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Effects of monomer composition on the mechanical and machinability properties of gel-cast alumina green compacts

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Abstract

In the present work, machinable green gel-cast alumina compacts were prepared by using polyethyleneglycol (400) diacrylate (P4) and polyethyleneglycol (600) dimethacrylate (P6) together with the acrylamide (AAm) comonomer. The glass transition temperatures of copolymers decreased with the increasing of P4 or P6 amount in total copolymer. The green samples obtained in an aqueous system were mechanically analyzed by means of three-point bending. Flexural strength values increased, from 2 MPa to 25 MPa, as the weight ratio of P4 or P6 in total copolymer (AAm-P4 or AAm-P6) decreased from 90% to 3.5%, respectively. The green gel-cast samples prepared by using P4 or P6 were machined easily by using a lathe, drill and milling machine without damaging the samples, which have good surface finish. The binder removal was achieved at lower temperatures than those samples prepared by using only AAm.

Keywords: Gel-casting; Monomer; Mechanical properties; Machinability; Al_2O_3; Green compacts

1. Introduction

A common and rudimentary requirement of ceramic products is the production of components of prescribed overall dimensions within specified tolerances.[1] When these parts possess larger and complex geometry, it becomes difficult to achieve such requirement by means of traditional processing operations.[2] Gel casting, technique used in the present study, is an alternative near-net-shape forming process since it has the potential for providing control over the micro- and macro-structural properties of green parts as well as faster and straightforward manufacturing process.[3]

The use of an organic monomer solution (a binder vehicle) is the important part of the gel casting; the monomer can accordingly be polymerized in the form of a strong "crosslinked polymer–solvent" gel. Ceramic slurry with a low viscosity and high fluidity is then obtained with the combination of the prepared monomer solution (not polymer solution) and the ceramic powder. The acrylamide (AAm) and its derivatives are preferred as the monomer for this purpose due to their easy polymerization and solubility in water. *N*,*N*′-methylene bisacrylamide (MBAM) and polyethyleneglycol (1000) dimethacrylate are amongst the examples of crosslinkers. Ammonium persulfate (APS) is one of the free radical initiator used for polymerizing the monomer system together with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) which is the corresponding catalyst used for catalyzing the APS to accelerate the polymerization and crosslinking reactions. The final ceramic aqueous slurry mixture is then transferred to a mould. The monomer used in the slurry mixture is then polymerized and crosslinked forming a firm "polymer–solvent (water)" gel matrix. As a result, ceramic particulates are formed into a desired geometry. This dried matrix contains

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only 2–6% of polymer, by weight, which can easily be removed by means of standard thermal procedures.[4] The green compact may then be sintered. Although there has been significant progress on the gel-casting process of green preforms, only a few papers on the mechanical properties, especially on green strength, of gel-cast ceramics could be found in preceding publication.[5–8] One of the main purposes of using the gel-casting method is the preparation of the components having high green strength, but increasing the green strength causes the structure to be very brittle which makes the machinability properties poor, especially for conventional drilling, milling and lathing. Plasticizers can be added to reduce the brittleness of green samples. However, important questions remain regarding the "constitutive behavior" and hence "structure-property" relations of these green structures.

The purpose of the present paper is primarily to describe, by means of experiment, the effects of monomer composition, which is the main organic component of the gel-casting ceramic slurry, on the mechanical properties of final gel-cast ceramic green compacts. Alumina powder was used as the ceramic system throughout the experimentation. It is anticipated that this information may be used for the description of structural response of the gel-cast ceramic green components as a function of material properties present within the process.

2. Experimental procedures

2.1. Materials used

An alumina powder (99% purity, HTM-30, Indial, India) with a 0.8 m^2/g BET surface area and a mean diameter of 4 μm was used. For gel-casting purpose, a monomer of acrylamide (AAm, $C_2H_3CONH_2$) and polyethylene glycol (400) diacrylate (P4) and polyethylene glycol (600) dimethyacrylate (P6) of Sartomer (SR-344 and SR-252, respectively), as a crosslinking agent or comonomer were used. In cases where only AAm was used as monomer, *N*,*N*′-methylenebisacrylamide (Merck, MBAM, $(C_2H_3CONH)_2(CH_2)$) was used as the crosslinking agent. Ammonium polyacrylate, potassium persulphate (Merck, $K_2S_2O_8$) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (Merck, TEMED) were used as dispersant, initiator and catalyst, respectively.

2.2. Gel-casting procedure

The alumina suspension was prepared with an (alumina)/(total water) ratio of being 1 by volume. The dispersant amount used for this purpose was 0.23% by weight of alumina. The suspension was first ball milled for 6 h. Later, AAm-P4 and AAm-P6 were added in the weight ratios of AAm/(P4 or P6) between 10/90 and 96.5/3.5, respectively. For comparison purposes, various suspensions were prepared by using P4 and P6 with weight ratios between 4% and 10% with respect to the alumina. AAm and MBAM were also used in the molar ratio of AAm/MBAM being equal to 200 and total AAm amount being between 2% and 8% of alumina by weight.

After the addition of 6 mg initiator and 2.5 ppm catalyst for 1 g of monomer or monomer mixtures, the oxygen was purged by using nitrogen. These suspensions were later cast into a glass mould then gelled in an oven at 50 °C. Finally, the desired samples were cut from gelled green structures and dried at 110 °C for 2 h.

2.3. Copolymer preparations

For the determination of glass transition temperature of crosslinked polyacrylamide and its copolymers, these polymers were prepared without the use of alumina and dispersing agent under the aforementioned conditions and then dried under vacuum.

2.4. Measurements

The viscosity values of ceramic suspensions were measured by means of a Brookfield synchrolectric viscometer (Model QSK 57) by using RV4 rod with a speed of 10–50 rpm.

Fracture tests were carried out by using a Universal testing machine (Hounsfield H10KS, UK). Samples with 5–7 mm thickness and 10–13 mm width and 60 mm length were prepared from the cast green alumina samples. Fracture tests were implemented according to ASTM D2344-80 with a 40 mm span length and 50 mm/min crosshead speed by repeating the tests for minimum three times for each sample. The results are given as the mean values of three measurements.

Thermogravimetric analysis for dried green samples were carried out by using a Shimadzu TGA-50 equipment with a 10 °C/min heating rate up to 700 °C in air.

Green samples were also cast in cylindrical and ring forms with various formulations in order to test the machinability. These samples were turned by using a lathe (500–900 rpm), drilled (100–300 rpm), milled (65–2400 rpm) and ground (3000 rpm). Attempts were also made to see whether it is possible to obtain sharp edges during machining. Easy chip forming without any crack propagation was examined. Final forms were examined to see whether there are any cracks and/or fractures, especially at the edges.

The glass transition temperature of prepared copolymers was determined by means of a Setaram DSC 131 with samples of 19–21 mg weight in a nitrogen atmosphere with a 20 °C/min heating rate. Samples were first preheated, with a heating rate of 20 °C/min, up to 220 °C and held at this temperature for 10 min for the removal of absorbed water. It was then cooled down to the room temperature.

3. Results and discussion

3.1. Copolymer preparations

One of the most important parameters being effective on the mechanical properties of polymeric materials is the bonding type of the composing units within polymers. Within this context, the structure of polymers is important whether it is linear, branched and/or crosslinked. The crosslinking density and the structure of crosslinking agent are also important as well as the main chain structure for crosslinked polymer structures as in gel-cast ceramic green compacts. Because of the structural similarity between AAm and MBAM (MBAM is the dimerised form of AAm), only the crosslinking process by means of MBAM affects the mechanical properties. This effect does not come from its structural contribution. In cases where other type of difunctional monomers (crosslinking agent with long chain structures) are used, the mechanical properties will be affected not only by the contribution from crosslinking reaction but also by the structure of crosslinking agent which can also be the main effective parameter for the mechanical properties depending upon their amount.

The use of crosslinking agents with long chain structure and etheric bonds, instead of MBAM, affects the mechanical properties of polymer. P4 or P6 are examples of this type of crosslinking agents. Due to the long chain structure and flexible etheric bonds, the glass transition temperature of crosslinked copolymer decreases and as a result, final mechanical properties will be affected. The AAm polymers crosslinked by MBAM has a glass transition temperature, T_g, of 195 °C where AAm/MBAM = 200 mol/mol, which is the same value as given in literature.[9] This high T_g value of crosslinked PAAm can be explained by the presence of hydrogen bonding, causing a great number of interaction points, reducing the mobility of polymer chains. When P4 is used with the same molar ratio as MBAM, the glass transition temperature becomes 188 °C. Fig. 1 shows the change in T_g as the molar ratio of P4 and P6 increased; T_g decreases almost linearly while the crosslinking density increases. The T_g value of the copolymer prepared by using AAm and P4 were 150, 107 and 72 °C where the percentage weight ratio of P4 in the copolymer are 25, 50 and 75, respectively. These T_g values for the copolymer containing P6 in the same weight ratio as P4 were determined as a little bit lower than those in the case of P4, as 140, 90 and 68 °C, respectively. The long chain structure of P4 and P6 will prevent, to some extent, the formation of hydrogen bonding between amine units and carbonyl oxygen of AAm. This prevention will cause the polymer structure to be more elastic than rigid one, which is also increased by hydrogen bonding contribution. These decreases in T_g value of copolymers are also expected from the T_g value of polymers obtained from oligo (ethylene glycol) diacrylates.[10] The change in T_g affects the mechanical properties of copolymer as well as gel-cast green ceramic structures and as a result, the final cast ceramic green structure will become less brittle.

These T_g values were determined from the samples dried at 220 °C for 10 min in an inert atmosphere. The mechanical tests were performed on the samples held in ambient laboratory conditions after drying at 110 °C for 2 h (see Section 2). It should be noted here that the water content would affect the T_g of polymers.

3.2. Preparation of green ceramics and mechanical properties

Viscosities of samples prepared with 4% AAm and with equal amounts of AAm (2%) and P6 (2%), with respect to alumina, remained at a constant value of about 0.2 Pa s in the range of 10–50 rpm. This indicates that the viscosity of these samples is independent of the shear rate within the current experimental ranges and there is no notable effect of partial replacement of monomer with a higher molecular weight than AAm to the viscosity. As a result, it can be said that the monomer composition, at least within the current experimental study, has not considerable effect on the rheological properties of ceramic suspension.

The flexural strength values obtained from three-point bending tests of samples prepared by using only AAm in the

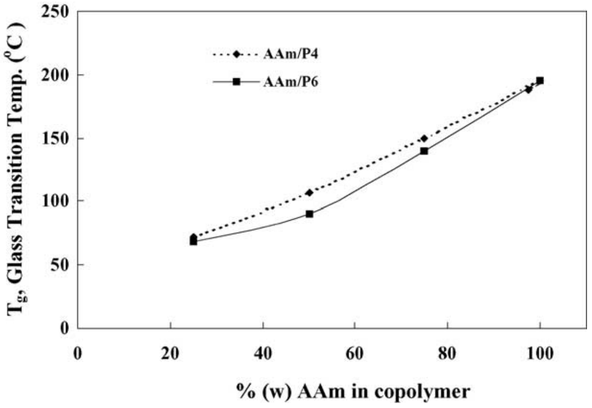

Fig. 1. The variation of T_g with the copolymer composition.

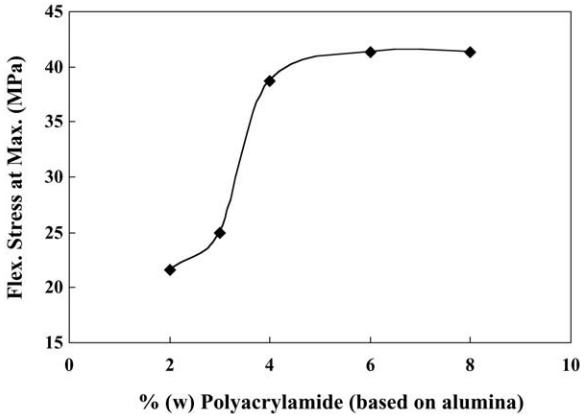

Fig. 2. The variation of flexural strength of green ceramics with polyacrylamide amount.

Table 1
Mechanical properties of gel-cast green samples

Sample	P4 in copolymer (wt.%)	P6 in copolymer (wt.%)	Flextural stress at Max. (MPa)	Elastic modulus (GPa)
P4-3.5	3.5		25.5 ± 2.60	0.905 ± 0.01
P4-10	10		22.7 ± 2.30	0.834 ± 0.08
P4-20	20		20.0 ± 2.00	0.667 ± 0.06
P4-35	35		19.1 ± 1.90	0.509 ± 0.05
P4-50	50		6.8 ± 0.60	
P4-75	75		4.4 ± 0.40	
P4-90	90		1.7 ± 0.10	
P4-100	100		0.5 ± 0.05	
P6-5		5	23.7 ± 2.40	0.806 ± 0.08
P6-10		10	22.7 ± 2.30	0.714 ± 0.07
P6-20		20	21.5 ± 2.10	0.611 ± 0.06
P6-35		35	14.6 ± 1.50	0.506 ± 0.05
P6-50		50	4.6 ± 0.40	
P6-75		75	3.3 ± 0.30	
P6-90		90	1.9 ± 0.16	
P6-100		100	1.4 ± 0.13	

range of 2–8% of alumina are given in Fig. 2. As the amount of AAm increases, the flexural strength values increase especially in the range of 3–4% of AAm ratios.

The effect of P4 or P6 addition into the copolymer structure is given in Table 1 and Fig. 3. As the weight ratio of P4 or P6 increases, from the value of 3.5 to 90% of copolymer, the flexural strength values decreases from 24–25 MPa to 1.5–2.0 MPa although the total polymer amount is equal to the 4% of alumina. The flexural strength values for samples P4-3.5 and P6-5 are interesting (see Table 1) while the amounts of P4 and P6 (1/200, in moles) in crosslinked copolymers and total amount of copolymer in ceramic suspensions were the same as in the case where AAm and MBAM were used. This indicates that the crosslinking density, in other words the distance between the crosslinking points, should almost be the same. The reason for the noticeable decrease in flexural strength values (from about 40 MPa to 25 MPa) should be arising not only from the flexible C–O–C bonds in the P4 and P6 but also from the prevention of hydrogen bonding between AAm units due to their high molecular weight, in another words, long chain structure (see Section 3.1).

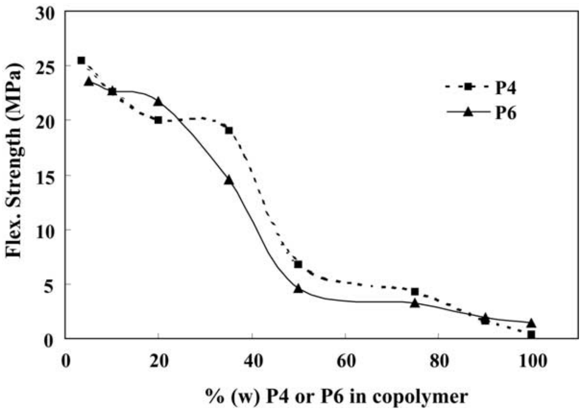

Fig. 3. The variation of flexural strength of green ceramics according to the change in copolymer composition.

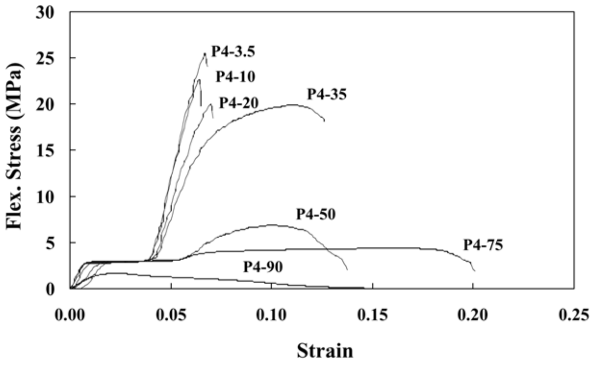

Fig. 4. Stress–strain curves of green samples with copolymer composition of AAm-P4.

It is seen from Fig. 4 and Table 1 that the flexural strength and modulus values of the samples are decreased as the ratio of P4 amount increases. Similar trend occurs for the samples with P6 (see Fig. 5 and Table 1). The modulus values for these samples vary almost linearly with the ratios of P4 or P6 while the flexural strength values show a decrease in notable amounts around 35–50% of used P4 or P6 amount in

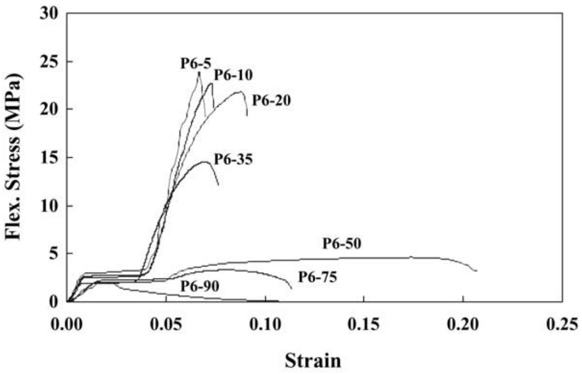

Fig. 5. Stress–strain curves of green samples with copolymer composition of AAm-P6.

copolymer (see Fig. 3). It should be noted here that the flexural strength and especially the elastic modulus values for the samples prepared by using P4 are higher than those of the samples prepared by using P6, as expected. The reason for this is the longer and more elastic chain structure of P6 than that of P4. The glass transition temperatures of copolymers prepared by using P4 are higher than those of prepared by using P6 with the same molar ratios. The mechanical test results of the cast green samples prepared using only P4 or P6 also show effect of monomer structure onto the mechanical properties. Flexural strength of the samples prepared using P4 or P6 in the weight ratio between 4% and 10% of alumina were only 0.5–1.5 MPa. The increase in weight ratio of P4 or P6 in the gel-cast samples has not affected their flexural strength, which shows that the dominant factor for their mechanical properties is the monomer structure rather than its amount under the current experimental conditions. As a result of these, it can be said that difference in the copolymer and/or polymer properties reflect upon the mechanical properties of cast ceramic green structures.

3.3. *Machinability properties*

The machinability studies were carried out on the cast green samples prepared by using P4 or P6 together with AAm, where their weight ratios are lower than 50% in the copolymer, because of their high mechanical strength. The machinability studies of the cast samples were performed using conventional tools and equipments. No fractures and cracks were developed during the fixing of the samples for the test machines. The samples prepared by using only AAm being crosslinked with MBAM showed fractures or cracks. Sharp edges can easily be obtained by lathing and milling, especially from the samples containing 10–35% of P4 or P6 in the copolymer. No cracks were observed after drilling and grounding. Machined samples exhibited good surface finish in all cases, showing their chip resistance. These results show the contribution of the addition of P4 or P6 in the copolymer structure, which lowers the brittleness of cast green ceramic samples having high enough flexural strength. The representative photographs of some machined green samples prepared using P4 or P6 are shown in Fig. 6. Screws, rings and recessed steps were prepared by lathing, internal screws by tap, and slots by milling.

3.4. *Thermal removal of organic additives*

The weight loss for the green ceramic samples prepared using P4 starts at below 200 °C as the P4 used is in higher amounts. As the amount of P4 decreases, the starting point of weight loss, for the ceramic green samples, increased up to about 240 °C (see Fig. 7). The completion point for the weight loss of ceramic green samples increased with the decrease in the amount of P4 ratio. The degradation point for the samples prepared by using P4 shows a notable decrease, in another words, the binder (copolymer) can be removed more easily

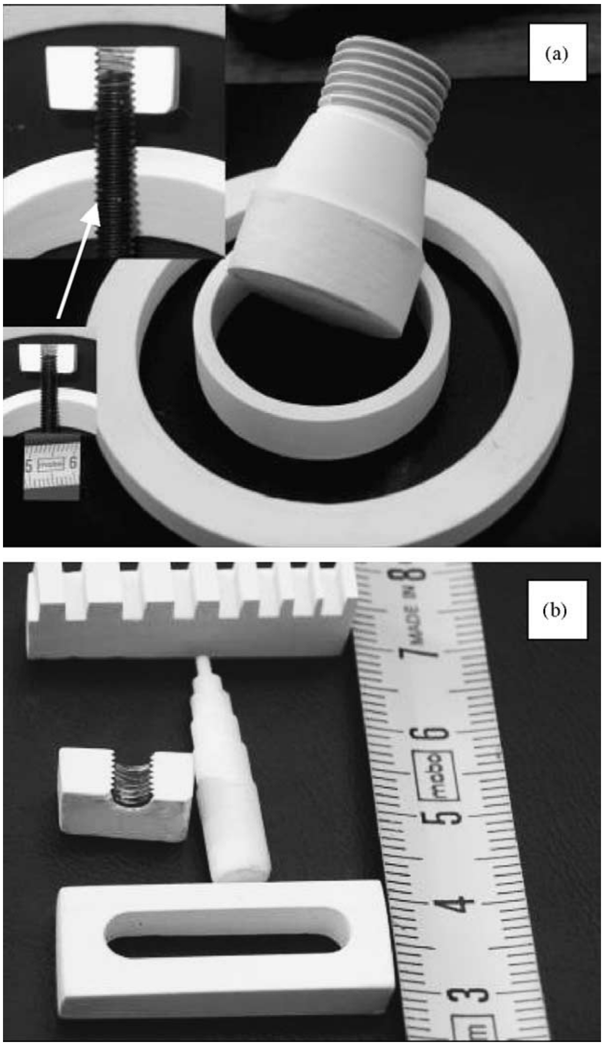

Fig. 6. Photographs of machined green samples prepared by using P4 or P6: (a) internal screw, screw and rings and (b) Slots, recessed steps and internal screw.

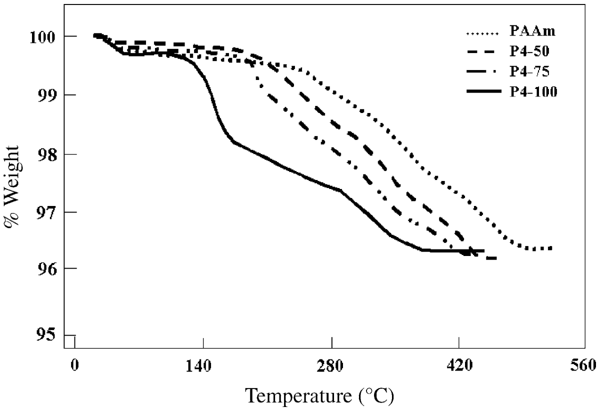

Fig. 7. TG curves of green samples with copolymer composition of AAm-P4.

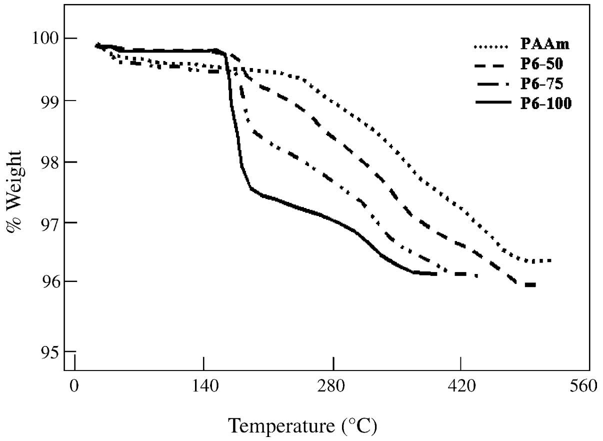

Fig. 8. TG curves of green samples with copolymer composition of AAm-P6.

from the cast ceramic samples. Similar trend is observed for the samples prepared by using P6; the starting and end points of degradation decrease as the P6 used increases (see Fig. 8).

4. Conclusions

The copolymers having various glass transition temperatures were prepared by the polymerization of AAm and P4 or P6. The cast green ceramic compacts obtained using these monomer mixtures with the various weight ratios in the copolymer show flextural strength high enough for handling and machining. Flextural strength decreased with the increasing of P4 or P6 in the copolymer compositions, but brittleness of the samples also decreased, which resulted in good machinability properties. Elastic modulus of green ceramic samples also decreased with the increasing of P4 or P6 weight ratios almost linearly as similar as T_g value of copolymers, which shows the contribution of the copolymer structure to the mechanical properties of cast green ceramic samples. Introducing the P4 or P6 comonomer in the structure of copolymer also made the burn out of binder polymer easier.

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