PHYSICAL AND MECHANICAL PROPERTIES OF TAPE-CASTED ALUMINA CERAMIC SHEETS+

Dr. Hadi S. Al-Lami*

Abstract

Tape-casting has been used to prepare different alumina ceramic sheets using block and random copolymer of butyl methacrylate/methacrylic acid as dispersants prepared by group-transfer polymerization. They were bounded with 40-60 vol.% of poly(butyl methacrylate) solution. Their mechanical properties were investigated in three-point bending test, and this was compared with oleic acid as well known dispersant for alumina particles. Higher moduli and higher bulk densities were obtained from tapes prepared with copolymer dispersants than those using oleic acid.

المستخلص

استخدمت عملية الصب الشريطي لتحضير رقائق سيراميكية ألومينية المشتتة مسبقاً بواسطة البوليمر القالبي والبوليمر العشوائي المشتركين لمونيمري ميثاأكريلات البيوتيل وحامض الميثاأكريليك المحضرين بطريقة البلمرة المشتركة بطريقة انتقال المجموعة كمواد مشتتة، وباستعمال 40-60 % من محلول بولي(ميثاأكريلات البيوتيل) كمادة رابطة لجسيمات الألومينا. فُحصت الخصائص الميكانيكية باستخدام فحص الانثناء بواسطة اختبار النقاط الثلاثة ، وقورنت مع تلك الرقائق المصنعة مع حامض الأوليك المعروف بكونه مادة مشتتة لجسيمات الألومينا. تم الحصول على معاملات مرونة وكثافة عاليتين لتلك الرقائق المحضرة مع البوليمرات المشتركة كمواد مشتتة عن تلك المستعمل فيها حامض الأوليك.

Introduction

In recent years, there has been a rapid development in research on high-performance ceramics, both for mechanical applications and for use in the electronics industry, in applications such as substrates, dielectrics for capacitors and packages for integrated circuits [1]. The production of such ceramics having high-density by sintering of powders depends on forming a ceramic 'green body' with closely packed fine particles. Production of such fine powders tends to give aggregates, bound together by covalent or hydrogen bonds at the point of contact [2]. Typical ceramics production involves breaking up these aggregates by milling the powders into a suitable liquid to form a slip. The slip solvent usually also contains a polymer, which acts as a binder to give mechanical strength to the green body [3]. This slip is converted into the appropriate form by processes such as centrifugal casting or doctor-blade coating, and the suspending liquid is removed by drying. To achieve close

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* **Prof./ Technical College , Baghdad**

packing, it is believed that the individual particles must be allowed to come together under conditions where the interparticle forces are repulsive, so that the particles pack into the green body as individuals rather than agglomerating into loosely packed clumps [4]. The extent of dispersion of the powder into the slip liquid is crucial in determining the microstructure and sinterability of the green body.

In principle, polymers of controlled structure are interesting dispersants, but there have been relatively little studies in the context of ceramic processing. Any dispersant has to be compatible with the binder polymer, and the choice of binder is limited by the condition that it must be burnt out of the green body during firing, without leaving any carbonaceous or ion-containing residues.

Since methacrylate polymers degrade very cleanly, they are attractive candidates as binder and dispersants. A novel system was described for forming thin ceramic sheets by casting a slip of alumina or barium titanate in a methacrylate monomer followed by polymerization process [5,6]. One disadvantage of this system is that few dispersants are effective for alumina in methacrylates. The use of methacrylate polymers as dispersants has also been limited by the synthetic problems of making them with controlled structures. This problem has been overcoame by using group-transfer polymerization to make block and random copolymers of different methacrylates with small fraction of methacrylic acid units. These polymers were found to bind strongly to aluminum oxide surfaces through the acid groups and act as efficient dispersants for alumina particles in polar organic solvents such as esters and ketones [7].

In this work, the preparation of ceramic green tapes and sintered alumina ceramic sheets is discussed using butyl methacrylate/methacrylic acid copolymers as dispersants and poly(butyl methacrylate) as a binder.

Experimental Procedures

Polymeric Dispersants

Block and random copolymers of butyl methacrylate/methacrylic acid were prepared by group-transfer polymerization as described in literature [7]. They have the properties shown in Table (1).

Table (1): Molecular masses of copolymers used as dispersants.

Polymer	**Mn GPC**	**Dispersity**	**Acid content (wt%)***
Poly(BuMA-co-MAA)	24600	1.26	5.58

Poly(BuMA-b-MAA)	23700	1.12	5.63

* Theoretical acid content = 5.709%.

Adsorbent

The ceramic powder used was Reynolds DPM alumina, it was purchased from Alcan of England. 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.

Tape-Casting Process

The procedure described by Mistler et. al. [8] was used in the tape-casting process. Suspensions were prepared in the first stage by dispersion of the 60 g of dried alumina powder, 1.2 g of the polymeric dispersant and 15 g of *2*-butanone as a solvent as shown in Table (2). They were mixed in a polyethylene container, then ball milled together for 24 hours in horizontal rolling mill type Luckham, Unimix model 840, using zirconia balls to form a homogeneous mix. In the second stage, poly(butyl methacrylate) solution as a binder was added, Table (2), followed by another 24 hours of milling to insure the homogeneity of the slip.

Three different binder ratios were used to make three different tapes for each particular dispersant. Table (2) shows the functions of the materials used and the different stages of the milling procedure.

Table (2): Summary of the tape-casting conditions.

Process Step	**Materials**	**Function**	**Part of weight Total =100%**
First stage (milling for 24 hrs.)	Alumina Poly(BuMA-co-MAA) or Poly(BuMA-b-MAA) or Oleic acid* 2-Butanone	Substrate material Dispersant Solvent	60 g 1.2 g 15 g
Second stage (milling for 24 hrs.)	Poly(butyl methacrylate) 2-Butanone	Binder Solvent	9.63 g 14.17 g

* Molecular weight = 282.47.

In the last step, the milled slip was degassed using a conventional vacuum pump, usually until agitation due to the cease of air escape. The degassed slurry was poured into a reservoir located above a moving carrier tape of a doctor-blade casting machine designed originally for making thin layer chromatography plates. The slips flowed from the reservoir onto the carrier tape which passed under a doctor blade. The thickness of the tape was controlled by adjusting the height of the knife blade above the carrier tape.

After casting, the layer of slip was left to dry slowly at room temperature in a closed system by covering the TLC machine. This controls the rate of solvent evaporation by keeping the difference of solvent content between the slip and the surrounding air during the drying process, and helps to minimize curling and cracking of the slip as it dries.

Mechanical Testing

The mechanical properties of the green tapes were measured by a three points method bending test before firing, using an Instron 1122 mechanical testing machine. This method allows the determination of flexural properties of the tape in the form of rectangular bars of known dimensions, typically 50 x 10 x 0.5 mm.

Sintering of Ceramic Tapes

All the samples were fired and sintered according to the following heating schedule in a Neobtherm electrical furnace: Firstly, the temperature was raised 50°C/hr up to 500°C and kept for one hour, and secondly, it was raised 100°C/hr up to 1500°C and kept for another one hour. The tapes were sandwiched between alumina slab during firing to prevent any wrapping.

Tape Characterization

Density Measurements

The density of the tapes is an important parameter for characterizing a tape-casting process. Two methods are involved; first, the tape volume for calculation of the apparent density was estimated by measuring the tape dimensions with a flat-faced micrometer caliper. About 10 thickness measurements were taken and averaged (for a substrate area about 5 cm^2). Combined with sample weight, this method gives bulk density of the solid, including any porosity.

Archimedes method [9] is the other technique used for measuring the density of the tapes, using water as buoyant fluid. From the difference in the sample weight before immersion (dry weight) and immersed in water, the tape density was calculated. No attempt was made to impregnate the porosity of the sample so that this method also gives an average density for the bulk solid.

Microstructural Characterization

The microstructures of the green and fired tape samples were examined using a Scanning Electron Microscope 'SEM', Jeol model 100C with ASID-4D ultrahigh resolution scanning attachment.

Results And Discussion

Ceramics tapes were prepared using block and random copolymers of butyl methacrylate and methacrylic acid as dispersants as well as oleic acid, which is considered as a well-known dispersant for alumina tape-casting [10] for comparison. Poly(BuMA) having high molecular weight (inherent viscosity of 5.3) with glass transition temperature (Tg) of 27 °C was used as a binder in three different volume ratios to prepare three different types of ceramic tapes. This binder should provide good toughness and strength for the tape due to its lower Tg, and good compatibility with the dispersant since they are all of the methacrylates group, and to ensure that sufficient mobility will remain in the tape for diffusion and flexibility after solvent evaporation (drying). It also retains the alumina particles in position, in other words, hold the tape together until it is fired into hard ceramic. For all of these reasons, no plasticizer is needed [8].

It is well known that properties of the final tape rely on rheological control of the dispersion, typically viscosity. On qualitative examination, oleic acid slurry has the highest slip viscosity and was somewhat difficult to mill by rotation. In contrast, using our acid copolymers as dispersants provided a paint like fluidity with good milling action, with random copolymer being the best, in spite of the high solid-to-liquid ratio used for all slurries, Table (2). These slips give a ceramic green sheets with good surface smoothness.

Some of the mechanical properties of the ceramic tapes were evaluated using a three-point bending test. This test was carried out on the tapes in the green state in form of rectangular bars cut from the sheets directly after solvent was removed. For each test, six specimen were tested. Specimens were bent to break on a 40 mm span in an Instron 1122 mechanical machine, operating at a cross-head speed of 5 mm min^{-1} at room temperature. The initial modulus of elasticity in bending (E_b) as well as the flexural strength (δ_b) and the strain (ε) in the outer face of the tape at break were calculated from the force-deflection curve shown in Fig. (1), which is a representative curve for all the types of dispersant used, i.e. (a) poly(BuMA-co-MAA), (b) poly(BuMA-b-MAA) and (c) oleic acid. It is quite obvious from Fig. (1) that random copolymer of poly(butyl methacrylate/methacrylic acid) has the higher modulus of elasticity than the block copolymer of the same monomers, and oleic acid being the worse as dispersant, which reflects their abilities for dispersing the alumina particles in the first stage of milling process. This is also true for other properties calculated from the force-deflection curves of all tested specimen. The results obtained are tabulated in Tables (3) and (4).

Examining Figures (2), (3) and (4), shows obvious differences between the properties of the tapes produced with each particular dispersant, especially between those having polymeric dispersant and those produced with oleic acid. This must be attributed to the homogeneity of the tape, arising from the better quality of the original dispersions [11]. Random copolymers give better results than block copolymer. This result is in a good agreement with adsorption and packing studies [12]. Thus, an improvement in the final tape's packing density depends upon maximizing the dispersion of the particles in the slip. Further evidence for the better packing came from SEM examination of the smooth top surface of the green and fired tapes, Fig. (5), which confirms the better packing of particles obtained with polymeric dispersants. The better packing of the particles obtained is also reflected in the bulk density of the green tapes, which increase in the order oleic acid < block copolymer < random copolymer for all tested specimen, Fig. (6 a). As expected, the tapes having highest binding content have the highest bulk densities and the lowest level of porosity. For example, using random copolymer as a dispersant produced a tape with a bulk green density equal to 2.551 g/cm^{-3}. If one takes the organic materials into account, this bulk density corresponds to an alumina volume percent of 51, which is a densely-packed green body, considering the fact that no pressing is involved during its formation. Similar bulk densities ranging from 2.5 to 2.6 g/cm^{-3} have been reported in the literature [8,13].

The final ceramics produced by firing the green tapes have good surfaces and no cracks occurred during the sintering processes. No attempt was made to measure the porosity level directly, but bulk density measurements for the sintered tapes was also made using Archimedes method in water. The results obtained are shown in Fig. (6 b). The same previous tape had a bulk density equal to 3.849 after firing, which corresponds to an alumina volume percent of 96.9, i.e. a porosity level of around 3%, which is also found to be related to the vol.% of binder used, Fig. (7). These results imply that the tapes from slips with the least deflocculating have the worst packing of alumina particles and thus the lowest fired bulk density. This was obtained with oleic acid being a dispersant.

Table (3): Bulk densities and the solid content of the alumina tapes.

Dispersant	*%Binder*	*Green Bulk Density* **(g cm^{-3})**	*Fired Bulk Density (g cm^{-3})*	*% Solid Alumina*
Random	***40*** ***50*** ***60***	***2.369*** ***2.414*** ***2.551***	***3.728*** ***3.785*** ***3.849***	***93.9*** ***95.3*** ***96.9***
Block	***40*** ***50*** ***60***	***2.340*** ***2.398*** ***2.506***	***3.709*** ***3.774*** ***3.821***	***93.4*** ***95.1*** ***96.3***
Oleic	***40*** ***50*** ***60***	***2.301*** ***2.390*** ***2.441***	***3.660*** ***3.735*** ***3.754***	***92.2*** 94.0 ***94.6***

Table (4): ***Modulus data of some alumina green-tapes.***

Dispersant	*%Binder*	**Flexural Strength (MPa)**	*Modulus of Elasticity* **(GPa)**	*Bending Strain*
Random	***40***	***22.00***	***8.15***	***3.51***
	50	29.90	9.26	4.74
	60	36.84	10.75	5.64
Block	***40***	***12.80***	***4.24***	***4.32***
	50	21.60	7.57	5.78
	60	34.14	10.16	6.23
Oleic	***40***	***4.21***	***2.45***	4.62
	50	4.80	2.75	6.24
	60	7.63	4.97	8.20

Conclusion

In qualitative terms the copolymers are very much better materials than conventionally used dispersant. They give very smooth dispersions which could be cast with ease to give ceramic green bodies of good quality. The final ceramics properties and SEM studies suggest that they are dense, well packed materials

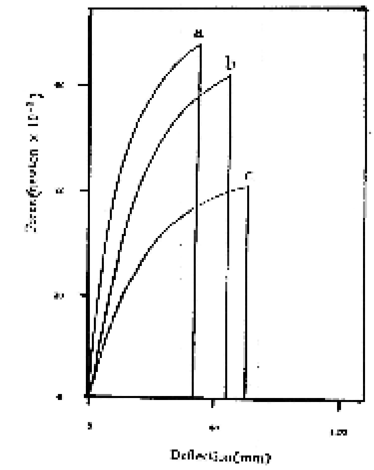

Fig. (1): Typical force-deflection curve produced from alumina sheets prepared with different dispersants: (a) random copolymer; (b) block copolymer (c) oleic acid.

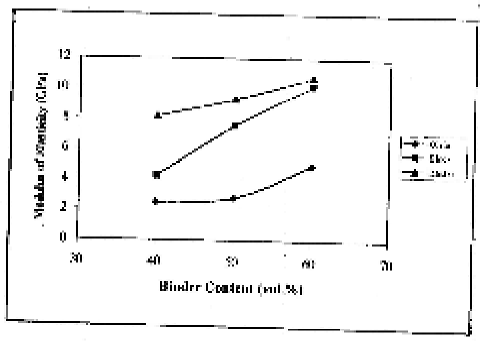

Fig. (2): Modulus of elasticity of green alumina tapes having different vol% of binder dispersed with various dispersants.

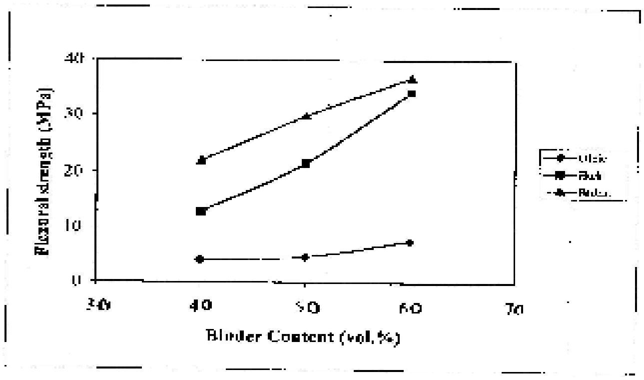

Fig. (3): Flexural strength of green alumina tapes having different vol% of binder dispersed with various dispersants.

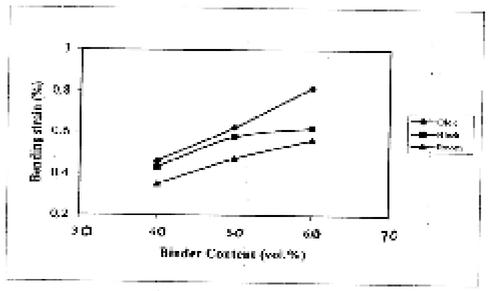

Fig. (4): Bending strain of green alumina tapes having different vol% of binder dispersed with various dispersants.

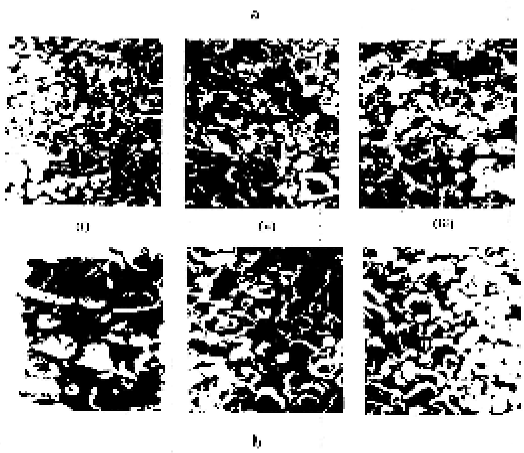

Fig. (5): SEM micrographs of some top surfaces of ceramic tapes: (a) green tapes and (b) fired tapes; prepared with different dispersants; where: (i) random copolymer; (ii) block copolymer, and (iii) oleic acid.

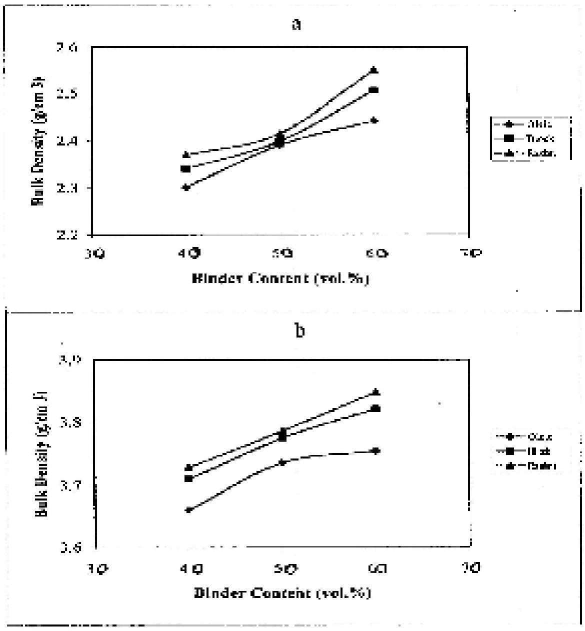

Fig. (6): Bulk densities of alumina sheets having different vol% of binder dispersed with various dispersants: (a) green tapes, and (b) fired tapes.

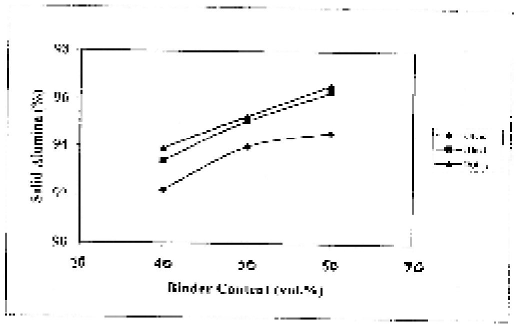

Fig. (7): % Solid alumina in fired sheets prepared with different vol% of binder dispersed in various dispersants.

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