Effects of Modified Poly(methacrylic acid) Copolymer on Rheological Properties of Ceramic Suspension and Sintered Ceramic Strength

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Received 2 November 2005; accepted 31 December 2005
DOI 10.1002/app.24089
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Modified waterborne poly(methacrylic acid) (MPBMA) with hydrophilic and hydrophobic groups is prepared by reacting maleic anhydride/polyglycol, α-olefine benzenesulfone, and methyl methacrylate. Using MPBMA as a ceramic dispersant, the effects of the MPBMA concentration on the rheological behavior of a ceramic suspension and the ceramic breaking strength are studied, and the reasons and its dispersing mechanism are analyzed. The results show that MPBMA can improve the suspension's rheological properties and enhance the ceramic strength. The optimum copolymer concentration is 0.20 wt % at pH 9–10. When adding 0.20 wt % MPBMA, the suspension's absolute ζ potential increases from 23.7 to 64.2 mV, and its zero shear viscosity decreases from 714.3 to 73.4 mPa s. At the same time, its thixotropy area reaches the minimum, and the suspension exhibits Newton flow behavior and good dispersivity. Compared with inorganic dispersant, the ceramic with added MPBMA has higher breaking strength, which is increased from 160 to 352 MPa. Scanning electron microscopy photographs show that the flocculate of particles is disintegrated and the particles scatter mutually. They also show that no aggregation phenomenon appears in the ceramic with MPBMA added and the pores distribute uniformly. J Appl Polym Sci 102: 2661–2667, 2006

Key words: polymeric dispersant; ceramic suspension; rheological properties; strength

INTRODUCTION

The preparation and application of concentrated ceramic aqueous suspensions with low viscosity has become a paramount problem in the process of ceramic casting, especially in the control of the properties of the final products.[1–10] Thus, it is necessary to study the rheological properties of the ceramic suspensions and the strength of the sintered ceramic body. Because of the presence of van der Waals attraction, ceramic powders tend to aggregate and form aggregates in a suspending medium. Thus, it was essential to add dispersant to keep the ceramic particles repelled by each other.

General ceramic dispersants are limited in their own dispersivity because of their molecular structure and relative molecular mass. Conversely, polymeric ceramic dispersants are naturally bestowed with better dispersivity. They have adequate ability to cover and envelop the surface ceramic particles, the position and size of their hydrophilic and hydrophobic groups can be adjusted, and their molecular structures are comb shaped with highly branched chains.

Among the polymeric dispersants, poly(acrylic acid) (PAA) is in common use. The influence of solid loading, pH, and PAA addition on the properties of many ceramic powders has been investigated systematically.[8,11–13] Recently, acrylic copolymers have attracted much attention because of their excellent dispersivity for ceramic powders.[14–19] However, most of these studies focus on the copolymer adsorption and its dispersivity. The influence of these dispersants on the rheological properties and the properties of the sintered ceramic body have been scarcely investigated. In this work, a novel polymeric dispersant was synthesized by simultaneously introducing maleic anhydride/polyglycol and α-olefine benzenesulfone, which had surface activity and long-branched chains, into a poly(methacrylic acid) (PMA) copolymerization reaction, which is seldom investigated. Furthermore, researchers have often used acrylic acids as polymeric monomers whereas in our research polar groups such as $—CH_3$, $—COOCH_3$, and $—SO_3H$ were introduced into the chain, which is also theoretically beneficial to improve the dispersivity.

In this study, diamond/feldspar/clay compound powders were chosen as ceramic basal material.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50473049.

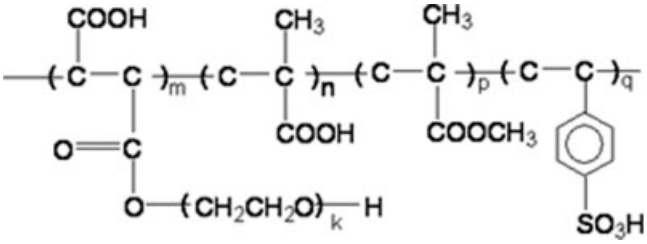


Figure 1 The molecular structure of the MPBMA dispersant.

Through radical copolymerization, modified waterborne PMA (MPBMA) with hydrophilic and hydrophobic groups was prepared by reacting maleic anhydride/polyglycol, α-olefine benzenesulfonic, MA, and methyl methacrylate. The dispersivity and mechanisms of MPBMA as a ceramic dispersant were studied, as well as the effects of the MPBMA concentration on the ζ potential and rheological behavior of ceramic suspensions and ceramic breaking strength.

EXPERIMENTAL

Materials

Diamond/feldspar/clay compound ceramic powders were obtained from The Heavy Pressure Electric Porcelain Factory of Xi'an, China. Chemical grade maleic anhydride, polyglycol, α-olefine benzenesulfone [(NaPO3)6], methyl methacrylate, and sodium hexametaphosphate were used without purification. Isopropanol was analytical grade.

Synthesis of modified polymeric dispersant MPBMA

A certain amount of maleic anhydride, polyglycol, and water were charged into a four-necked reaction vessel equipped with a reflux condenser, a mechanical stirrer, and a digital thermometer. Then, the reaction temperature was raised to 8°C under acid conditions. After 1 h, a mixed solution of methyl methacrylate, α-olefine benzenesulfone, and isopropanol was introduced into the vessel and stirred for 30 min at pH 8.5. A certain amount of ammonia was added in the processing to keep the reaction system alkalescent. Ammonium peroxydisulfate was slowly dropped into the vessel in 1 h, and the reaction was sequentially carried out for 4 h. Finally, a canary-yellow solution with 20 wt % solid loading was obtained, which is the polymeric dispersant MPBMA. Its molecular structure is shown in Figure 1. The MPBMA concentration in this article refers to the mass fraction of the pure polymer on the basis of the dry ceramic mass.

Preparation of ceramic suspension

The suspensions were prepared by adding 70-part ceramic powders into 30-part water. The suspensions were then ball milled by using a corundum ball mill for 24 h. After mixing, the pH of the suspensions was adjusted to 9.5 with $NH_3 \cdot H_2O$ solution.

Preparation of sintered ceramic body

Preparation of the sintered ceramic body was mainly divided into four steps. First, a certain amount of ceramic powders, dispersant with different dosages, and different species were poured into the corundum ball and then were passed through a 130-mesh screen after ball milling for 20 min. Second, a certain amount of poly(vinyl alcohol) solution was squirted into the above-mentioned ceramic powders to make the powders aggregate to form pseudoparticles with a certain size, and they were kept in a shady and cool place for 72 h. Third, the worked powders were poured into the mold of a double-column hydraulic press. Then, the ceramic bodies were cast under 20-MPa pressure and dried at room temperature under controlled humidity. Fourth, the ceramic bodies were sintered at 1000°C for 3 h after the organics were burn out at 650°C for 4 h. The surface microstructure of these sintered bodies was observed with scanning electron microscopy (SEM).

The ceramic bodies can be divided into four species according to the dosage and kind of dispersant. They are provided in Table I.

Dispersivity study

Dilute suspensions (0.01 mol/L) were prepared and dropped on the conductive copper gauze to make them disperse freely. The dispersivity of the MPBMA dispersant was observed with SEM.

ζ-Potential measurement

The ζ-potential measurements were conducted on a BIZetaplus ζ-potential analyzer (Brookhaven Instruments Corp). Dilute suspensions (0.01 mol/L) were prepared, and the mixture was ultrasonicated for 15 min prior to measurements. Each ζ potential was measured 4 times and the average of the four values is reported. The pH of the suspension was adjusted using HNO_3 or $NH_3 \cdot H_2O$ solutions.

Rheology measurements

The viscosity, pseudoplasticity, and thixotropy of the ceramic suspensions were analyzed in a Brookfield

TABLE I
Species of Ceramic Bodies

Designation	m(MPBMA)/m (Na hexametaphosphate)
a	0 : 10
b	3 : 7
c	5 : 5
d	10 : 0

DV-III Ultra Programmable Rheometer. The measurements were carried out at 20°C in rotational mode using type SC4-21 concentric cylinders. Ceramic suspensions (100 cm^3) were used in the measurements. Controlled shear rate experiments were carried out as follows: to provide a uniform and standardized state in all the solutions, the samples were presheared at an identical shear rate of 350 s^{-1} for 2 min and left standing for an additional 2 min prior to measurement. Then, the shear rate was gradually increased from 0 to 350 s^{-1} (up curve in the flow curve) followed by a gradual decrease from 350 to 0 s^{-1} (down curve in the flow curve). Some experiments were repeated and an excellent reproducibility was always obtained.

The pseudoplasticity of the ceramic suspensions was quantified by means of the shear-thinning index. The thixotropic area (TA) is the area between the up and down branches of the flow curve.

Breaking strength measurements

The breaking strengths of the ceramic bodies were measured on a 401/3 breaking strength tester (Scientific and Technological Limited Company of High Iron). Tensile test bars (110 × 10 mm^2) were demolded from the 4-mm thickness molds. Each breaking strength was measured 4 times and the average of the four values was reported. The breaking strength can be calculated by the following equation:

$$\sigma_f = \frac{3PL}{2bh^2} \tag{1}$$

where σ_f is the breaking strength (MPa), P is the breaking load (N), L is the distance between the two supporting blades (mm), B is the breadth of the cross section (mm), and h is the thickness of the cross section (mm).

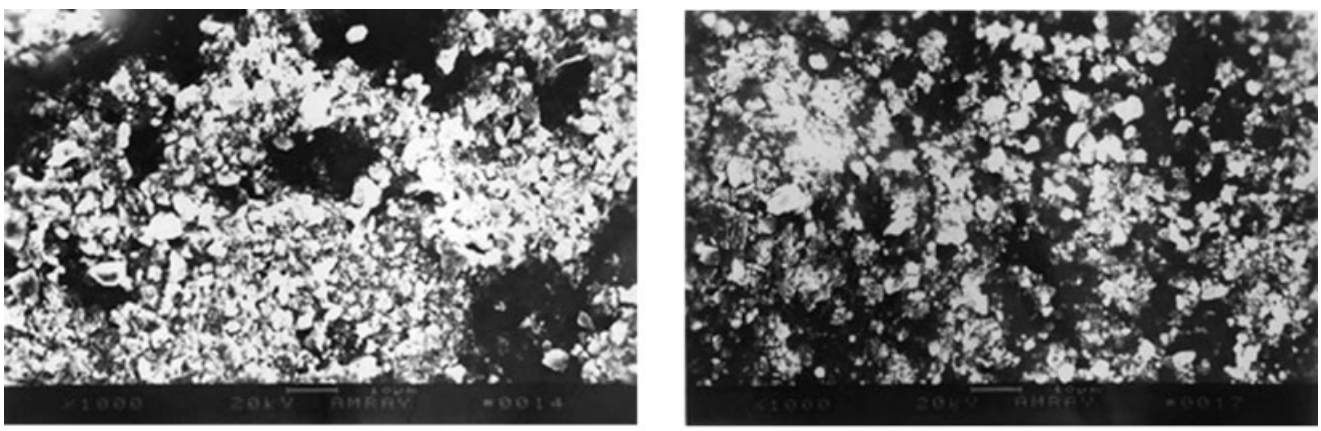
RESULTS AND DISCUSSION

Dispersing and stabilizing mechanism studies

Our hypothesis is that the particles in the suspension system have rheological properties similar to that of a sphere. These particles have a narrow but not monodisperse size distribution. According to the Kriegeer and Dougherty theory for a hard sphere, the viscosity (η) is correlated over a wide range of volume fractions (ϕ) by

$$\eta = \eta_s - \left(1 - \frac{\phi}{\phi_m}\right)^{-[n]} . \phi_m \tag{2}$$

where η_s is the viscosity of the liquid medium, [η] is the intrinsic viscosity, and ϕ_m is the volume fraction at close packing.[20] Equation (2) shows that increasing the ϕ_m of a ceramic suspension produces a duplex effect in improving the suspension's rheologial properties and stabilization. In fact, the aggregates formed by the powders are the main factor that affects the suspension's viscosity and stabilization. Thus, it is essential to add dispersant to make the aggregates break down and enhance the fluidity and casting ability of ceramic suspensions. MPBMA is a kind of polyelectrolyte that possesses a charge that is present along the length of the polymer chain. When adsorbed on ceramic powders, these species can impart electrostatic and steric stabilization to the resulting system, known collectively as electrosteric stabilization.[8] On the one hand, the polymeric chains with surface activity absorbed on the particle's surface give rise to strong electrostatic repulsions. On the other hand, because MPBMA is a kind of polymer simultaneously endowed with hydrophilic and hydrophobic groups, one end of its chain absorbs on the particle's surface and the other end directs it to the liquid phase. As a result, a steric layer with certain mechanical strength is formed on the particle's surface, which hinders particles from adjoining



(a) (b)

Figure 2 SEM photographs of particles in ceramic suspensions (a) without MPBMA added and (b) with MPBMA added.

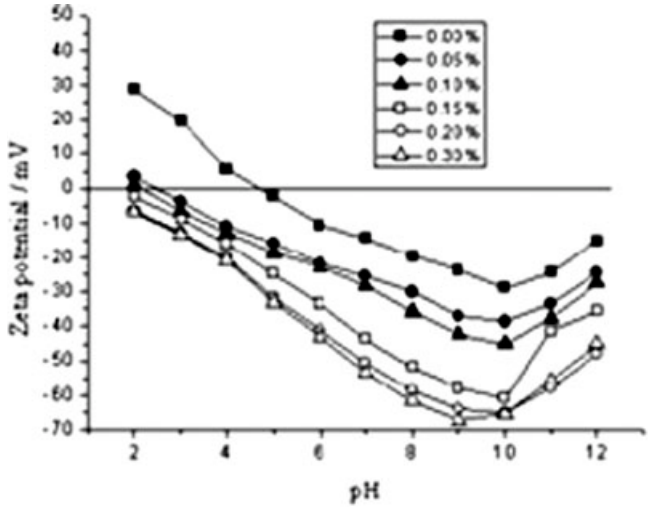


Figure 3 The effects of the MPBMA concentration on the ζ potential of the ceramic slurry.

and agglomerating. Figure 2 shows SEM photographs of the particle distribution in ceramic suspensions in the absence and presence of MPBMA. It is obvious that the flocculate of particles is disintegrated and the particles scatter mutually with the addition of MPBMA.

Effects of MPBMA concentration on ζ potential

The ζ potential of the ceramic powder as a function of the pH in the absence and presence of MPBMA is depicted in Figure 3. We found that the ζ potential decreased with increasing MPBMA concentration, and it began to be almost invariable when the MPBMA concentration exceeded 0.20 wt %. For example, the ζ potential of the bare powder at pH 9 reached −23.7 mV, in contrast to −64.2 mV in the presence of 0.20 wt % MPBMA. With the increase of the MPBMA concentration, the negative charge of the powder increases, which contributes to the higher absolute value of the ζ potential. Thus, the electrostatic repulsion between particles was enhanced with increasing MPBMA concentration.

The isoelectric point (IEP) for the bare powder was found to be at pH 4.6, and the addition of MPBMA led to a shift of the IEP to the more acidic region. In addition, there was a decrease in the ζ potential when the pH ranged from 2 to 10. The adsorption of the negatively charged dispersant increased the net negative charge on the particle and thus shifted the IEP to lower pH values. The decreases of the ζ potential were attributed to the anionic groups of the added dispersant. At a pH of < 3, the adsorbed anionic MPBMA on the solid surfaces often possessed a higher degree of dissociation, compared to the case in a bulk aqueous solution.[21] This explains the significant decrease of the ζ potential with the addition of MPBMA. At a pH of less than the pH_{IEP}, electrostatic repulsion exists between the dispersant and the powder surface. This behavior is indicative of a chemical contribution to the free energy of adsorption to overcome adsorption barriers caused by electrostatic repulsion.[8] However, the ζ potentials at a pH of > 10 greatly increased because of the presence of excessive ions.

Effect of MPBMA concentration on rheological behaviors

Figure 4 presents the rheological properties of 70 wt % ceramic suspensions. It shows that the suspension's viscosity decreases with increasing MPBMA concentration. Moreover, the viscosity is almost invariable for the whole shear rate range investigated when the MPBMA concentration is more than 0.20 wt %, which

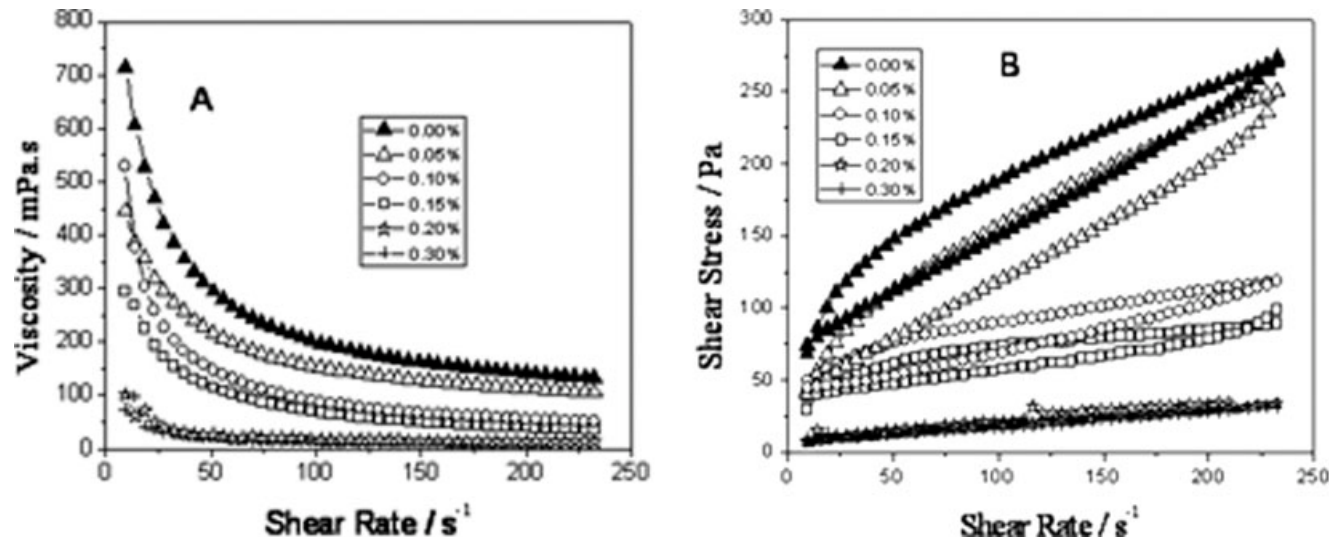


Figure 4 The effects of the MPBMA concentration on the rheological behaviors of ceramic suspensions: (a) the apparent viscosity and (b) the shear stress.

indicates that the ceramic suspension exhibits Newtonian behavior and excellent dispersivity. MPBMA, a kind of polyelectrolyte, can dissociate and turn into $RCOO^-$ and NH^{4+} in aqueous solution at a pH of > 3. $RCOO^-$ can be easily absorbed on the surface of ceramic particles and then increase the net negative charge on the particle, which makes ceramic particles repel each other.

In addition, we found that the systematic apparent viscosity (η_a) decreased acutely at the beginning and then became invariable with increasing shear rate, which was manifested in the endowment of ceramic suspensions with pseudoplasticity. The Mooney equation can explain this phenomenon, which is described as follows:[22]

$$\ln \eta_a = \ln \eta_e + k_e V_i/(1 - V_i/\phi) \quad (3)$$

where V_i is the particles' interior phase volume, ϕ is the stacking coefficient, k_e is the shape factor, and η_e is

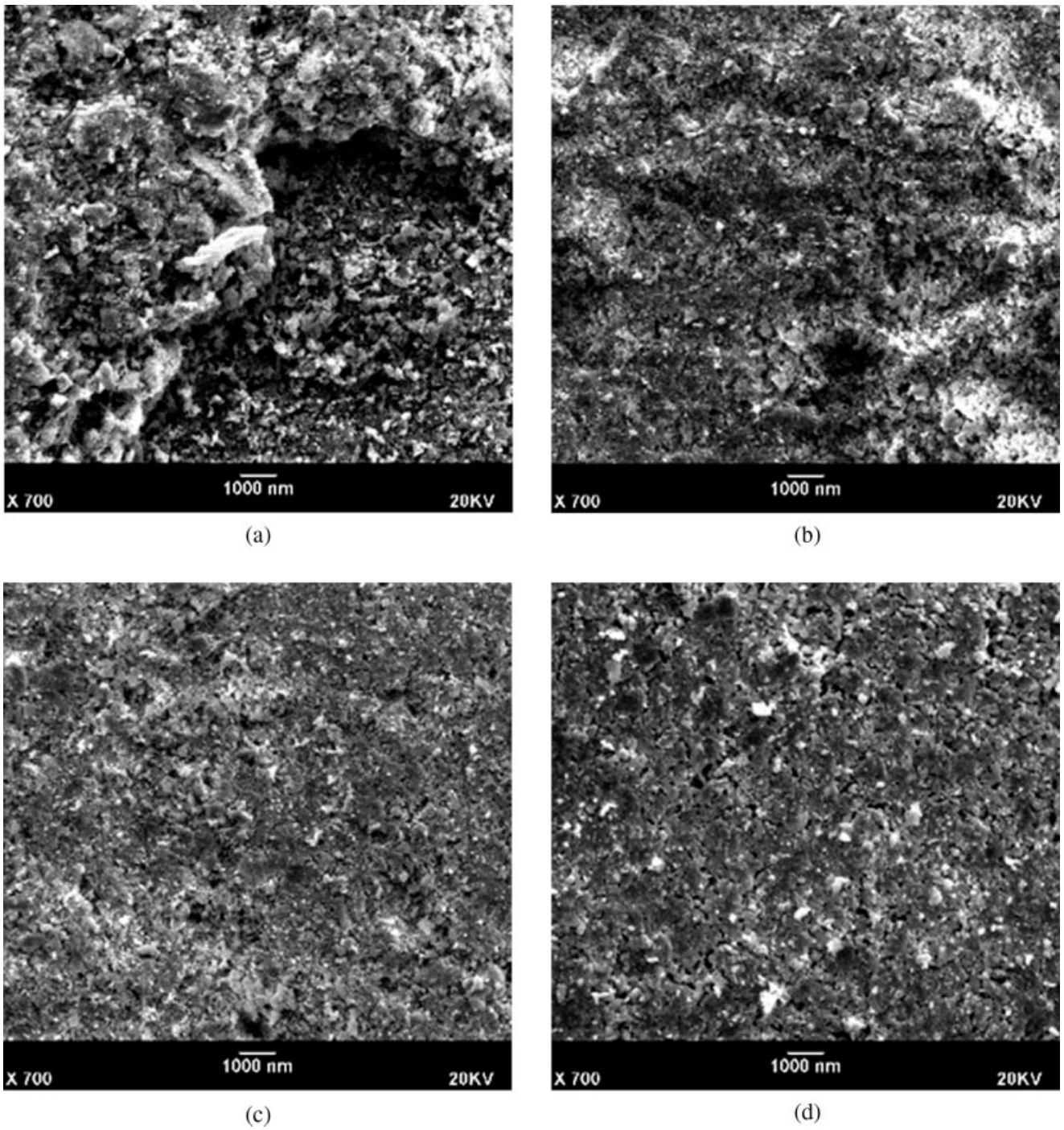


Figure 5 The SEM microstructure of sintered ceramic bodies with the addition of different dispersants.

the particle's outside viscosity. Deformation took place in the particles with the action of shear stres and the k_e decreased and ϕ increased, which eventually led to the decrease of η_a. The η_a remained invariable when the particles maintained a steady shape. Furthermore, polar groups exist in the polymer molecular chain; hydrogen bonds and solvation are then created, which eventually form hydrated layers. The hydrated layers are destroyed when the shear rate increases, which makes the particles' relative movement easier and therefore the η_a decreases. However, when the shear rate increases to a certain degree, that is, the hydrated layers are totally destroyed, η_a will not decrease any further.

Thixotropy is also imparted to ceramic suspensions [i.e., the up curve of the flow curve is higher or lower than the low curve, as shown in Fig. 4(b)]. A thixotropic system is characterized by the presence of a positive hysteresis loop between the up and down branches of the flow curves. The area of this loop is called the TA. Figure 4(b) shows that the TA decreases with increasing MPBMA concentration, and the TA values were almost the same when the MPBMA concentrations were 0.20 and 0.30 wt %. The main reason for this is that less dispersant cannot totally cover the surface of the ceramic particles. Because of the particle's Brownian movement and the action of static and gravitation, the amount of nude dots on the particles increases more and more, which makes the formation of a thixotropic structure easier.

Effect of MPBMA concentration on ceramic strength

Residual pores exist for almost all of the ceramic products prepared by the agglomerate approach. To a great extent, the ceramic strength depends on the amount, size, and distribution of these holes. Figure 5 displays the SEM microstructure of sintered ceramic bodies with the addition of different dispersants, and Figure 6 shows the variation of the ceramic breaking strength with the dosage of MPBMA. It is obvious that serious local agglomeration appears in the Figure 6(a) sample, and the pores distribute heterogeneously. The phenomenon is improved to a certain extent in the Figure 6(b) sample. Moreover, the Figure 6(c,d) samples show a high homogeneity without any agglomerates and exhibit a relatively smooth surface. Therefore, we can conclude that the sintered ceramic strength was gradually enhanced with the increasing ratio of MPBMA to sodium hexametaphosphate. This conclusion can be drawn from Figure 6 as well.

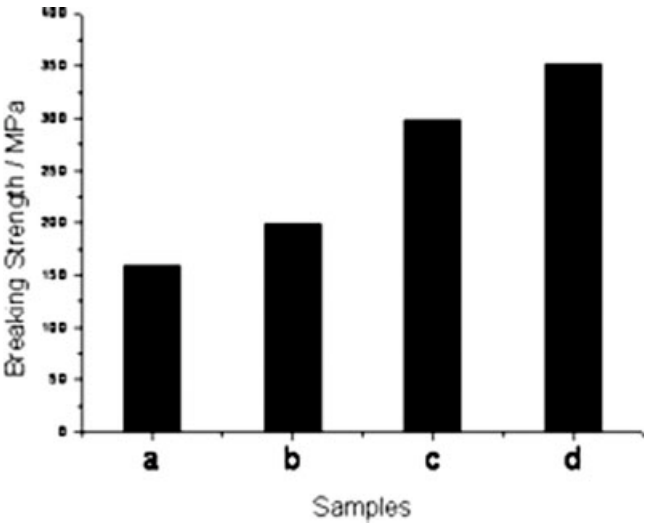


Figure 6 The variation of the ceramic breaking strength with the ratio of MPBMA.

CONCLUSIONS

A copolymer prepared by reacting maleic anhydride/polyglycol, α-olefine benzenesulfone, MA, and methyl methacrylate is used as a dispersant to prepare aqueous ceramic suspensions. The flocculate of particles in ceramic suspensions was disintegrated and the particles scattered mutually with the addition of MPBMA. Added MPBMA led to a shift of the IEP to the more acidic region, as well as a decrease in the ζ potential. The decreases of the ζ potential were attributed to the anionic groups of the added dispersant. Furthermore, the ζ potential and the suspension's viscosity decreased with increasing MPBMA concentration, as well as the TA. They were almost invariable for the whole shear rate range investigated when the MPBMA concentration was more than 0.20 wt %, which indicated that the ceramic suspension exhibited Newtonian behavior and excellent dispersivity. Therefore, an optimum copolymer concentration was found to be 0.20 wt % at pH 9–10, which was independent of the solid loading. A concentrated slurry with a solid loading of 70 wt % was prepared using this dispersant. The microstructures of sintered bodies were characterized by SEM. Compared with the inorganic dispersant, the sintered ceramic strength was gradually enhanced by increasing the ratio of MPBMA to sodium hexametaphosphate.

We express our sincere thanks to the National Natural Science Foundation of China for financial support.

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