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Rheology of alumina suspensions stabilized with Tiron

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Abstract

Pressure filtration technique was used to obtain defect-free microstructure of green cast ceramic bodies. Stable alumina suspensions of desired rheology (<5 Pa s at 1 s^{-1}) containing 60 - 80 mass. % solid loading were prepared in the alkaline region (at pH$\approx$9) with an optimum amount of 0.5 dmb % of Tiron added. Acidic region (at pH$\approx$4) enabled the preparation of 60 mass. % suspensions with addition of 1.5 dmb % of Tiron. The best quality slip was processed from an 80 mass.% suspension with 63% of theoretical density. The homogeneity of particle packing and the absence of defects in microstructure were proven by narrow pore size distribution (ranging from 32 to 64 nm, with up to 85% abundance), confirming advantages of the wet consolidation route.

Keywords : rheology, alumina, Tiron, suspensions, porosity

1. Introduction

In recent years, the colloidal processing has been recognized as a technologically important route of green shape forming for advanced ceramics powders (Sigmund *et al.*, 2000; Harbach and Weiler, 1986; Lange, 1989; Roosen and Bowen, 1987). In various wet techniques such as gelcasting, slip casting, tape casting or pressure filtration, it is an imperative to have a slurry with good dispersion and desirable rheological behavior because the quality of dispersion controls the casting behavior and the resulting green-body properties (Velamakanni *et al.*, 1990). Many factors can affect the colloidal stability of ceramic powders such as particle size, solid volume fraction, nature and amount of surface-active agents, *etc.* To obtain a ceramic suspension with high solid content, which can be successfully processed, low viscosity must be achieved and its stability maintained. This requires efficient dispersants; therefore, a good knowledge of the stabilizing mechanisms is of the utmost importance, because efficient deagglomeration and dispersion of the ceramic powder are crucial for defects minimization.

The aim of the present work is to use pressure filtration as a convenient way to obtain defect-free ceramics. An experimental set-up has been assembled to process aqueous alumina suspensions. Successful preparation of concentrated suspensions was achieved by utilizing a commercially available dispersant, Tiron. The stability of suspensions was studied as a function of pH, dispersant concentration, and solid phase content via rheological behavior of the suspensions.

2. Experimental

The ceramic powder used in this study was 99.7% α-Al_2O_3 (Alcoa CT 3000 SG) with average particle size, $d_{50}=0.6$ μm, and BET specific surface area, $S_p=6$ m^2/g. Tiron (Aldrich Chemie) was chosen as a water-soluble dispersant, frequently used for the preparation of highly concentrated alumina suspensions.

The suspensions were prepared both in the acidic and in the basic pH region. This was done by 24 h ball milling, followed by 24 h ageing to allow complete adsorption of Tiron onto the alumina surface. The powder content varied from 60 to 80 mass %, whereas the amount of added Tiron ranged from 0 to 1.5 dmb % (dry mass base percent) of alumina. Rheology of the suspensions was studied using a Brookfield Dial Reading viscosimeter, RV Series, with an SC4-21 spindle (Brookfield Engineering Laboratories,Inc., USA). The shear rate and viscosity measurements range is 0.93 N, s^{-1} (N=0.5 - 100 rpm) and 50 - 10^5 mPa s, respectively. The filtration step was performed in a laboratory set-up with a glass cylinder (allowing up to 10 bar air-pressure), and a system for air-supply and pressure regulation, Fig. 1. The filtration process was typically performed at a constant pressure of 5 bar. The density of disk-like green bodies was measured based on Archimede`s principle. The microstructure of cast bodies was studied by scanning electron microscopy (SEM) and mercury porosimetry (Carlo Erba, model 2000).

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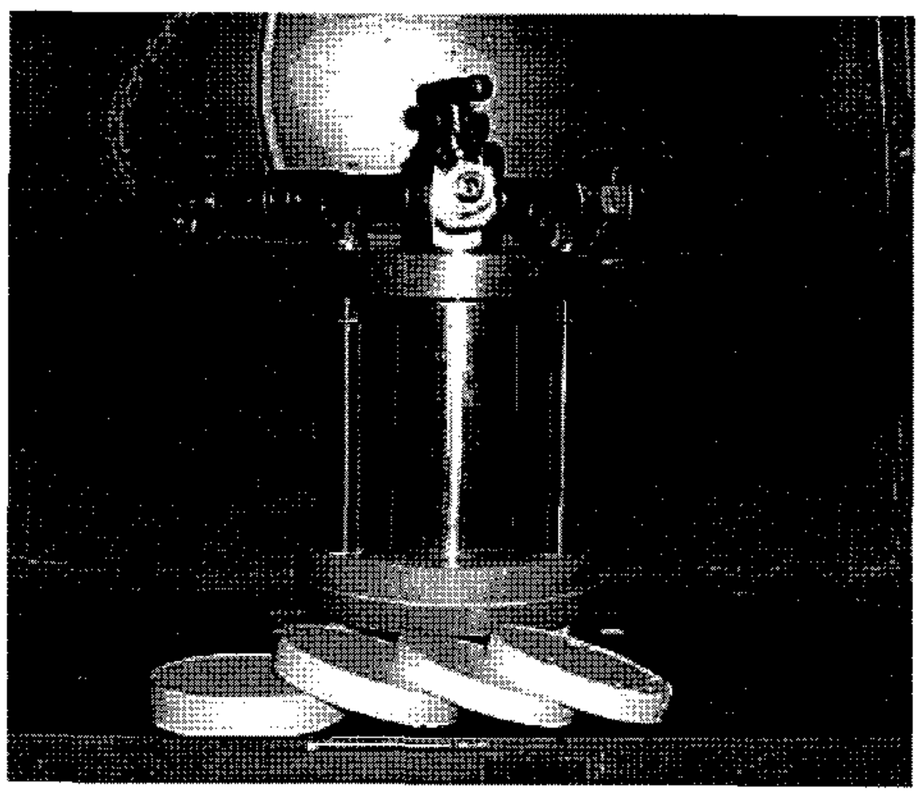


Fig. 1. A laboratory set-up for pressure filtration. Detailed description is given in experimental.

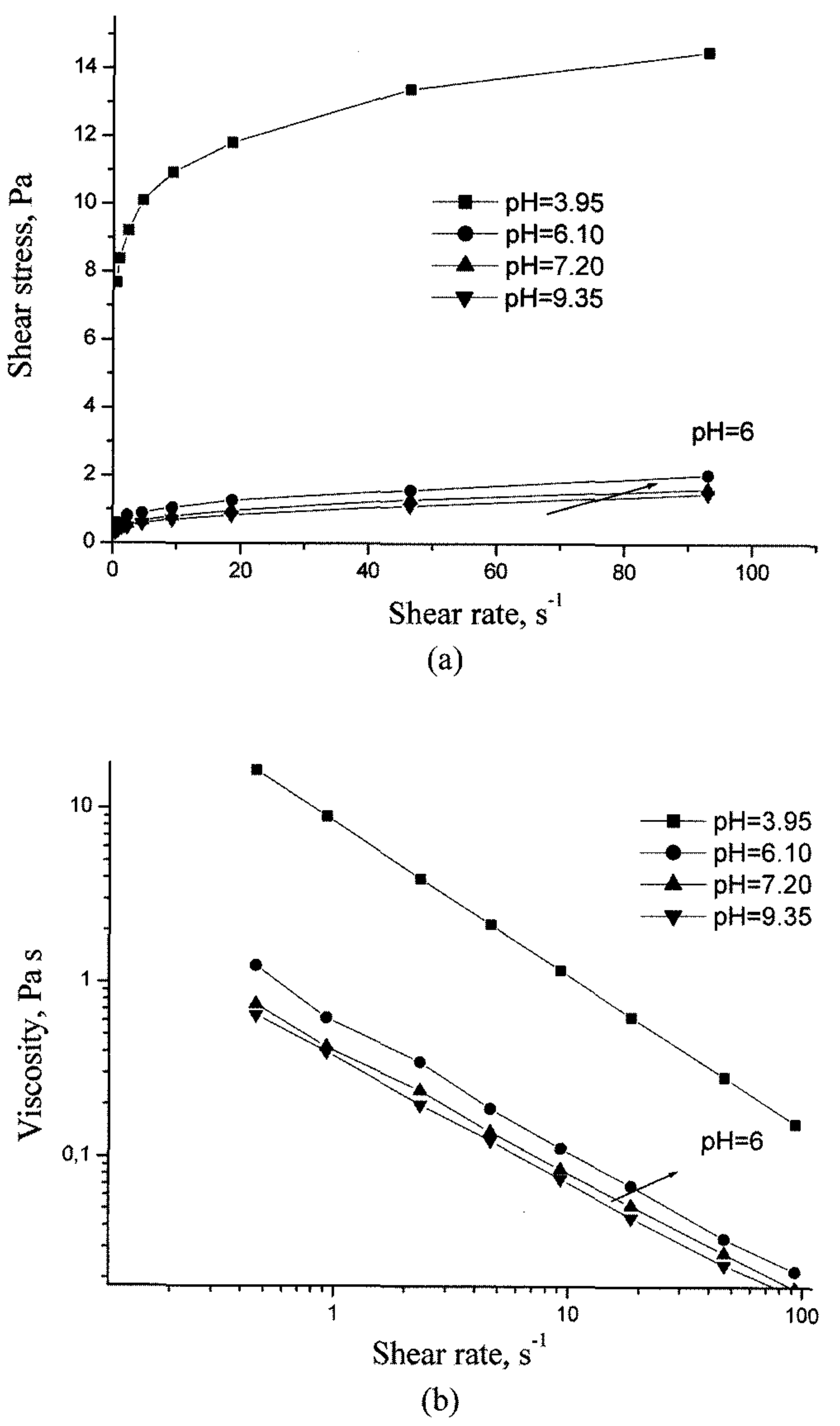


Fig. 2. Flow curves of 60 mass% alumina suspensions as a function of different pH values; in the presence of 1.5% dmb Tiron: dependencies of (a) shear stress and (b) viscosity on shear rate.

3. Results and Discussion

3.1. Rheology of suspensions

The rheological behavior of aqueous alumina suspensions with Tiron was studied as a function of pH, solid phase content, and added-dispersant amount. In our previous study (Gulicovski *et al.*, 2008), sedimentation behavior of diluted alumina suspensions was evaluated via screen sedimentation tests as a function of pH and Tiron concentration. As shown, the suspensions were unstable in the acidic region (pH = 3 – 5), contrary to very stable ones in the basic region (pH = 6 – 10). Based on these results, the effect of pH on rheology of 60 mass. suspensions was studied. Flow curves, expressed as a dependence of shear stress (a) and viscosity (b) on shear rates applied, are shown in Fig. 2.

All suspensions displayed pseudoplastic character, typical of ceramic systems. However, their rheology was significantly different at pHs lower and higher than pH 6. At pHs ≥ 6, the suspensions exhibit almost the same shear thinning behavior, while at pH ≈ 4 this shear thinning behavior is stronger and the viscosity level much higher. This is in good agreement with the corresponding sedimentation behavior, as well as opposite pHpzc shifts found in acidic and basic pH regions (Gulicovski *et al.*, 2008). The surface chemistry data, obtained from the potentiometric titration in the same study, confirmed that the Tiron molecule was essentially uncharged below pH ≈ 6, with the first dissociation constant pKa1 = 7.6. The differences in suspension rheology are thus to be attributed to different mechanisms of Tiron adsorption onto the alumina surface, due to existence of two different ion species dependent on pH values. According to (Laucournet *et al.*, 2000; Laucournet *et al.*, 2001; Greenwood and Bergstrom; 1997, Jiang and Gao, 2003), the adsorption of Tiron in the alkaline region proceeds via specific interactions, *i.e.*, an inner sphere complex is built between alcohol groups of the molecule and hydroxyl groups of alumina. The authors claim that an outer sphere complex is probably formed in the acidic region due to strong electrostatic adsorption of ionized Tiron by positively charged alumina surface.

In colloidal ceramic processing, the concentration that yields the lowest suspension viscosity is the optimum concentration of dispersant. At that concentration, which corresponds to the monolayer surface coverage of the surfactant (Greenwood and Bergstrom, 1997), the particles are effectively kept apart and high fluidity is obtained. To establish the optimum dispersant concentration for the preparation of 60 mass. % suspensions, in acidic as well as in basic media, Tiron was added in the range 0.5 – 1.5 dmb%. The chosen range is based on our and literature data (Briscoe *et al.*, 1998; Gulicovski *et al.*, 2008; Jiang *et al.*, 2002; Jiang and Gao, 2003; Rocen, *et al.*, 2005; Tari *et al.*, 1998). The obtained variations in suspension viscosity

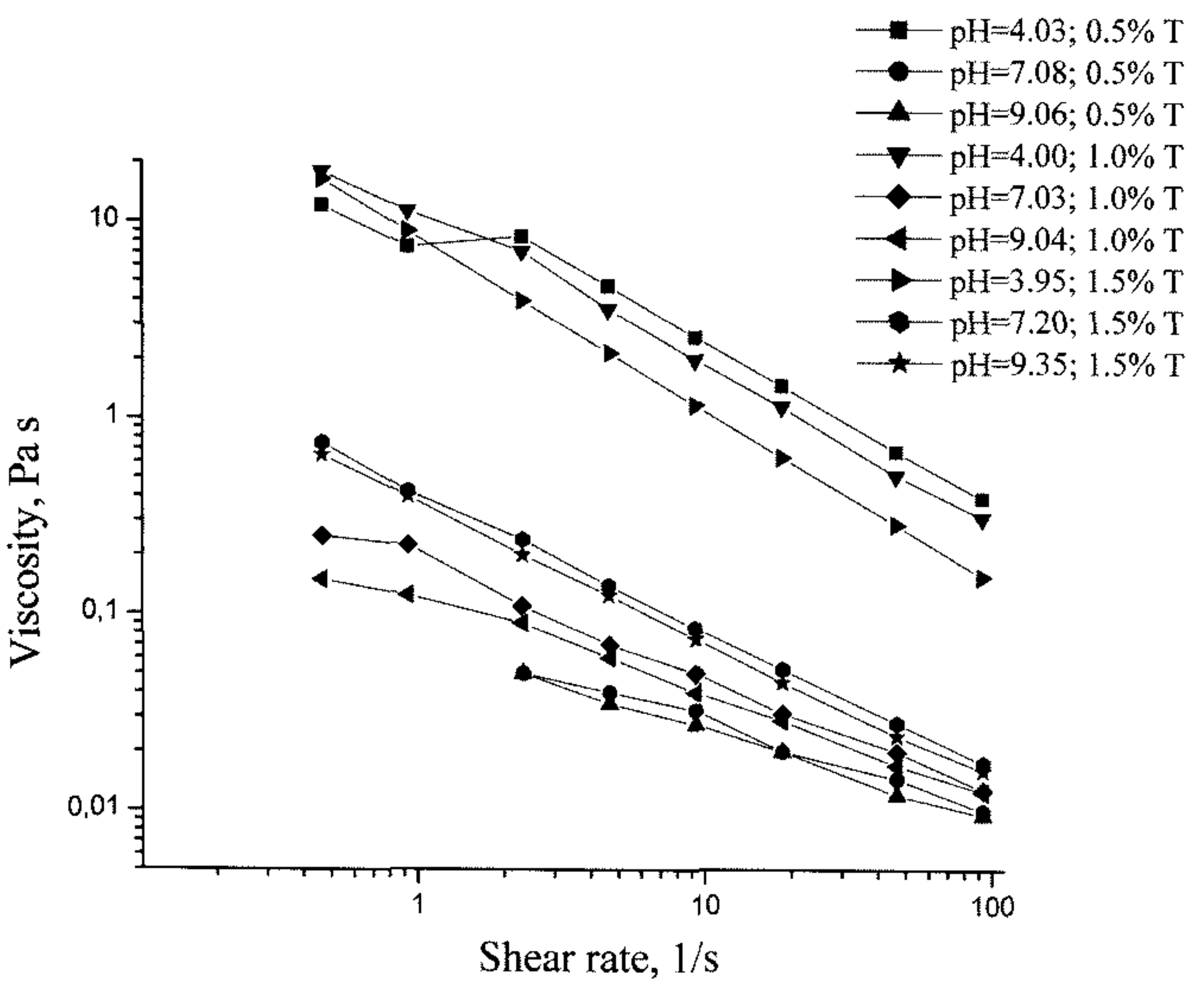


Fig. 3. Effect of different pH values and different amounts of Tiron on viscosity of 60 mass. % alumina suspensions as a function of shear rate.

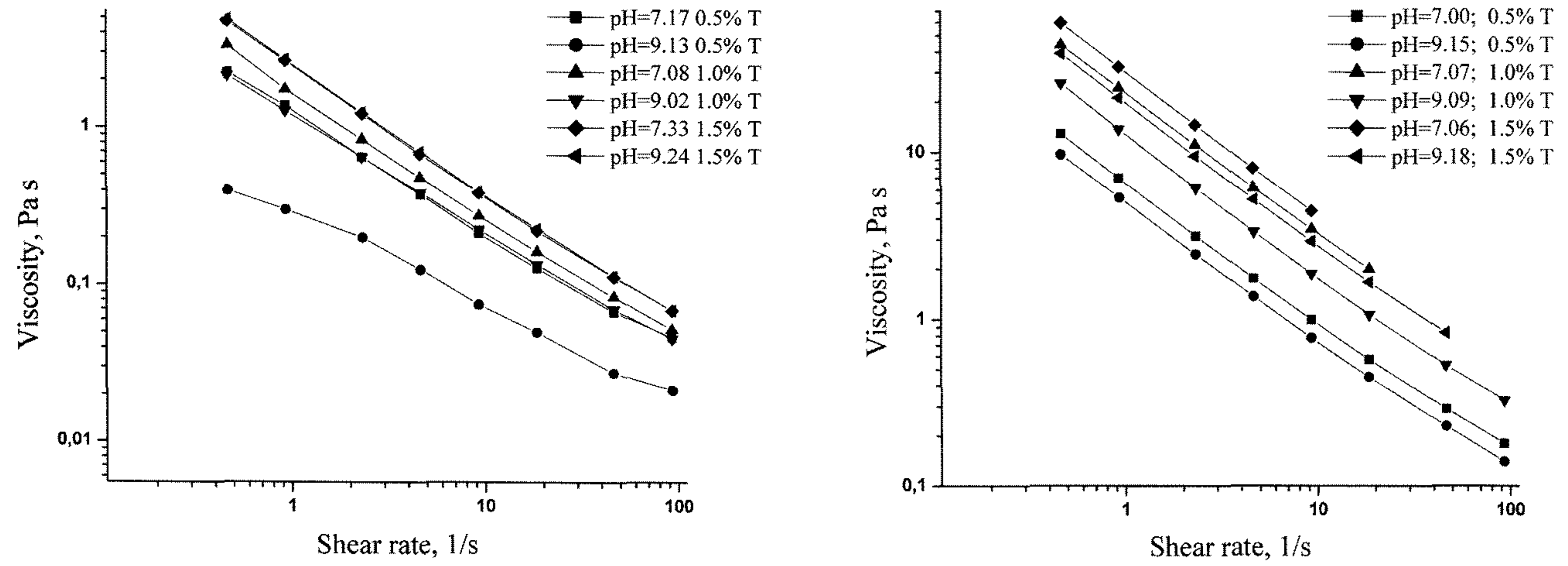
as a function of pH and Tiron concentration are shown in Fig. 3. It is easily seen that the viscosity of suspensions at pH≥pKa1 (pH≈7 and pH≈9) decreases with decreasing amount of Tiron; the lowest achieved with the smallest amount of Tiron, 0.5 dmb %. For acidic suspensions, a reverse dependence was found; the minimum viscosity required the largest amount of Tiron of 1.5 dmb %.

It is well known that any amount of dispersant, lower or higher than the optimum one, will lead to the suspension instability. Insufficient amount of the dispersant often results in a decrease in suspension stability and fluidity, as charges of the particles are not high enough to overcome the attractive van der Waals force. Too much dispersant, however, is also unfavorable for the stability of alumina suspensions. In the case of Tiron as a dispersant, the excess of Na^+ will lead to a decrease in thickness of electrical double layers of particles, or may reduce the repulsion between two particles (Jiang and Gao, 2003).

The authors (Palmqvist *et al.*, 2006) state that at lower dispersant concentrations the surface is not completely covered by surfactant so the flocculation may occur due to attraction between positively charged bare surface patches and negatively charged surface with adsorbed polyelectrolyte (pH≈4). At pH≈7 and pH≈9, the excess of dispersant can cause flocculation due to bridging or depletion effects, *i.e.*, the viscosity of suspensions increases.

The rheological behavior of suspensions has also been studied in regard to solid content, Fig. 4. Therefore, the suspensions containing 70 and 80 mass % alumina were prepared at pH≥pKa1. Preparation of the suspensions at pH≈4, with Tiron of 1.5 dmb %, found optimal for the 60 mass% ones, was also attempted. However, the suspension viscosity was too high to be measured by the available viscosimeter.

All tested suspensions exhibited shear thinning behavior, with an expected increase in yield stress and viscosity with increased solid content from 60 to 80 mass%, Fig. 5. This accentuated shear thinning behavior is usually associated with a more complex structure of the suspensions with increased particle concentration (Reed, 1998). The authors (Conway and Bobry-Duclaux, 1960) attributed this enhance to the higher frequency of collisions between particles, which causes higher resistance to flow. Particles are forced to approach each other and overlap their electrical double layers (electroviscous effect). If the particles approach the distance corresponding to the primary minimum in the total energy, they will coagulate/flocculate. As a result, the stabilization of suspensions becomes more difficult, *i.e.*, the number of flocks will increase with increasing quantity of entrapped liquid not available for flow



(a) (b)

Fig. 4. Effect of different pH values and different amounts of Tiron on viscosity of (a) 70 and (b) 80 mass. % alumina suspensions as a function of shear rate.

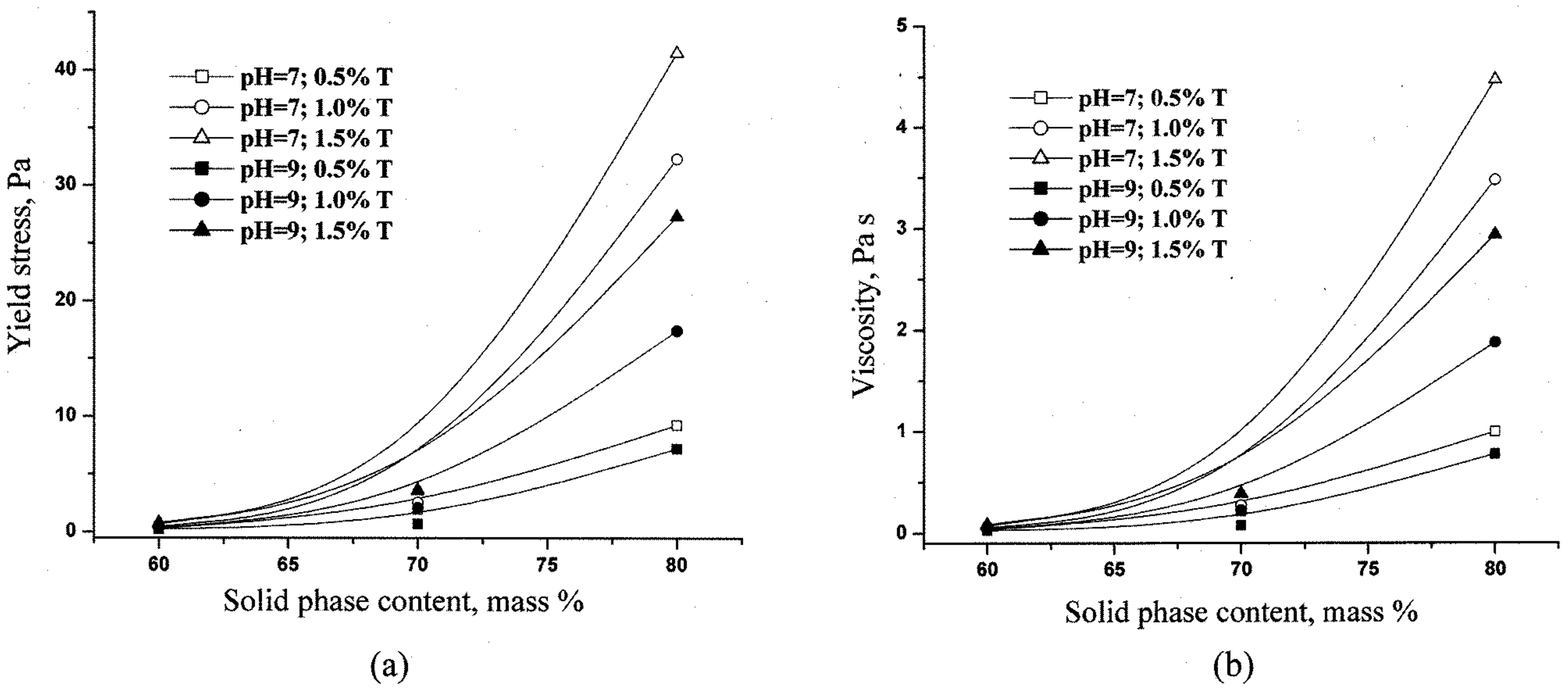


Fig. 5. Plots of (a) yield stress and (b) viscosity vs. solid phase content (mass %) with different dispersant concentrations and pH values.

(Conway and Bobry-Duclaux, 1960; Sacks, 1984)

The effect of the Tiron concentration on the fluidity of 70 and 80 mass % suspensions was found to be the same as that determined for 60 mass % suspensions. So, the decrease in viscosity with decreasing percentage of dispersant, from 1.5 over 1.0 to 0.5 dmb %, is observed for suspensions prepared at $pH \geq pKa1$, Fig. 4. The result indicates that the optimal dosage of Tiron in the basic region is independent of the alumina content and corresponds to 0.5 dmb %. (Jiang and Gao, 2003) have also reported the same amount of Tiron as optimal for diluted and concentrated alumina suspensions at $pH = 8.5$.

It is also worth noting that the viscosities of suspensions with the same solid and dispersant content prepared at $pH \approx 9$ were always lower than the ones prepared at $pH \approx 7$. The alkaline region thus appears suitable for preparation of stable suspensions, which is consistent with the findings of other authors who also chose basic pHs when working with Tiron as a dispersant. Various authors (Jiang and Gao, 2003; Briscoe *et al.*, 1998; Tari *et al.*, 1998; Oberacker *et al.*, 2001) measured viscosity of alumina suspensions at different shear rates. The results summarized in Table 1 show that the data obtained in this study (60, 70 and 80 mass % 28, 37.5 and 51 vol. %, respectively) agree well with the literature ones.

Ceramic suspensions suitable for processing should be shear thinning, since high viscosity at low shear rates often destabilizes the suspension. The viscosity values for successful processing as stated in literature range between 1 and 10 Pas at 1 s^{-1}.

A comparison between the rheology of the suspension prepared in this study at $pH \approx 4$, with 60 mass % alumina

Table 1. Viscosity of Al_2O_3 suspensions with various solid contents

Al_2O_3, vol. %	pH	Tiron, dmb %	Viscosity, Pa s	Shear rate, s^{-1}	References
28	9	0.5	<0.03	10	This study
28	4	1.5	<8	1	This study
37.5	9	0.5	<0.3	1	This study
37.5	7.2	0.5	<1.5	1	This study
51	9	0.5	<5	1	This study
30	9-10	0.25	<0.05	10	Tari *et al.*, 1998
35	9-10	/	<2	100	Oberacker *et al.*, 2001
35	4	/	<0.03	100	Oberacker *et al.*, 2001
40	9-10	0.25	<0.5	1	Tari *et al.*, 1998
40	7.2	0.5	<1	1.46	Briscoe *et al.*, 1998
45	8.5	0.5	<0.175	50	Jiang and Gao, 2003
50	9-10	0.25	<5	1	Tari *et al.*, 1998

Table 2. Properties of green cast bodies processed from suspensions with different alumina contents prepared at pH≈4 and pH≈9

No. samp.	Al_2O_3, % mass	pH	Tiron, dmb %	Dens., g/cm^3	Open poros., %	Overall poros., %	TD, %	Pore range 120-64 nm, %	Pore range 64-32 nm, %	Other pore ranges, %
1	60	9	0.5	2.2	42.9	46.3	55.5	73.9	17.7	8.4
2	70	9	0.5	2.3	39.0	44.4	57.4	68.8	23.5	7.7
3	80	9	0.5	2.5	35.4	38.7	63.1	4.5	84.5	11.0
4	60	4	1.5	2.2	43.3	46.5	55.2	78.7	14.1	7.2

and 1.5 dmb % Tiron, and that of the suspension prepared at pH≈9, with 80 mass % solid and 0.5 dmb % Tiron, revealed almost the same shear thinning behavior. For that reason the suspension at pH≈4, as well as all those prepared at pH≈9, as listed in Table 1, were further processed. No available literature data have been found about the processing of acidic Tiron-stabilized alumina suspensions.

3.2. Consolidation of Al_2O_3 suspensions and green body characterization

After the filtration of suspensions (100 ml), performed under constant pressure of 5 bar and 30 min time hold, green cast compacts (disc-like bodies) were formed. The thickness of the green discs was dependent on the solid content

The reduction in moisture in wet cast bodies was achieved by holding the same air pressure for 30 min; the remaining water was pumped out from the smallest pores as well, decreasing the capillary tension during subsequent drying, which may be the cause for cracks. In parallel, the consolidation process was improved, *i.e.*, rearrangement of particles towards more even packing in different layers (parts) of the green cast body was made. Besides good deagglomeration and deflocculation, this is the main precondition for obtaining homogeneous and defect-free microstructure of a compact.

The degree of consolidation upon filtration was evaluated via density and porosity values of green cast bodies, as summarized in Table 2. It can be seen that the density of compacts increases with increasing solid content; the highest packing density was achieved for 80 mass % solid with the corresponding value of 63.1% TD (theoretical density, TD, of alumina, $\rho=3.90\,\mathrm{gcm^{-3}}$). The result accords well with the value of 63.8%TD, for slip cast bodies obtained from 50 vol.% suspensions for finer alumina (A16 SG, Alcoa), presented by (Tari *et al.*,1998; Luckfeldt and Ferreira, 1997).

The pore size distribution data, recorded for all samples by mercury porosimetry, also summarized in Table 2, show a close correlation with the measured densities. The higher the alumina content, the better the particle packing. This conclusion is based on the presence of a greater amount of smaller pore sizes at the expense of pores with bigger radii, as alumina content was increased from 60 to 70 mass %. The distribution of larger pores (64 – 120 nm) changed from 73.9 to 68.8%, while the percentage of finer pores (32 – 64 nm) increased from 17.7 to 23.5%, for the samples 1 and 2, respectively. The greatest amount of the smallest pores was accomplished for the sample 3 (Fig. 6) corresponding to the abundance of 84.5% pores in the range 32 – 64 nm. Similar graphs of for pore size distribution were obtained for other samples.

It is known that the pore size distribution in green body has a crucial impact on homogeneity and quality of the microstructure obtained. Due to the fact that during the sintering process it is not possible to eliminate either pores of big diameters or pores remaining in unbroken agglomer-

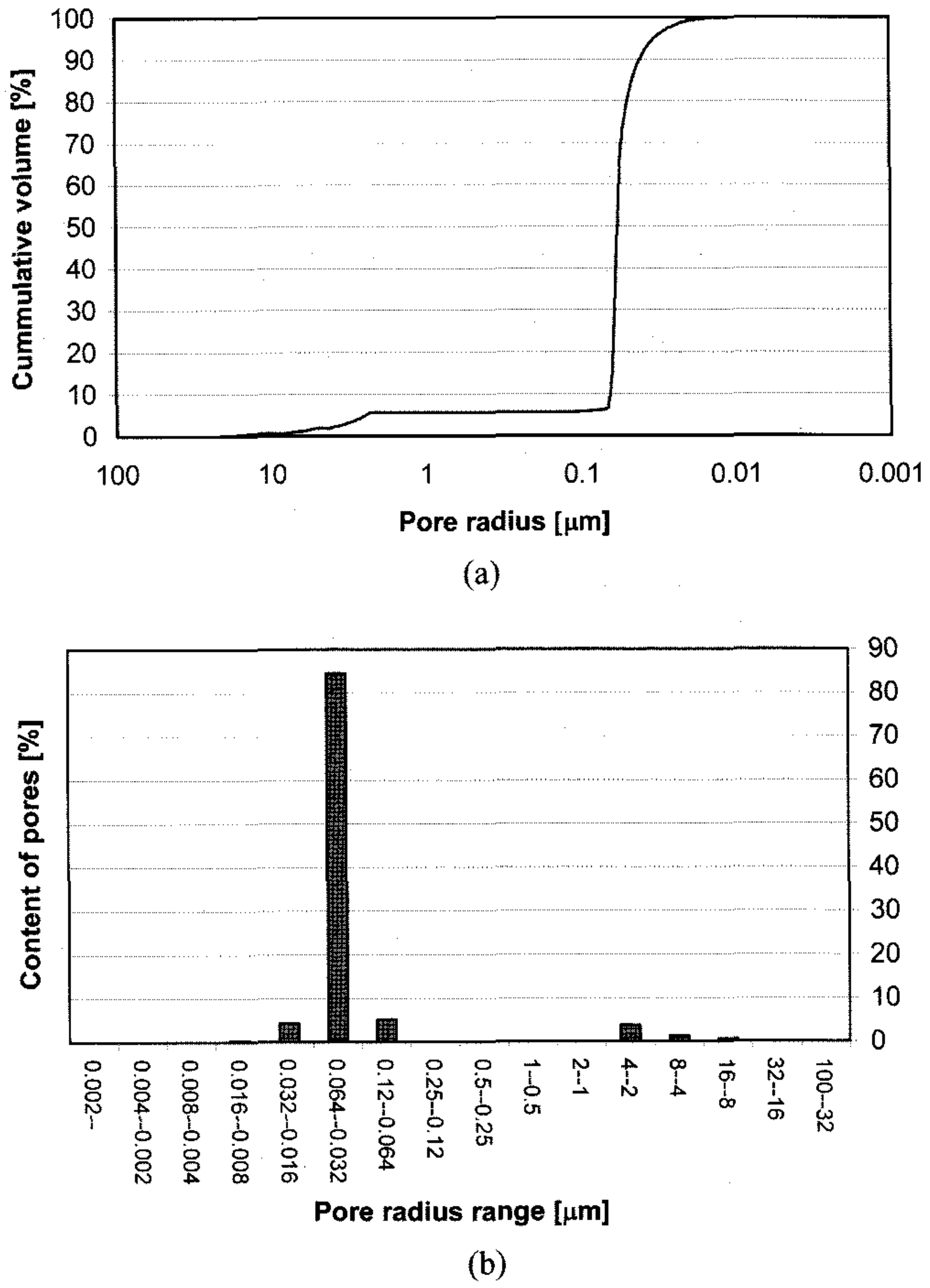


Fig. 6. Dependencies of (a) cumulative pore volume on pore radius and (b) content of pores on pore radius range for the sample prepared with 80% mass alumina and 0.5% dmb Tiron, at pH=9.

ates, it is of the utmost importance to obtain a slip with as narrow as possible pore size distribution.

It is important to note that the density of the disks, obtained by pressure filtration at pH≈4, was of the same value as that measured for the sample processed from the alcaline domain, also with 60 mass % solid. To our knowledge, this is the first result given in the literature.

3.3. Microstructure of green cast bodies

The influence of the morphology of powder particles on packing densities is well known from the literature (Reed, 1998). The spherical particles are the most densely packed, but in a real ceramic system, the particles are not spherical and the packing density is dependent on the degree of variation. The microstructures of obtained green cast samples are given in Figs. 7 and 8. A slight difference towards more compact microstructure is noticeable between 60 and 70 mass % suspensions at acidic or basic pHs. The closest particle packing coincides with the highest solid content in the suspension (sample 3). It is evident that the powder particles during the deposition stage are arranged in an ordered way in the direction of applied pressure, forming homogeneous microstructure with minimum porosity present.

The morphology of as-received alumina is shown in Fig. 8(a). It is obvious that the starting powder is polydispersed and agglomerated. The particles differ in size (ranging from several hundred nanometars to micrometric values) as well in shape (varying from rather elongated over plate-like to equiaxed ones). For the sake of comparison, a

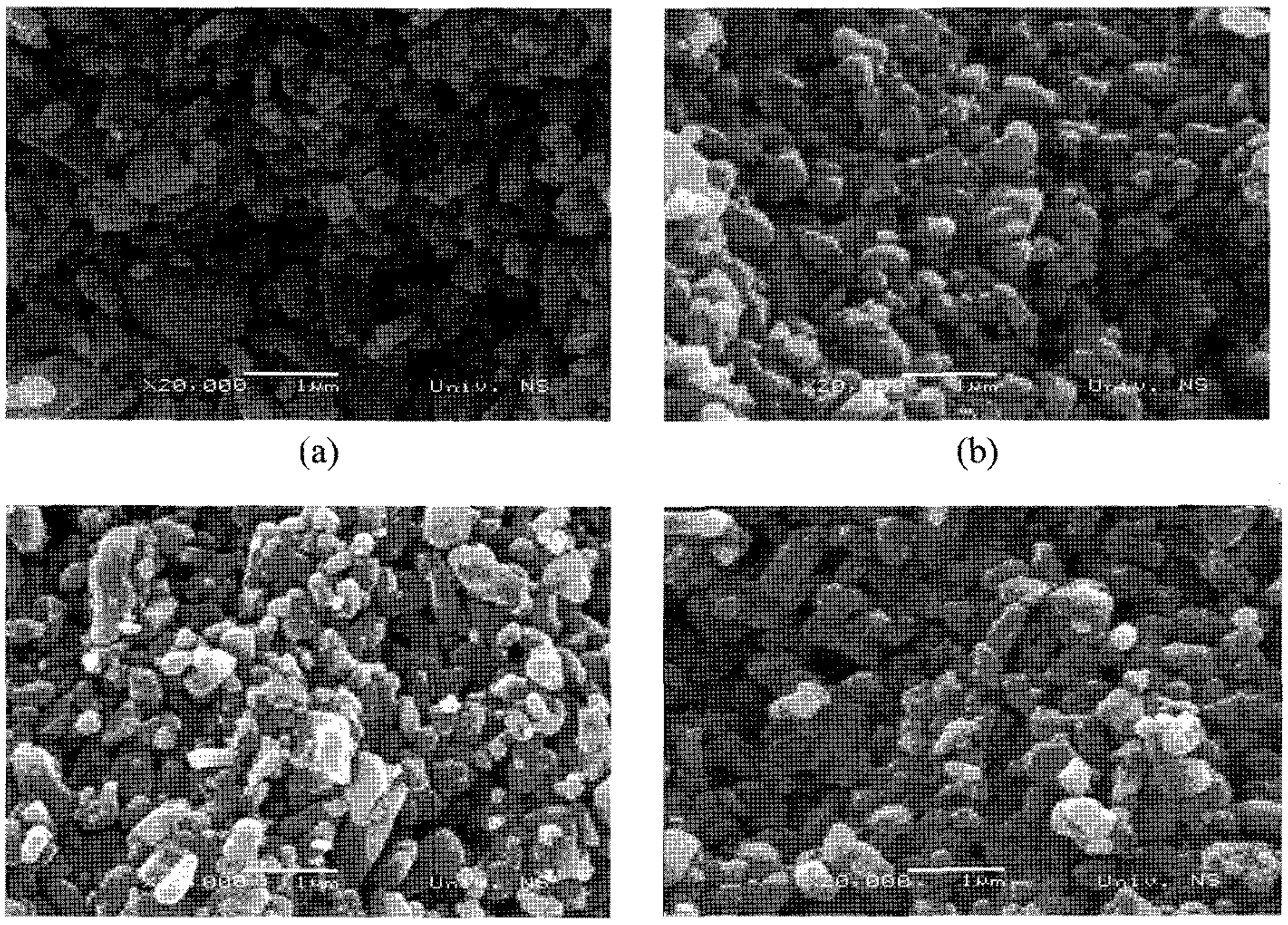
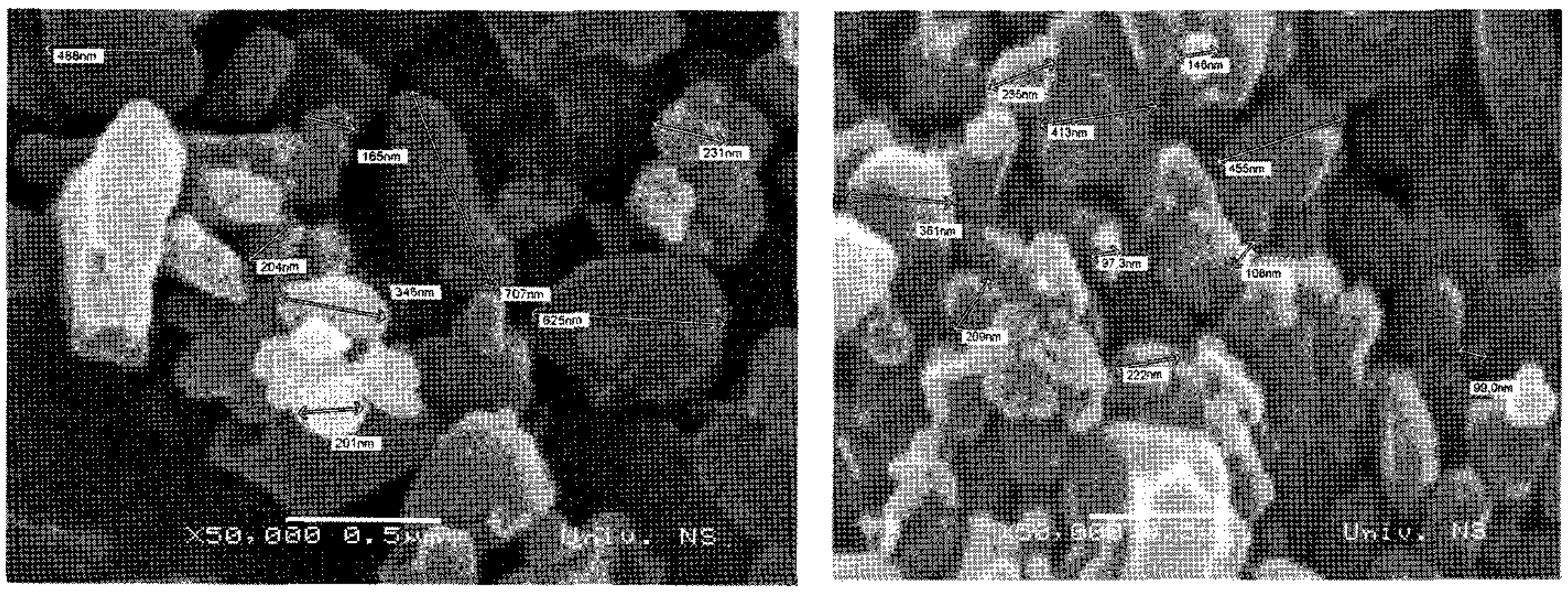


Fig. 7. SEM micrographs of green body samples processed from (a) 60, (b) 70, (c) 80 mass % alumina suspensions at pH=9 and 0.5 dmb % of Tiron, and (d) 60 mass % alumina suspensions at pH=4 and 1.5 dmb % of Tiron.



(a) (b)

Fig. 8. SEM micrographs of (a) as-received alumina powder and (b) sample No.3 of green cast body.

micrograph of the sample 3, taken at the same magnification, is also given in Fig. 8(b).

The homogeneity in microstructure of the green cast bodies is to be attributed to successful deagglomeration of the starting powder. The particles are well dispersed, which leads to their better packing and diminution of segregation phenomena. Uniform microstructure without significant defects, as well as narrow pore size distribution, was found in all samples. Good correlation is thus established between the powder dispersion, *i.e.*, suspension stability and rheology, and the green body microstructure.

4. Conclusions

Stable alumina aqueous suspensions in acidic and basic regions were prepared by using a commercial dispersant, Tiron. Rheological study has shown that the stabilizing mechanism in Tiron-alumina suspensions differs remarkably with respect to the suspension pH. The optimum powder dispersion to achieve the greatest suspension stability occurs in the basic region at pH 9. The required amount of Tiron to obtain minimum viscosity for 80 mass % suspension is 0.5 dmb %. On the other hand, the stable acidic suspension allows up to 60 mass % solid loading and Tiron of 1.5 dmb %. Structural analysis of green bodies processed by pressure filtration from the above mentioned suspensions proved advantages of the wet consolidation route. Uniform microstructure without significant defects, as well as narrow pore size distribution, was found in all samples. However, for the highest solid content the best particle packing, with the smallest pore radius in the range from 32 to 64 nm with up to 85% abundance, was achieved.

Acknowledgements

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