INFLUENCE OF POLYMER CHAIN LENGTH ON PACKING DENSITY OF GREEN ALUMINA BEDS[+]

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Abstract

The effect of the copolymer chain length of block and random copolymer of butyl methacrylate/methacrylic acid on dispersion of the alumina particles in tolouene has been studied. It was found that the chain length of the attached dispersant is important in affecting the packing density, The marked differences between the packing density in the presence of short or long polymer chains indicate some bridging flocculation might occurred with the latter one.

The results were discussed in term of radius of gyration of butyl methacrylate chains which are responsible on stabilizing the particles.

المستخلص

درس تأثير طول السلسلة البوليمرية لكل من البوليمر العشوائي المشترك والبوليمر القالبي المشترك لمونيمري ميثاكريلات البيوتيل وحامض الميثاكريلك على استقرارية جسيمات الألومينا في مذيب التلوين كوسط تشتيت. لقد وجد أن لطول السلسلة البوليمرية الممتزة على سطح الألومينا تأثير كبير على كثافة الرص، وأن الفرق الكبير بين هذه الكثافات بوجود سلاسل بوليمرية قصيرة أو كبيرة يدلل على حدوث عملية امتزاز تجسيري في حالة السلاسل الكبيرة.

نوقشت النتائج بدلالة نصف قطر التدويم لسلاسل ميثاكريلات البيوتيل المسؤولة عن استقرارية جسيمات الألومينا.

Introduction

In previous work [1,2], novel polymer systems were prepared by group transfer polymerization (GTP), these include copolymerization of different alkyl methacrylates, such as methyl, *n*-butyl and *2*-ethylhexyl with low concentration of methacrylic acid or γ–methacryloxypropyl trimethoxysilan. They were 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. The marked differences between the packing density from various organic solvents indicate that the solvent plays an important role in the dispersion process. For the same anchoring group, it was also found that the packing depends on the molecular structure of the attached dispersant which was an important factor affecting the dispersion quality. Increasing the size of the branched chains improves the dispersion stability providing the same surface active site density is maintained.

[+] **Received on 24/11/2005 , Accepted on 5/6/2006**

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Our experiments suggest that the homopolymers are weakly bonded to the surface but block and random copolymers formed very strong bonds, so that only a rather small portion of the polymer could be removed from the surface. In general, particles stabilized with *n*-BuMA and *2*-EHMA gave slower packing and greater density.

In this work, we discuss the effect of polymeric chain length on the dispersion stability, and hence the packing density of alumina particles from toluene solution.

Experimental

Dispersing Agent

The dispersants used were prepared by GTP as described before [1]. They were random and block copolymer of *n*-butyl methacrylate/ methacrylic acid units as anchoring groups. The ester to acid ratio was kept constant (100:10) in the initial feeds. These copolymers were fully characterized. Average molecular weight and its distribution were determined by gel-permeation chromatography. The properties, molecular weight, dispersity, and acid content are shown in Table (1).

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 $7.2 m^2 g^{-1}$. The alumina was dried at 150 °C in a circulating-air oven for 24 hour before use.

Table (1): Molecular weight, dispersity and acid content of poly(butyl methacrylate/methacrylic acid).

Polymer	$Mn/10^4$ (GPC)	Dispersity	Acid content (wt%)
P(BuMA)	0.6	1.23	0.00
Block copolymers			
1	0.62	1.29	5.08
2	2.37	1.26	5.58
3	3.40	1.58	5.16
4	24.2	3.09	4.86
Random copolymers			
1	0.59	1.18	5.60
2	2.46	1.12	5.63
3	3.22	1.22	5.63
4	28.9	3.13	5.98

Dispersion Media

Toluene was obtained commercially. It was dried by normal laboratory methods, and used as dispersion medium.

Dispersion Process

Dispersions were prepared by mixing eight grams of alumina with a solution of a known concentration of the dispersing agent in a stoppered 25ml-graduated cylinder or in a clean centrifuge tube. They were agitated manually and ultrasonically for at least 1 hour, and then the cylinders were allowed to stand at room temperature until settling was complete, while the centrifuge tubes were settled at 4000 rpm using machine type Baird & Tatlock H-700B/Japan. The centrifuge speed was increased slowly and the samples were centrifuged for one hour at the desired speed.

The volume of supernatant solutions, in both types of settlement, was measured using an analytical pipette, and the packing factor was calculated. The packing density of the final particle bed is measured and expressed as a fraction of the theoretical density of a fully dense ceramic.

Results

Adsorption as a function of molecular weight of copolymers of similar composition and structure has been studied in toluene solution, because this was found to be the best dispersion medium [3,4]. Copolymers were compared in term of %packing density after centrifugation settlement. The results obtained are shown in Figure (1) for block copolymers and Figure (2) for random copolymers. High molecular weight copolymers (2.5×10^4) gave poor packing density and a decrease in %packing density with concentration. The effect was greater with the random than block copolymer. This can be attributed to the flocculation induced by high molecular weight polymers [5], involving the so-called bridging mechanism [6]. Random copolymers would be expected to bridge particles more effectively than block copolymers and this may be the reason in our case.

The relationship between the number-average molecular weight (Mn) and the %packing density of alumina dispersed in 2wt% polymer are shown in Figures (3) and (4) for block and random copolymers respectively. It shows clearly that packing density, which has been calculated from both types of settlements, is molecular weight dependent. All the results were reproducible and each one has been repeated at least twice. Gravity settlement always gives lower values from centrifuge settling because no force has been used. It is clear that an optimum chain length of polymers of molecular weight around 0.6×10^4 gives the best dispersion more than the high molecular weight once. In all cases random copolymers of a given molecular weight give better packing than block copolymers.

Discussions

Studies using the adsorption copolymer systems show that increasing the chain length of the polymer over the a certain range leads to a reduction in packing density. Indeed at the highest molecular weight the polymer may have a negative effect on dispersion stability. This effect is relatively easily understood for the block copolymers as a combination of fact that long chains may lead to bridging flocculation and that a large number of short chains may be more effective than a smaller number of long chains in stabilizing the systems. For random copolymers we might expect the effect to be largely independent of chain length for short chains; clearly long chain random copolymers are much better as bridging flocculants.

As particles settle into their final packing shape, the polymer chains on the surfaces of separate particles must begin to interact. The distance at which this will occur is roughly four times the radius of gyration of the chain on the surface. This can be easily estimated for block copolymers.

If we assume that the polymer chain on the surface has the same dimensions as the isolated chain in solution, the root mean square end-to-end distance of the chain is given by [7]:

Where n is the number of backbone bonds, l is the length of the C-C bond and C is characteristic ratio of the chain, a measure of how far it is expanded by the steric influence of the substituents. The root mean square radius of gyration R_G is given by:

The value of C for a bulky substituent such as the butyl methacrylate group is typically around 10. On this basis, the radius of gyration of a poly(BuMA) chain is tabulated in Table (2).

Table (2): Radius of gyration of poly(BuMA).

Mn/10^4	**R_G/nm**
0.62	8.5
2.37	16.3
3.4	19.5
24.2	51.9

For all copolymers, especially those that are good stabilizers, the effective overlap distance is around 30-70 nm, compared to the particle contact distance of around 300 nm between centers. Thus the particles cannot approach complete close packing without significant interpenetration. The interpenetration region ($R_G \leq d \geq R_G$) involves an increase in polymer concentration, which involves a mixing free energy, ΔG_M, or osmotic effect [7]. This region also includes a small configurational loss. Lowering the interpenetration, which is sensitive to the solvent power of the dispersion medium, increases dispersion stability. One would therefore predict that a good solvent would improve packing by giving good dispersion but reduce it by inhibiting overlap of chains at close approach. Our results suggest that the first effect is dominant since packing was best in toluene, which is a good solvent.(1975).

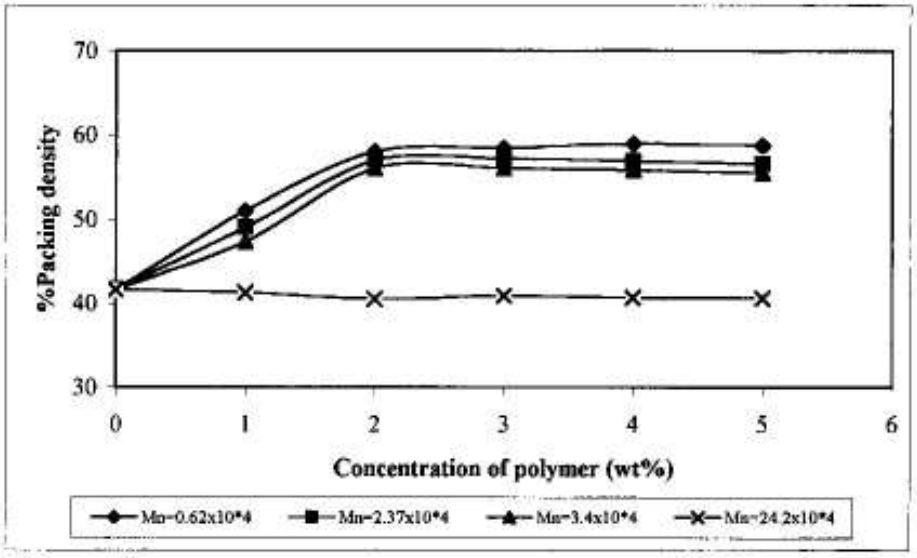

Figure (1): Effect of block copolymer concentration on centrifuge packing density of alumina in toluene.

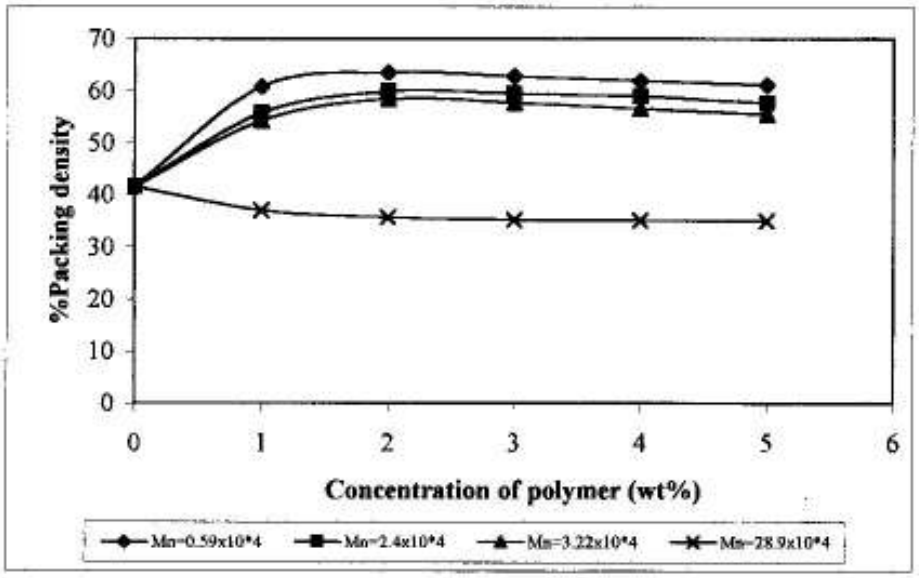

Figure (2): Effect of random copolymer concentration on centrifuge packing density of alumina in toluene.

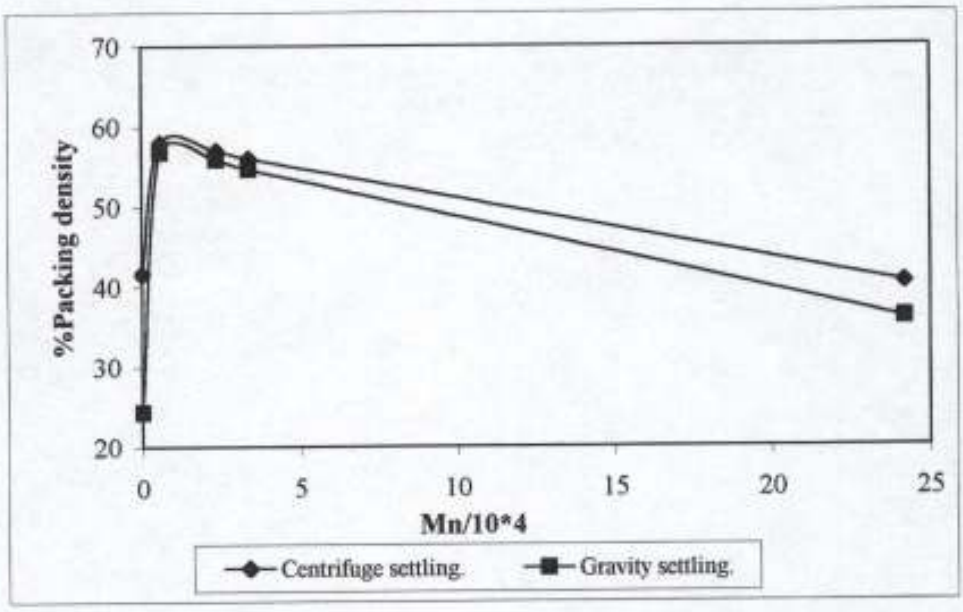

Figure (3): Effect of block copolymer chain lengths on packing density of alumina in toluene.

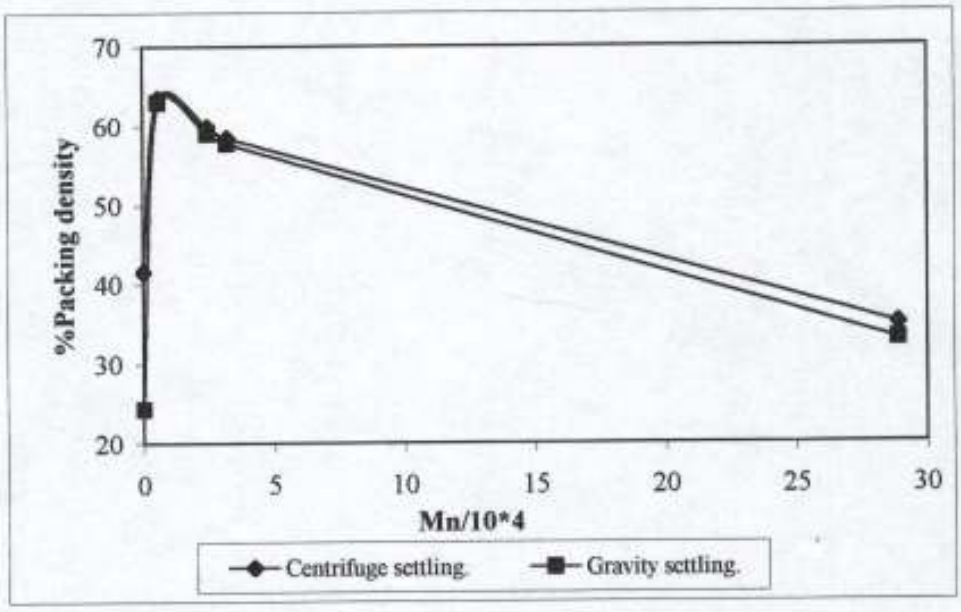

Figure (4): Effect of random copolymer chain lenghts on packing density of alumina in toluene.

Reference

[1] Al-Lami, H.S.; Billingham, N.C. and Calvert, P.D.; *"Controlled Structure Methacrylic Copolymers as Dispersants for Ceramics Processing"*, Chem. Mater., 4, 1200 (1992).

[2] Al-Lami, H.S.; Billingham, N.C.; Calvert, P.D. *"New Polymethacrylate Dispersants for Alumina Particles Prepared by Group-Transfer Polymerization",* Mu'tah Lil-Bhooth Wal Dirasat, 9(2), 199 (1994).

[3] Al-Lami, H.S. and Ibrahim, A.M.; *"Adsorption of poly(n-butyl methacrylate-Methacrylic Acid) copolymers on Alumina Powders"*, Basrah J. Sci., 11(1), 71 (1993).

[4] Al-Lami, H.S.; *"Polymeric Dispersants for Ceramic Processing"*, Ph.D. thesis, University of Sussex, England (1989).

[5] Ostubo, Y. and Watanabe, K.; *"Effect of Polymer Bridging on the Flow Behaviour of Silica Suspensions",* J. Colloid Interface Sci., 122(2), 345 (1988).

[6] Fleer, G.H., Koopal, L.K. and Lyklema , J.; *" Polymer Adsorption and Its Effect on the Stability of Hydrophopic colloids",* J. Colloid Interface Sci., 46, 1 (1974).

[7] Braudrup, J. and Immergut, E.H.; *"Polymer Handbook*