Biogenic Hydroxylated Carboxylate Monomers Serve as Dispersants for Ceramic Particles

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Abstract

A total of 20 biogenic carboxylic acids, which contain one to three negatively charged -COO$^-$ group(s), were investigated as dispersion additives in the processing of ceramic particles. Only carboxylic acids containing one or more hydroxyl groups were able to disperse α-Al_2O_3 particles in aqueous suspensions. Detailed studies of two carboxylic acids, citric acid and tricarballylic acid were undertaken: measurements of zeta potential, particle packing, and dispersant adsorption characeristics indicated that carboxylic acid groups and hydroxyl groups are both important for dispersion of the ceramic particles. Hydroxyl groups increased the adsorption of the molecules to the particles.

Introduction

Currently, synthetic polymers from petrochemicals, such as polymethacrylic acid (PMAA) and polyacrylic acid (PAA) are used as dispersants (1). Similarly, previous work from this laboratory has shown that biologically produced polyelectrolytes such as kelp and bacterial alginate and bacterial polyglutamic acid also function as dispersants in ceramic processing (2, 3). However, synthetic and biological polymers have several major limitations: 1) polydispersant layers may be too thick to allow high packing densities, especially when the particle size is reduced to the nanometer size range; 2) the polyelectrolyte may not be compatible with useful gelling biopolymer matrices; and 3) commercial cost.

Furthermore, PMAA may contain formaldehyde, and PAA may contain residual amounts of acrylic acid. Moreover, PMAA and PAA are toxic and are produced from precursors that are toxic and/or carcinogenic.

This study was undertaken to investigate the use of biogenic monomers as dispersants. The compounds tested comprise a group of carboxylic acids and come from biological sources.

Results

(1) Dispersion of alumina suspensions by carboxylic acids.

A total of 20 carboxylic acids containing one, two, three or four carboxylate groups were evaluated for their dispersion behavior. Sedimentation volumes with AKP-30 alumina results are shown in Table 1. Tartaric, citric, and mucic acids produced the best dispersion with the

Table I: Sedimentation volumes (cake height, mL) of selected carboxylic acids at various concentrations (dry weight basis [dwb] of the particle)

	0	0.1%	0.3%	0.5%	1.0%	2.0%	3.0%	4.0%	6.0%
Glutamate				1.8		1.8			
Mannuronate				1.8		1.85			
Adipaic acid			1.8	1.75		1.8			
Mucaic acid				0.5		1.6			
Fumarate (*trans*)				3.0		3.0			
Maleic acid (*cis*)				2.5		2.5			
Succinate	1.85	2.4	2.45	2.7	2.7			2.4	
meso-Tartarate				0.55		0.6			
d,l-Tartarate	2.2	2.6	1.5	0.55	0.55			0.45	
Malate				0.7		0.7			
Malonic acid				2.0		2.05			
Tartronic acid				0.7		0.5			
Mesoxalic acid				0.8		0.5			
Glutarate				2.5		2.5			
Sebacic acid				2.0		3.5			
Tricarballyic acid				1.7		1.2			
Aconitic acid (*trans*)				1.8		1.75			
Nitrilotriacetic acid	2.25		1.9	1.45	1.1			0.9	
Citrate	2.0	2.0		0.5	0.5		0.4		0.4
Ethylenediamine tetracetate	1.8	1.75	2.0	2.0	2.0			1.9	

ceramic suspension and malic, tartronic, and mesoxalic acids provided some dispersion effect. From the molecular structure, it can be seen that tartaric, citric, mucic, malic, tartronic and mesoxalic acids all contain hydroxyl group(s). In contrast, succinic, maleic, tricarballylic, aconitic, and adipic acids which are not satisfactory dispersants, do not contain this group. When the various organic acids that are structurally similar to one another are compared by molecular weight and pKa value, the hydroxyl group was the principal difference between those producing good versus poor dispersion.

Suspensions prepared with hydroxylated organic acids had the lowest viscosities. With citric or tartaric acids, α-Al_2O_3 (AKP-30 of Sumitomo Chemical, median size 0.4 μm) particle suspensions having solid concentrations as high as 50 vol% could be prepared with a viscosity lower than 1 mPa.s. On the other hand, it was difficult to prepare ceramic suspensions with a solids concentration higher than 20 vol% when succinic, malic, tricarballylic, aconic or adipic acids were used as dispersants (data not shown here).

(2) pH effects and zeta potentials

Two carboxylic acids, citric acid versus tricarballyic, were chosen for more detailed investigation of sedimentation properties and surface charge under various conditions. The sedimentation results of citric acid with various concentrations of the acids are shown in Figure 1. All samples (except the samples at pH 4) at pH 6, 8, 9, and 10 produced the lowest cake heights (about 0.5 ml in this test) when the concentration of citric acid in the suspension was increased to 0.3 % (dwb). At pH 4, the cake height was the lowest without any citric acid and eventually increased as the concentration of the acid increased to achieve a maximum at 0.4 %. After this, the cake heights of the samples plateaued at about 1.2 ml. As shown below, this low packing is due to insufficient charge development on the particles with citric acid adsorption at this pH in spite of the fact that adsorption is strong.

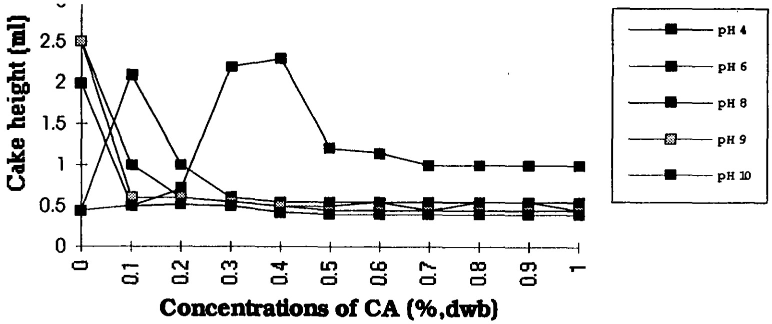

Figure 1: Cake heights of AKP-30 particle suspensions with citric acid (0.5%, dwb) under various pHs.

These dispersion behaviors correlate with and can be explained by zeta potential experiments. Figure 2 shows that with increasing citric acid concentration, the zeta potential decreases to zero (at pH 4 and 6) and then reverses sign and increases in the negative direction. In pH 8, 9, and 10 suspensions the zeta potential is near zero or already negative, so, as the concentration of the citric acid increases, the zeta potential continues to increase in the negative direction. Above 0.2% acid, the zeta potential approaches a nearly constant value of 65 mV (at pH 4 this is 33 mV). This value may reflect the state in which a saturated monolayer of citric acid occurs.

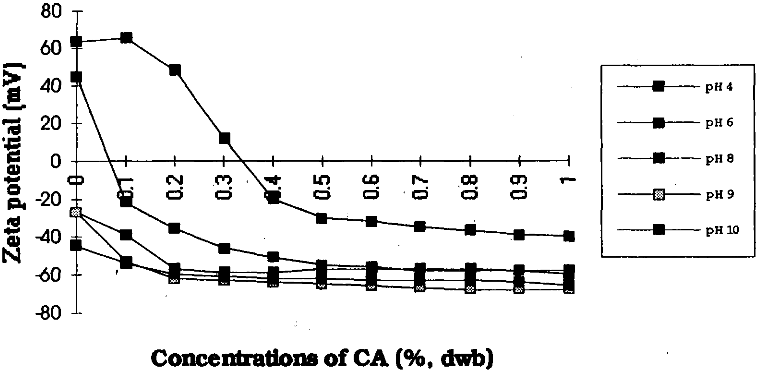

Figure 2: Surface charges of AKP-30 particles prepared with 0.5% (dwb) citric acid at different pHs.

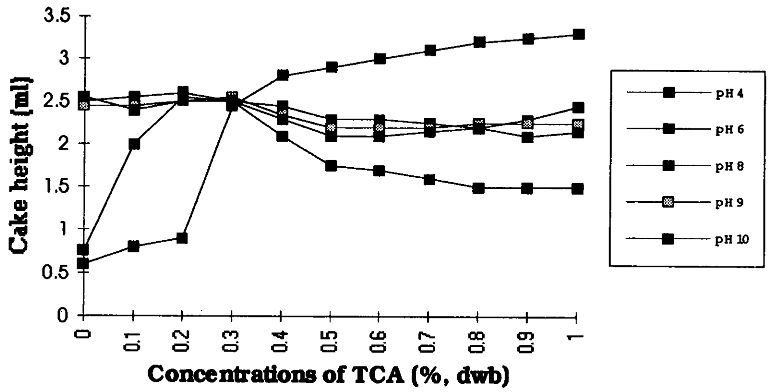

Figure 3: Sedimentation densities of AKP-30 particle suspensions when tricarballylic acid was used as a dispersant with a concentration of 0.5% (dwb) versus pHs.

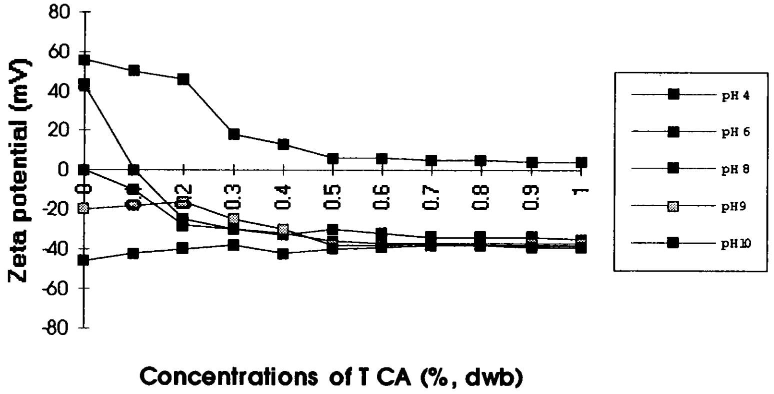

Figure 4: The surface charges of the AKP-30 particles prepared with tricarballylic acid at a concentration of 0.5% (dwb) with different pHs.

Tricarballylic acid did not produce the same packing densities as the citric acid (Figure 3) regardless of pH. At pH 4 the zeta potential changed from 55 mV to about 5 mV and never reversed sign, and the cake height increased from 0.6 mL to 3.5 mL (at 1.0%). At pH 6, the zeta potential decreased from about 43 mV to zero at about 0.2% concentration and then reversed sign and decreased to about -30 mV. This result is consistent with the sedimentation tests in which the cake height is first low (0.75 mL) and reaches its summit (2.5 mL) below 0.2% concentration and then decreases to around 1.5 mL but never decreases further although the concentration of the acid was increased to 6% (result not shown). At pH 8, 9, and 10, the zeta potential varies within the range of 0-40 mV, but the cake heights changed only slightly (from 2.7 mL to 2.3 mL).

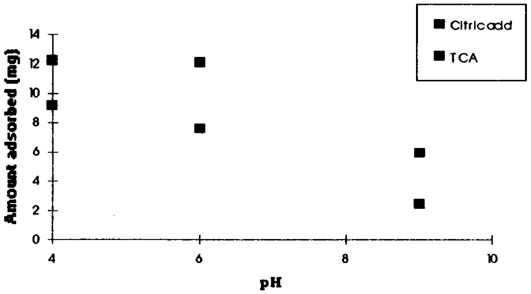

Figure 5: Comparison of the adsorption of tricarballylic acid and citric acid to 3.96 g AKP-30 particles

(3) Adsorption studies

According to this study, it can be concluded that the higher particle surface charge results in a higher packing density and the hydroxyl group may produce an increase in the surface charge. How do the hydroxyl groups affect the particle surface charges?

One explanation could be that hydroxyl groups affect the adsorption of the acid to the particles. To verify this, tests evaluating adsorption of the acid to the particles were performed by titration. Figure 5 shows the adsorption of citric acid and tricarballylic acid per 3.96 gram particles. The samples were examined at a concentration of 0.5% (dwb) at pH 4, 6 and 9. At each pH, the adsorption of citric acid was always greater than that of tricarballylic acid. These results clearly show that the hydroxyl group associated with the carboxylic acid can somehow increase the adsorption of the acid to the particle leading to an increase in the particle surface charge (zeta potential), and therefore results in better dispersion. From Figure 5, it can also be seen that more acid was adsorbed at lower pH values than at higher pH. This agrees again with the results from the zeta potential and sedimentation tests. It can be explained as follows: at lower pH, the surface of the particle has more positive charges than at higher pH and therefore can attract more negatively charged carboxylic acid.

Discussion

The results of this study show that all of the carboxylic acids tested cannot be used as dispersants. Only those containing hydroxyl group(s) disperse alumina particles in aqueous suspensions. Although some organic acids tested contain more than two carboxylic groups, they do not function well as ceramic dispersants without the presence of a hydroxyl group. This observation is in agreement with the recent results of Graule, et al (5).

Furthermore, it can also be stated that for compounds that contain the same number of charged groups and carbon atoms and have a similar molecular structure, the more hydroxyl groups the molecule has, the better it performs as a dispersant (e.g., tartronic acid and mesoxalic acid contain one hydroxyl group; tartaric, malic, maleic and succinic acids contain two hydroxyl groups; citric, tricarballylic and aconitic acids contain three hydroxyl groups; mucic and adipic acids contain four hydroxyl groups). Compared with the effect of the hydroxyl group, the effect of a double bond between the carbon atoms is insignificant.

The explanation of how the hydroxyl group of the carboxylic acid affects the adsorption and the dispersion behavior is not clearly understood. One possibility is hydrogen bond formation between substrate and adsorbate. A hydroxyl group on the carboxylic acid would increase the polarity of the molecule, thus increasing the adsorption by hydrogen bond formation or by other mechanisms. This increase of the adsorption is accompanied by an increase in the surface charge of the particles and therefore an increase in the dispersion capability.

It is also possible that a hydroxyl group associated with carboxylic acid could increase the affinity chelation of the acid to the particle surface and this could strengthen the reaction between the particle and dispersant. Or, a combination of these and other effects may play a role. Although citric acid is a chelating agent, it should be noted that other chelating agents, nitrilotriacetic acid and ethlyenediamine tetracetate were not good dispersants (Table 1).

The chemical composition of biogenic carboxylic acids makes them suitable for diverse industrial processes. These monodispersants contain only carbon, hydrogen, and oxygen in their molecular structure and no phosphorous, sulfur, halides, or metals. Therefore, they would not leave an undesireable residue which could impart defects in sintered ceramic products. Additionally, because most of them are small monomers they readily dissolve in aqueous solutions, and unlike most polymers, they do not impart high viscosities to ceramic suspension when mixed with gelling agents for injection molding.

Citric acid and other biogenic acids are currently in wide use in industry and medicine. They are inexpensive and can be readily produced by large scale microbial fermentation (6). Moreover, they are non-toxic and biodegradable.

References

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Supported by AFOSR through Grant #AFOSR-91-0258.