EFFECT OF POLYMERIC ALKYL SIDE-CHAIN ON DISPERSION STABILITY OF ALUMINA PARTICLES [+]

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Abstract:

The dispersion stability was examined for alumina particles in solutions of different alkyl methacrylates (methyl, *n*-butyl and *2*-ethylhexyl)/methacrylic acid copolymers. It was found that good dispersion can be obtained from solutions of *n*-butyl methacrylate/methacrylic acid and *2*-ethylhexyl methacrylate / methacrylic acid copolymers and that they settled as good deflocculated suspensions, whereas aggregation was much easier using methyl methacrylate/methacrylic acid copolymers.

Sedimentation test was used to determine the dispersion quality, which involved measuring the sediment volume of the packed alumina after gravity settling. The influence of dispersion media and copolymer structure was also studied.

المستخلص:

درست استقرارية تشتيت جسيمات الألومينا في محاليل البوليمرات المشتركة لميثاكريلات الألكيل (مثيل، *n*- بيوتيل و *2*- أثيل الهكسيل) و حامض الميثاكريلك. لقد تم الحصول على تشتيت جيد من محاليل البوليمرات المشتركة لكل من ميثاكريلات البيوتيل /حامض الميثاكريلك و ميثاكريلات أثيل الهكسيل/حامض الميثاكريلك، بينما على النقيض من ذلك كان البوليمر المشترك لميثاكريلات المثيل/حامض الميثاكريلك.

أستخدم فحص التركيد بواسطة الجاذبية الأرضية لتعيين جودة التشتيت، وهذه تتضمن قياس حجم الألومينا الراكدة مع الزمن. كذلك درس تأثير وسط التشتيت و تركيب البوليمر.

Introduction:

Dispersion stabilization usually results from adsorption of molecules or ions from solution onto the particle surface, thus creating repulsive forces between the particle in suspension either through electrostatic repulsion or from steric prevention of coagulation. The degree of dispersion of a particle suspension may be defined as the extent to which the individual powder particles become separated from one another in the liquid medium [1]. This process is very important in ceramic technology since it is considered as the 'critical' first stage in production of good ceramics [1].

The dispersion forces between two particles in a medium of different polarizability are always attractive [2]. In nonaqueous media and in aqueous suspension at high ionic strength or particle concentration, electrostatic repulsion is

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easily overcome. Most successful dispersants for these cases are believed to act by steric repulsion [3]. At present, it is generally accepted that the loop and/or tail sizes have wide distributions and that a polymer chains can have large or small loops, depending on the attraction by the surface and flexibility of the chains in the dispersion media. The preferred chain for stabilizing colloidal dispersions should not only be well anchored but should give a thick barrier by extending into the dispersion medium. A cloud of tails then surrounds each particle.

Observation of the particle settling rate and final packing density are commonly used methods for the determination of the behaviour of suspended solid in a liquid and measure the degree of stability of colloidal suspensions; slow settling and/or good packing density are taken to imply good dispersion stability. The stability of dispersion affects the settling and packing behaviour of particles, and this allows one to obtain qualitative information about the stability of the alumina dispersions in organic media.

In principle, polymers of controlled structure are interesting dispersants, but they have been relatively little studied in the context of ceramic processing. Simms and Spinelli [4] have described the use of group-transfer polymerization (GTP) for making acrylic block copolymers, which were used as dispersant for pigments in high-solid coatings. They claimed that narrow molecular weight distribution alloys gave higher solid content, better pigment dispersion, and better color development than do conventional dispersants.

In previous work [5,6], a novel polymer systems were prepared by GTP and used as dispersants for alumina particles in polar solvents such esters and ketones. It was found that the molecular structure of the attached dispersants was important in affecting the final packing density of the alumina particles, and the marked differences between the packing density from various organic solvents indicates that the solvent plays an important role in the dispersion process. Therefore, in this work we spot the light more clearly on the dispersion process using methacrylates having different side chains dispersed in polar and nonpolar solvents. The settling behaviour of copolymer dispersants are compared to each other and that of alumina suspension only. Acid copolymers were chosen for this purpose because of the availability of range of different molecular structure and compositions of copolymers of different alkyl methacrylate with methacrylic acid.

Experimental:

Dispersing Agent

The dispersant used were prepared by group transfer polymerization as described before [7]. They were random and block copolymer of methyl methacrylate, *n*-butyl methacrylate and *2*-ethylhexyl methacrylate having methacrylic acid units as anchoring groups. The ester to acid ratio is kept constant (100:10) in the initial feed for all copolymers. These copolymers were fully characterized. Average molecular weights and their distribution were determined by gel-permeation chromatography.

Adsorbent:

The ceramic powder used in all experiments was Reynolds DPM alumina. Scanning electron microscopy showed near spherical particles with diameter around 0.2-0.3 mm. The specific surface area was determined by a chromatographic BET method, calibrated with NPL standard alumina and found to be 7.2 ±0.1 $m^2 g^{-1}$. The alumina was dried at 150 °C in a circulating-air oven for 24 hour before use.

Dispersion Media:

Toluene and ethyl acetate were used in dispersion testing. They were obtained commercially and were dried by normal laboratory methods.

Dispersion Process:

Dispersions were prepared by mixing the desired quantity of alumina with a 2wt% solution of the dispersing agent in a stoppered 25 ml-graduated cylinder. They were agitated manually and ultrasonically for at least 1 hour, then they allowed to stand at room temperature until settling was complete. The height of the top surface of the solid bed, measured as the main front of particles above which the suspension is only thinly cloudy, was monitored as a function of time.

The packing density of the final particle bed is measured and expressed as a fraction of the theoretical density of a fully dense ceramic. Perfect packing of spheres would yield a density of 74%; random close packing of spheres gives 69% density. Agglomerated particles typically settle rapidly to packing densities of the order of 20%. Dispersants giving packing densities in the range from 30% to 60% are currently regarded as good.

Results and Discussion:

The sedimentation rates were taken to be the speed at which the interface between the supernatant liquid and the consolidation sediment moved down. This allows comparison in terms of settling rate and of the final sediment volumes directly. Although all the dispersants contributed to the dispersibility of alumina in toluene and ethyl acetate, some of them increased the stability of dispersions very much more than others. In these systems there is a general correlation between sedimentation rate and final packing density. For all the suspensions, the final packing densities were reproducible to within ±0.2 in repeated experiments with same conditions.

Upon examining the top surface of particles settled in solutions of the copolymers one could see a trend in their surface characteristic; the top surface of the compacts became smoother and flatter as the adsorption from solution increased. In addition, the supernatant solutions of the better dispersions remained opaque for several days. As sedimentation proceeded the uppermost part of the supernatant liquid became clearer, while the lower part remained opaque. The boundary between the cloudy and opaque portions of the supernatant liquid gradually moved downward, leaving very fine particles floating in the suspensions. In some cases, these fine particles stayed in the supernatant liquid for two months (the maximum time given for these type of experiments).

Figure (1) compares the top particle height versus settling time for alumina particles suspended in MMA/MAA copolymers of similar molecular weight as dispersants. It can be seen that the particles complete their settling within few days after standing in solution of poly(MMA-co-MAA) copolymer in toluene, figure (1 a) and poly(MMA-b-MAA) copolymer in ethyl acetate, figure (1 b). In both cases sedimentation gave a sharp interface that moved through the solution, leaving a clear supernatant liquid above it. The resulting sediments were loosely packed and quit fluid. In other cases illustrated, poly(MMA-co-MAA) copolymer in ethyl acetate, figure (1 a) and poly(MMA-b-MAA) copolymer in toluene, figure (1 b), it took about two weeks for the powder to settle, although sedimentation still involved a sharp interface and a clear supernatant liquid. The resulting sediments were much more densely packed. In both cases, the better packing was obtained from the system that

had the slower sedimentation rate. Without the dispersant, agglomeration takes place very rapidly and leads to almost instantaneous settling, with a lot of the alumina adhering to the inside walls of the graduated cylinders, thus making sedimentation volume determination of the reference difficult.

When MMA copolymers were replaced by copolymers of n-BuMA the sedimentation behaviour was different. In this case sedimentation was generally markedly slower and after some time three layers could be distinguished, the compacted sediment at the bottom, a clear layer at the top and an intermediate cloudy layer of fine particles.

The settling rate of the sediments is also very sensitive to the dispersant as can be seen by comparison of figure (2) and (1). For example, with poly(MMA-co-MAA) in toluene, settling was complete in a few days whereas with poly(BuMA-co-MAA) the same system needed over 20 days to settle. In general, dispersions stabilized by BuMA polymers needed longer settling time though the final packing densities were not necessarily better. For those sediments the top surface volume measurements plotted are different from the actual sediment volumes from which the packing density is calculated. The final packing volumes of compact beds were significantly higher than these obtained for the MMA copolymers, showing very much better packing of the particles, table (1). This type of sedimentation behaviour is typical of deflocculated dispersion [8]. One can easily distinguish between dispersions with the random and block copolymers of BuMA/MAA; more time was needed to achieve final settlement with random copolymer than in the case of block copolymer from both solvents. This was not noticeable with MMA/MAA copolymers.

From the results mentioned above, one can conclude that increasing the size of the branch chains improved the dispersion stability in terms of sedimentation rate, although the anchoring group was the same, providing the surface active sites density is kept the same. This explains why better dispersions is obtained from a polymer having butyl side chains than from the methyl methacrylate polymers. This might be possibly due to increase of the branch chain length, which might cause the surface concentration to drop due to crowding (though keeping the layer thickness constant). Doroszkowski and Lambourn [9] made similar observation for TiO_2 powder, using the acetate ester of hydroxystearic acid as dispersant in aliphatic hydrocarbons. They found that increasing the length of the acetate side chain by just three ($-CH_2-$) links caused very large increase in stability. This indicates that surface concentration is very important in influencing dispersion stability. Not much obvious differences can be seen for dispersions using *2*-ethylhexyl methacrylate copolymers, figure (3). They are very similar to those using the butyl methacrylate copolymers, although the final packing densities were slightly lower, table (1). This is may be also related to the original configuration of solubilized tails, more syndiotactic configuration was found with BuMA polymer than 2-EHMA and MMA polymers [10].

By examining figures (2) and (3), one can conclude that solvent and copolymer structure both had an effect on the settling of the particles. In suspensions with random copolymers, the particles tend to settle at similar rates from ethyl acetate and toluene solutions, although the final packing is different. In contrast, block copolymer suspensions settle more slowly from toluene, which is a better solvent for the stabilizing chain [11].

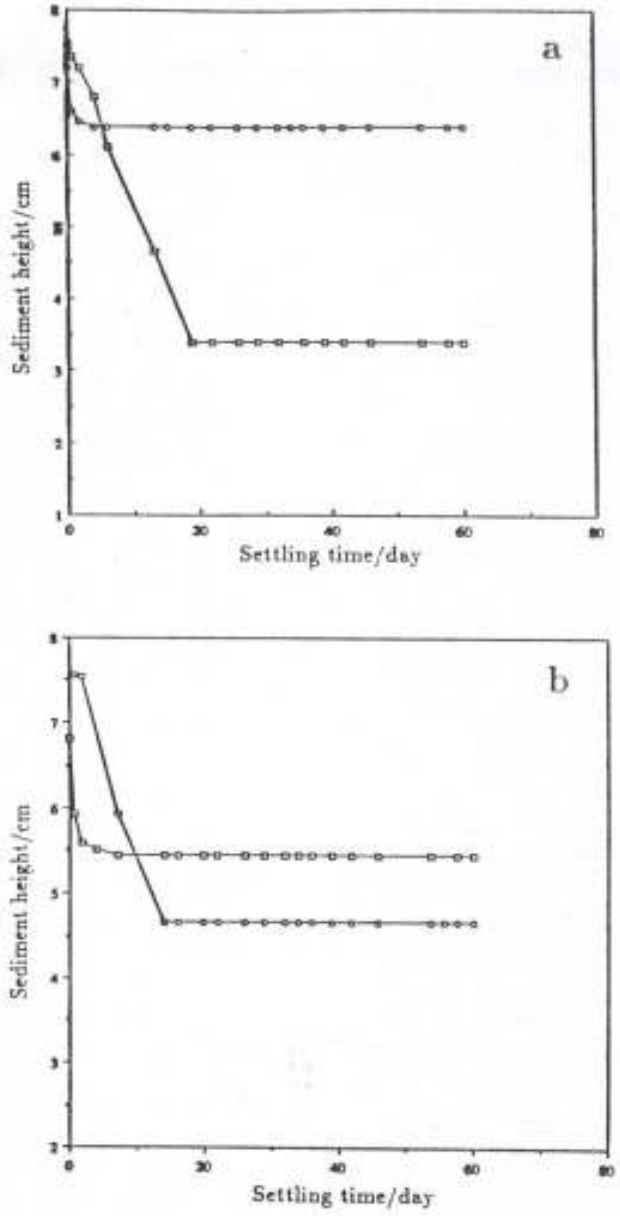

Figure (1): Height of alumina sediment as a function of settling time using toluene (-o-) and ethyl acetate (-o-) solutions of: (a) poly(MMA-co-MAA), (b) poly(MMA-b-MAA).

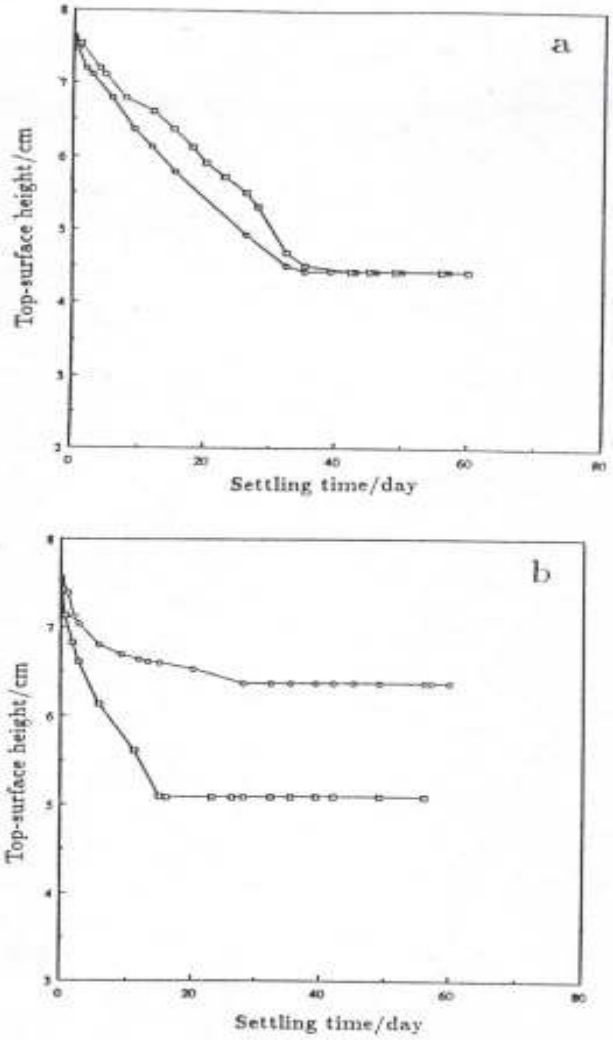

Figure (2): Height of alumina sediment as a function of settling time using toluene (⊸) and ethyl acetate (⊸) solutions of: (a) poly(BuMA-co-MAA), (b) poly(BuMA-b-MAA).

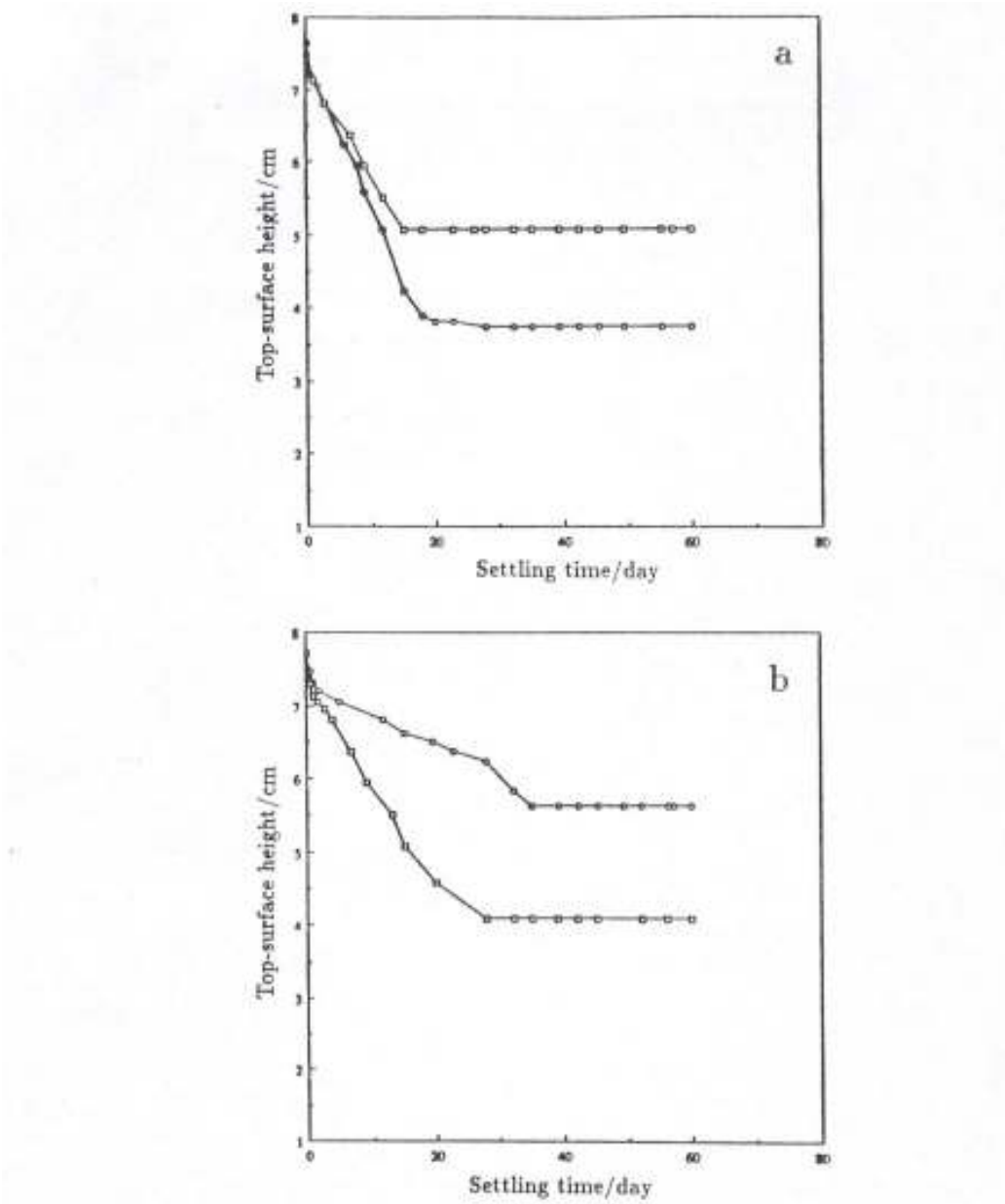

Figure (3): Height of alumina sediment as a function of settling time using toluene (-○-) and ethyl acetate (-●-) solutions of: (a) poly[(2-EHMA) -co-MAA], (b) poly[MAA-b-(2-EHMA)].

Table (1): Packing densities of settled alumina sediments from different dispersant solutions

Polymer	Mn (GPC)	(D)	Solvent	% Packing* density

Poly(MMA-b-MAA)	10300	1.28	Toluene Ethyl Acetate	37.2 30.9
Poly(MMA-co-MAA)	10800	1.23	Toluene Ethyl Acetate	27.1 52.1
Poly(BuMA-b-MAA)	13700	1.26	Toluene Ethyl Acetate	53.0 43.5
Poly(BuMA-co-MAA)	14600	1.12	Toluene Ethyl Acetate	59.9 57.5
Poly[MAA-b-(2-EHMA)]	17900	1.20	Toluene Ethyl Acetate	53.8 56.9
Poly[(2-EHMA)-co-MAA]	19800	1.23	Toluene Ethyl Acetate	55.4 57.0

*** % Packing density with no polymer in Toluene=24.3% and in Ethyl acetate=24.5%**

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