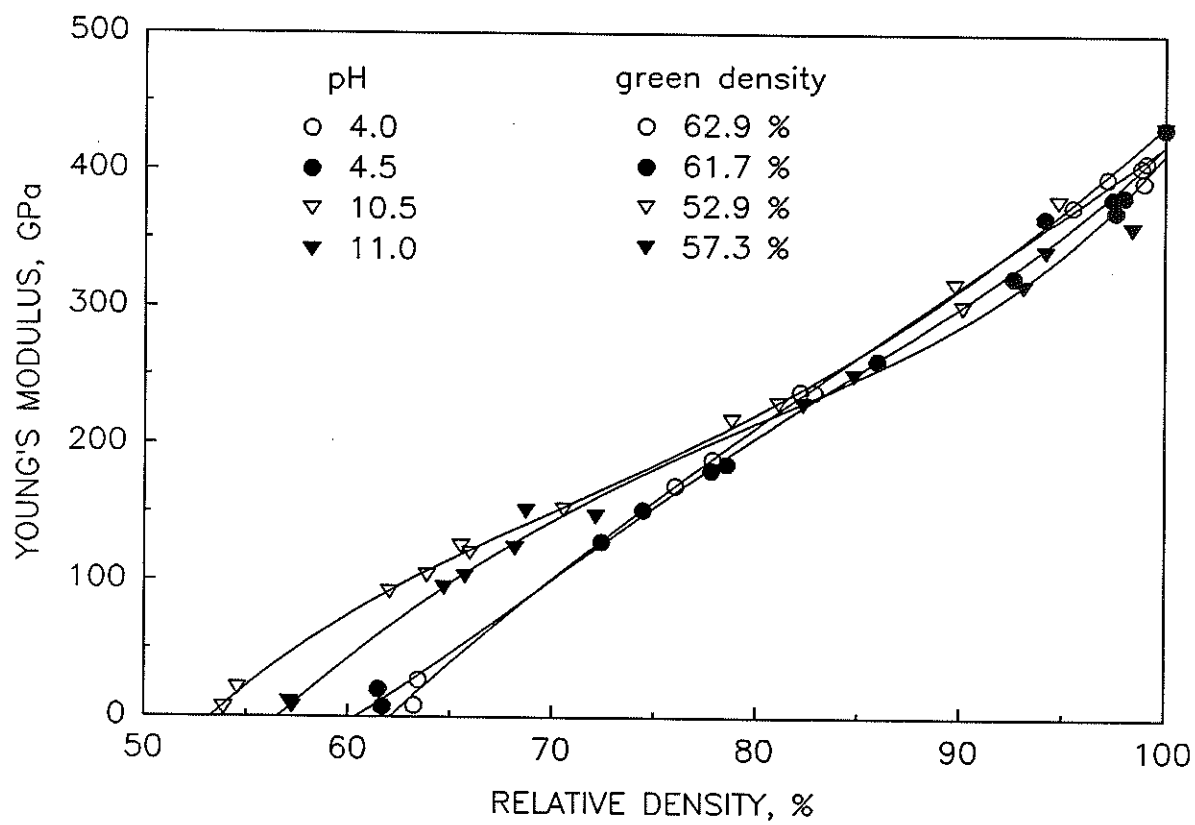
Figure 8.   Young's modulus of elasticity as a function of percentage relative density.

Figure 9.   Poisson's ratio as a function of percentage relative density.

LIST OF TABLES

Table 1. Mercury Porosimetry analysis of green samples.

pH	Median Radius (nm)	% Relative Density
3.5	34.2	63.2
4.0	35.8	62.9
4.5	39.2	61.7
5.0	40.1	58.7
10.5	51.1	53.9
11.0	46.5	57.3
11.5	42.7	58.8

Table 2. Archimedes analysis of green samples. Samples were partially sintered at 700°C for 2 hrs.

pH	% Relative Density	% Total Porosity	% Open Porosity	% Closed Porosity
3.5	64.7	35.3	35.1	0.2
4.0	63.4	36.6	36.4	0.2
4.5	61.5	38.5	38.0	0.5
5.0	59.2	40.8	38.6	2.2
10.5	54.6	45.4	42.2	3.2
11.0	57.1	42.9	41.2	1.7
11.5	59.1	40.9	39.9	1.0

Table 3. Ultrasonic velocities of green samples.

pH	Median Pore Radius (nm)	% Relative Density	Longitudinal Velocity (m/s)	Shear Velocity (m/s)
3.5	34.2	63.2	1926	1233
4.0	35.8	62.9	1881	1194
4.5	39.2	61.7	1791	1144
5.0	40.1	58.7	1736	1101
10.5	51.1	53.9	1689	1071
11.0	46.5	57.3	1784	1138
11.5	42.7	58.8	1850	1176

Table 4. Ultrasonic velocities of sintered samples. (a) dispersed (b) partially flocculated

(a)

Sintering		Dispersed Samples (pH 4)		
Temp. (°C)	Time (hrs.)	Density (%)	Longitudinal Velocity (m/s)	Shear Velocity (m/s)
700	2	63.4	3318	2148
1200	1	76.1	7846	4862
1200	3	77.9	8312	5013
1200	12	82.2	9008	5513
1200	24	82.9	9027	5467
1350	1	95.5	10366	6452
1350	3	97.2	10656	6531
1350	12	98.8	10690	6541
1350	24	99.1	10844	6517
1500	3	99	10870	6335

(b)

Sintering		Partially Flocculated (pH 10.5)		
Temp. (°C)	Time (hrs.)	Density (%)	Longitudinal Velocity (m/s)	Shear Velocity (m/s)
700	2	54.6	3220	1976
1200	1	62	6430	3904
1200	3	63.9	6620	4167
1200	12	66	7102	4376
1200	24	65.5	7281	4479
1200	60	70.6	7928	4699
1350	1	78.8	9005	5298
1350	3	81.1	9214	5343
1350	12	90.1	10121	5757
1350	24	89.7	9914	6078
1500	3	94.8	10640	6426