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Thermal and morphological studies of binary and ternary composites of poly(vinylalcohol) with alumina and zirconia

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Abstract

Composites of PVA with alumina (PVA–Al_2O_3), zirconia (PVA–ZrO_2), and both alumina–zirconia (PVA–Al_2O_3–ZrO_2) were prepared by ball milling the dispersed solid powder of Al_2O_3, ZrO_2 and Al_2O_3–ZrO_2 in a PVA matrix at room temperature. The composites were cast into films. The films were later decomposed and the residual ceramics were sintered at 1400°C. The surfaces of the composites have been examined using scanning electron microscopy at various stages. The nature of decomposition of PVA as influenced by ceramic particle surfaces has also been studied. There is clear evidence that controllable morphologies and microscopic porosities can be achieved in these composites. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: D. Al_2O_3; D. ZrO_2; Thermal and morphological studies; PVA composites

1. Introduction

Polymers like polypropyleneoxide (PPO) provide a convenient route to prepare composites in which salts are dispersed to a high degree of uniformity and fineness. Polymer salt composites of this kind consisting of fast ion conductors have now been widely investigated. The most attractive of them are the salt rich (polymer in salt) composites, first reported by Angell et al. [1]. Similar polymer in ceramic composites can be employed for preparing ceramic tapes and subsequently complex ceramic shapes because when the polymer is burnt out under suitable conditions pure ceramic objects are realised. Polymer thus play an important role in ceramic processing [2–4]. Tape casting processes involving polymers have been discussed widely in the literature. Anderson et al. [5] have discussed formulations for the tape casting process and production of alumina substrates from powders. The function of polymer in the tape casting of alumina has also been discussed by Meyer et al. [6]. These methods can eventually be of great use in ceramic welding also. Many methods have been employed to sinter the alumina ceramic viz. plasma activated sintering [7], microwave sintering [8,9] apart from conventional furnace sintering where powders compressed into pellets are heated to high temperatures.

PVA is a water soluble polymer which can be blended with ceramics into thin and uniform slurries which can be cast into tapes and water can be removed easily by vacuum evaporation. This provides a new route for the preparation of polymer bonded tapes of single and multiple ceramics of desired compositions in order to obtain ceramic composites of desired properties.

In this communication we describe the preparation of PVA–Al_2O_3, PVA-ZrO_2 and PVA-Al_2O_3-ZrO_2 composites in the form of tapes which are later subjected to heat treatment in order to decompose the polymer and obtain ceramics in film form. We have examined the microscopic structures of the composites both before the decomposition of PVA and after sintering of the ceramic at 1400°C. These preliminary studies indicate that it should be possible to further optimise this technique to obtain ceramic composite in desired shapes. We have also examined the thermal decomposition behaviour of PVA in the presence of dispersed ceramic and compared it with the decomposition characteristics of pure PVA itself, which has been reported earlier from this laboratory [10].

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2. Experimental

The required PVA was obtained from SDFine Chemicals India. The molecular weight was reconfirmed using the intrinsic viscosity method [11] and found to have a value of 137770. The commercial grade Al_2O_3 and ZrO_2 powder of purity 99.99% was obtained from Lobo Chemie India. The average particle size as determined by TEM was 1–2 μm. One gram of PVA was dissolved in 30 ml of mixture (1:1) of distilled water:*n* propanol. Weighted quantities of Al_2O_3 and ZrO_2 were added and the mixture was ball milled for about 4 h in a zirconia container using zirconia balls. The resulting slurry was quite uniform and we observed that ceramic particles exhibited no tendency for sedimentation. The initial concentration of PVA and the oxides were optimised such that a sedimentation free suspension was obtained. The optimised concentrations are given in Table 1. Since the mixtures were milled for a sufficiently long time the initial particle size distribution was of no consequence. The slurries were cast on teflon substrates and were dried in a vacuum oven set at 65°C. It required about 12 h to get rid of all the water from the films and to be able to easily lift them from the Teflon substrate. Complete absence of water in the dried films was confirmed using IR spectroscopy (absence of $\approx 1650\text{cm}^{-1}$ peak). The films were quite flexible and could be handled very easily.

The decompositional characteristics of the films were studied using thermogravimetric analysis (TGA). Small pieces of the films were cut and loaded into a TGA pan on a Stanton Redcroft, STA1500 instrument at a programmed heating rate of 5°C/min in nitrogen atmosphere. The films were heated to 800°C and in most cases there was no variation in the weight beyond 500°C.

The films themselves were placed on a high density alumina plate and kept inside a programmable thermolyne furnace (model No.46100). The films were heated initially slowly 2°C/min upto 600°C and soaking it for 2 h at this temperature and heating was continued at an increased rate of 3°C/min and taken to 1400°C and soaked at 1400°C for 1 h. The power was switched off and the ceramic films were furnace cooled. The effect of longer soaking times on the final microstructure has not been studied in this study.

The structures of the films were examined at two stages using SEM, first the upper (free surface) and the lower (Teflon substrate side surface) surfaces of the dried films were examined. Next, the surfaces of 1400°C sintered films were examined. In the case of ternary films of PVA–Al_2O_3–ZrO_2 which was decomposed to obtain binary Al_2O_3-ZrO_2 ceramics, EDAX analysis was used to ascertain the uniformity of the compositions. We report here behaviour of five compositions each of the three systems (see Table 1 for compositions).

X-ray diffraction (XRD) pattern were recorded for the powdered samples of the sintered films on a scintag Inc. (USA) XDS 2000 XRD machine in the range between $2\theta = 5°–70°$. The final density was measured for sintered samples by the Archimedes method. The theoretical densities of the composites were calculated using the equation [12].

$$\rho = \frac{100}{\left(\frac{x}{3.965}\right) + \left(\frac{y}{5.89}\right)} \tag{1}$$

x and y are the mole fractions (in percent) of Al_2O_3 and ZrO_2 respectively. The theoretical densities of Al_2O_3 and ZrO_2 used are 3.965 and 5.89 g/cc respectively.

3. Results and discussion

3.1. Thermal analysis

The TGA plots of the three different sets of composites with PVA are shown in Fig. 1. In Fig. 1a decomposition behaviour of pure PVA is shown. Pure PVA is somewhat hygroscopic and is always associated with adsorbed water which is removed when heated upto 100°C. The first step like decrease in weight in the case of pure PVA is associated with this stage. The next major stage of decomposition involves degradation and burning of the polymer. The third, somewhat smaller step like loss in weight is due to the decomposition of the acetate portion in PVA. We may note here that the present PVA is obtained by the hydrolysis of polyvinyl acetate and about 20% of acetate groups in PVA remain unhydrolysed. We have earlier reported and

Table 1
The various composites compositions

Sample code	Mol%	Wt%
	PVA:Al_2O_3	PVA:Al_2O_3
PA1	0.01:99.99	11:89
PA2	0.02:99.98	20:80
PA3	0.03:99.97	27:73
PA4	0.04:99.96	33:67
PA5	0.05:99.95	38:62
	PVA:ZrO_2	PVA:ZrO_2
PZ1	0.09:99.99	9:91
PZ2	0.02:99.98	17:83
PZ3	0.03:99.87	23:77
PZ4	0.04:99.96	29:71
PZ5	0.05:99.95	34:66
	Al_2O_3:ZrO_2	Al_2O_3:ZrO_2
AZ1	7:93	6:94
AZ2	18:82	15:85
AZ3	41:59	37:63
AZ4	63:37	59:41
AZ5	74:26	70:30

analysed these features along with residual weight obtained during the decomposition of PVA. We note from Fig. 1a that in composites there is a virtual absence of any adsorbed water in these films which is consistent with the spectroscopic evidence mentioned earlier. The first decomposition occurs in the same temperature region as observed in pure PVA although the decomposition appears to be initiated at slightly higher temperatures. In the case of ternary composites the variation in the proportion of the polymer is very small (in terms of mol%, the proportion was actually held constant) and only the molar ratio of Al_2O_3 to ZrO_2 was varied. We, therefore, notice in Fig. 1c. that the TGA curves are very close to each other. The fact that the decomposition is initiated at slightly higher temperature than in pure PVA is suggestive of the presence of chemical interaction between PVA and the oxides; oxide ions on the surfaces of the ceramic particles and the hydrogen atoms of the polymers. Such interactions have been noted by us in a aluminiumisopropoxide doped in PVA [13]. There is no adsorbed water in these films because the hydrogen bonding tendencies of polymer is now satisfied by the oxide ion of the ceramic.

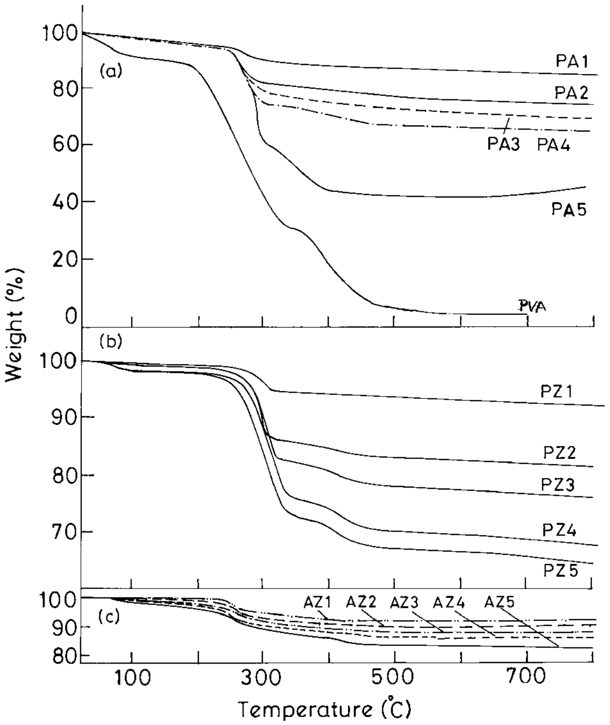

Fig. 1. Thermogravimetric curves of various composites (sample codes are given in Table 1).

The decomposition kinetics in these films has been examined by making use of the kinetic expression suggested by Freemann and Carroll [14]. It is assumed in such kinetics that the solid decomposes to give another solid and the rate U is related to an instantaneous weight fraction of the material w by the expression

$$U = -dw/dT = A\exp\left(-\frac{E}{RT}\right)\frac{w^n}{U_h} \tag{2}$$

Where, U is the rate of reaction, U_h is the heating rate = 5°C/min, A = frequency factor in min^{-1}, E is the

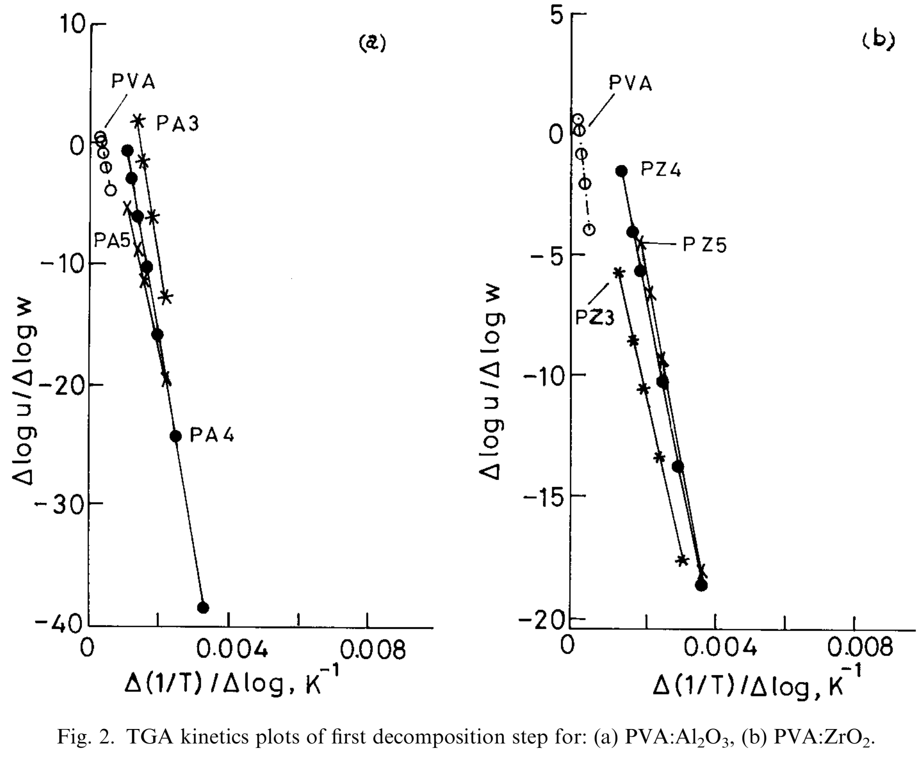

Fig. 2. TGA kinetics plots of first decomposition step for: (a) PVA:Al_2O_3, (b) PVA:ZrO_2.

activation energy in cal/gm mol, T is the temperature in Kelvin, R is the gas constant = 1.987 cal/degmol, n is the order of reaction, w is the weight fraction of material undergoing degradation at time t and is taken as the ratio of the weight of the material present at time t to the weight of the sample taken($t = 0$).

TGA data has been plotted as $\Delta \log U / \Delta \log w$ versus $\Delta (1/T) / \Delta \log w$ in Fig. 2a for PVA–Al_2O_3 and in Fig. 2b for PVA–ZrO_2 composites. This calculation were performed for those compositions in which the percentage of polymer was sufficiently high and a typical two stage character of the decomposition was evident in Fig. 1. The activation barriers for the first stage are listed in Table 2 for these cases. The insufficiency of the total variation in weight makes evaluation of kinetic parameters for several of the compositions inaccurate and unreliable and therefore are not reported. It may be noted that the activation barrier of the first decomposition is lower in these cases than in pure PVA (which is typically of the order of 37 kcal/mol for the first stage) suggesting that the decomposition of the polymer on the surface of the ceramic particle is catalysed in some complex manner.

Table 2
Activation energies of PVA in composites

Composite compositions	No. of decomposition steps	E_a (kcal/mol)	Temperature range (°C)
PA3	1	25.69	266–282
PA4	1	33.18	247–305
PA4	1	36.00	248–312
PZ3	2	29.96	261–318
PZ4	2	35.38	261–310
PZ5	2	36.13	257–330
PVA	2	37.00	249–333

3.2. Morphological studies

The SEM micrographs of top and bottom surfaces of the films for the two types of polymer ceramic composites are shown in Fig. 3. We notice that there are differences between the lower and upper surfaces of the completely dried films in which ceramic particles are held by PVA. The polymer and ceramic particles are well differentiated in the micrographs with polymer appearing as smooth shinning featureless surface. During the evaporation of the solvents an induced sedimentation

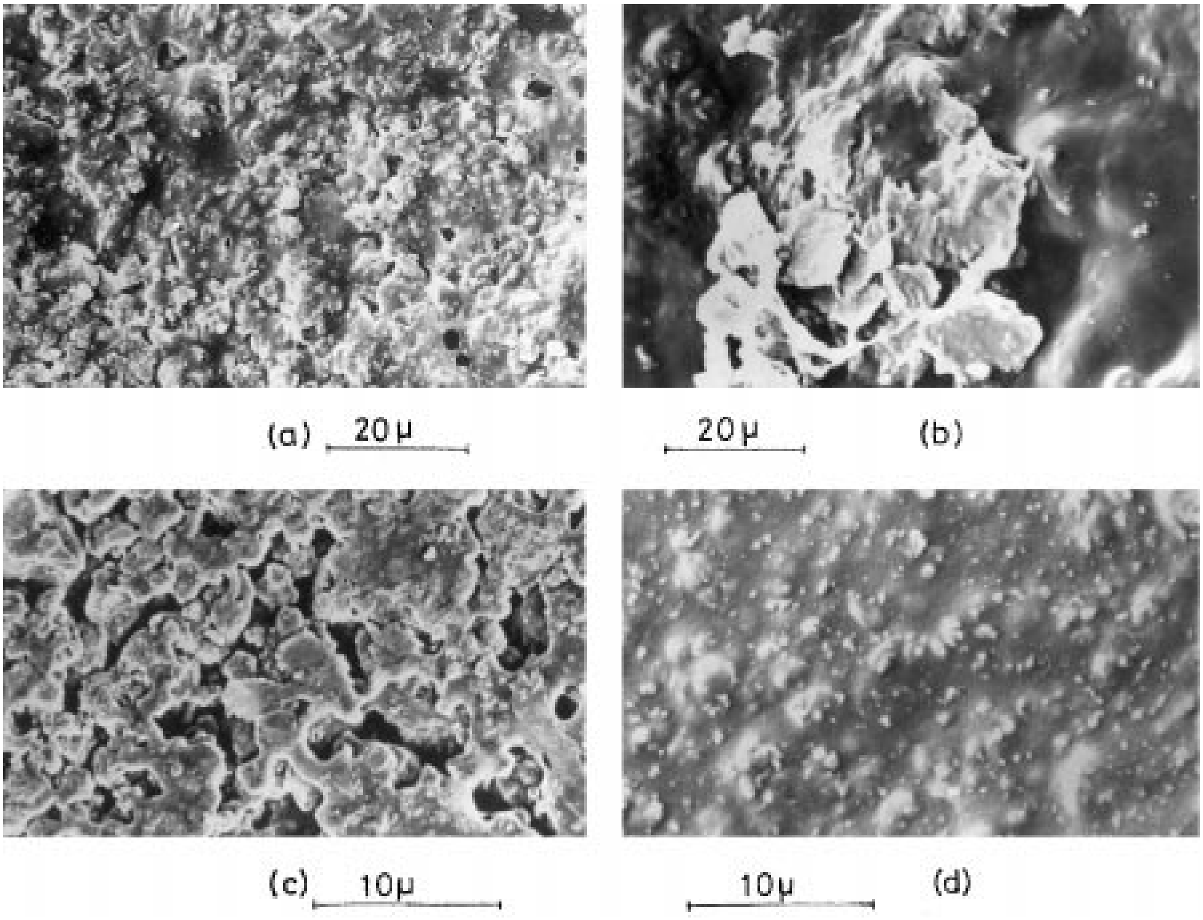

Fig. 3. SEM micrographs of lower surfaces for: (a) PA5, (c) PZ4 and upper surfaces for: (b) PA5, (d) PZ4 composites.

seems to have occured and the ceramic particles are settled densely at the bottom of the film. This is manifest more clearly in ZrO_2–PVA films as ZrO_2 particles are denser than Al_2O_3 particles. Since the films are cast on smooth teflon surfaces, the bottom surfaces of the films appear quite smooth compared to top surfaces. The top surfaces are rough due to the projections of the individual particles. The ternary Al_2O_3–ZrO_2 with PVA films also exhibit similar characteristics but there is evidence of further differentiation of Al_2O_3 and ZrO_2 particles due to density differences. Typical surfaces of ternary composites of low moderate and high Al_2O_3 compositions are shown in Figs. 4(a and b), 5(a and b) respectively. The composition determined by EDAX are given alongside the micrographs. The nominal compositions with which the slurries were made, were, slightly different and we feel that in small batch preparations involving ball milling and several transfers it is preferable to rely upon the EDAX determined values of film compositions. The SEM also confirmed that the ceramic particles were well mixed and evenly distributed.

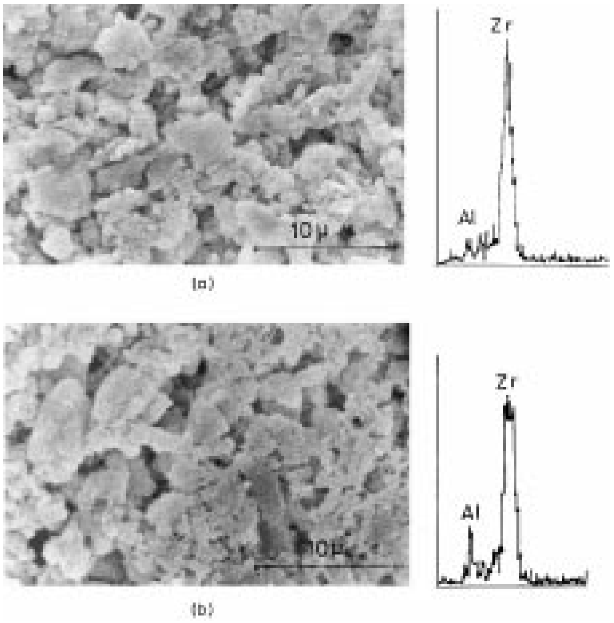

Fig. 4. Unsintered SEM micrographs of (a) AZ1, (b) AZ2 (along with their EDAX).

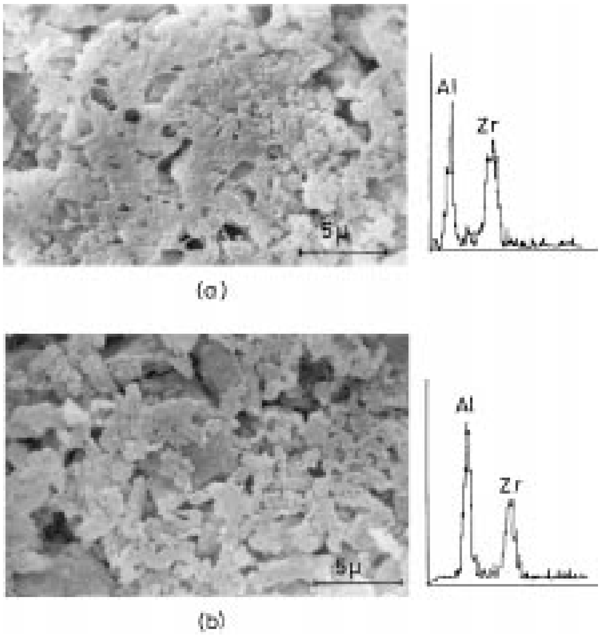

Fig. 5. Unsintered SEM micrographs of (a) AZ4, (b) AZ5 (along with their EDAX).

Fig. 6 gives the SEM of the sintered alumina. The micrographs reveal that the sintered products can have remarkably different microstructures depending upon the quantity of PVA present initially in the film. When a high proportion of PVA is present it leads to a sintered product which is flaky in appearence with significant porosity. A low proportion of PVA gives rise to a dense

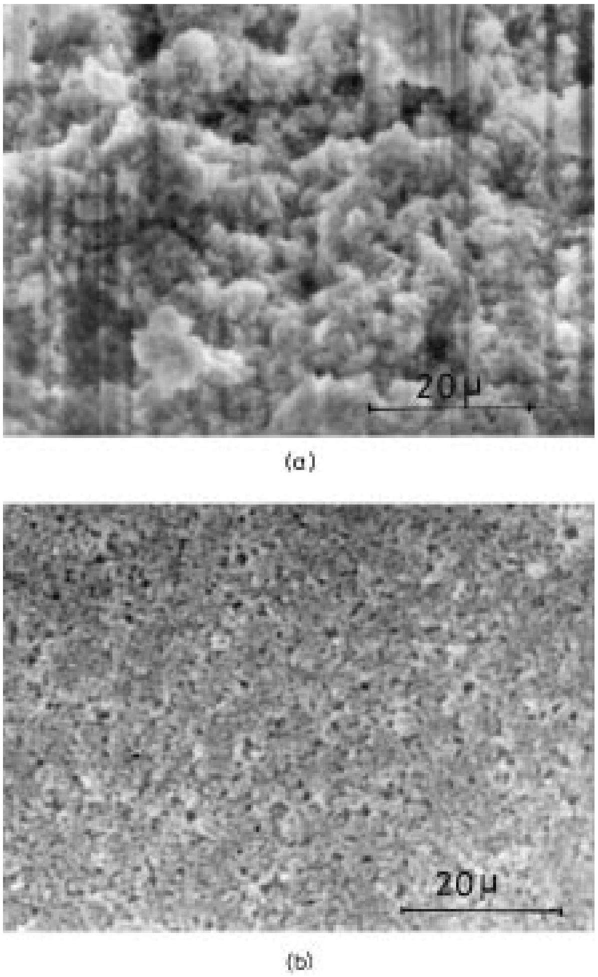

Fig. 6. Sintered (fired at 1400°C 6 h) SEM micrographs of (a) PA5, (b) PA1.

Al_2O_3 product with a small proportion of included voids. A similar observation can be made with regard to ZrO_2-PVA composites. The microstructures of sintered ZrO_2 films are shown in Fig. 7 for four of the initial film compositions. Here again a large fraction of PVA in the film leads to significantly higher porosity and higher grain sizes. The grains are, however, irregularly shaped but appear to be continously connected in the structure. In compositions with lower PVA content there is very little included porosity and a dense structure of an essentially void free sintered product is obtained. Grain sizes are also small when PVA content is low. Microscopic cracks observed in one of the samples has perhaps occurred during handling of the thin wafer like sintered products. It is not clear if the tetragonal to monoclinic phase transition in zirconia [15] has introduced the cracks during cooling. No such crack patterns are seen in other micrographs.

These sintered products were very thin and of the order of 0.2 mm in thickness. Their mechanical properties have not yet been measured. Both alumina and zirconia in the sintered products were monophasic α-Al_2O_3 and m-ZrO_2 structures. The shrinkage, weight loss and density characteristics of the films subjected to sintering are summarised in Table 3. The weight losses suggest that the PVA polymer residues are completely burnt out when heated to 1400°C. The shrinkages are somewhat lower for the films made with larger proportions of the polymer. It appears that the extent of sintering is controlled by the number and areas of interparticle contacts which in turn determines the porosity of the resulting products.

The micrographs of sintered composites containing both Al_2O_3 and ZrO_2 in various proportions are shown in Figs. 8 and 9. These compositions are the same for which, micrographs in Figs. 4 and 5 were presented in their unsintered stage. The sintered products have very remarkable structures. In all of them except the one with the highest AZ5 Al_2O_3 content (Fig. 10) a three dimensionally connected matrix of particles and pores are seen. The surfaces of particles have got smoothed during sintering. The pores seem to make connected microscopic channels of irregular geometry.

However, when alumina content is higher the connecting elements of such a net work appear thinner and the openings smaller. In the case of AZ5 (Fig. 10) the sintered product appears to be made up of a wide distribution of flaky particulates with evidence of partial connectivity

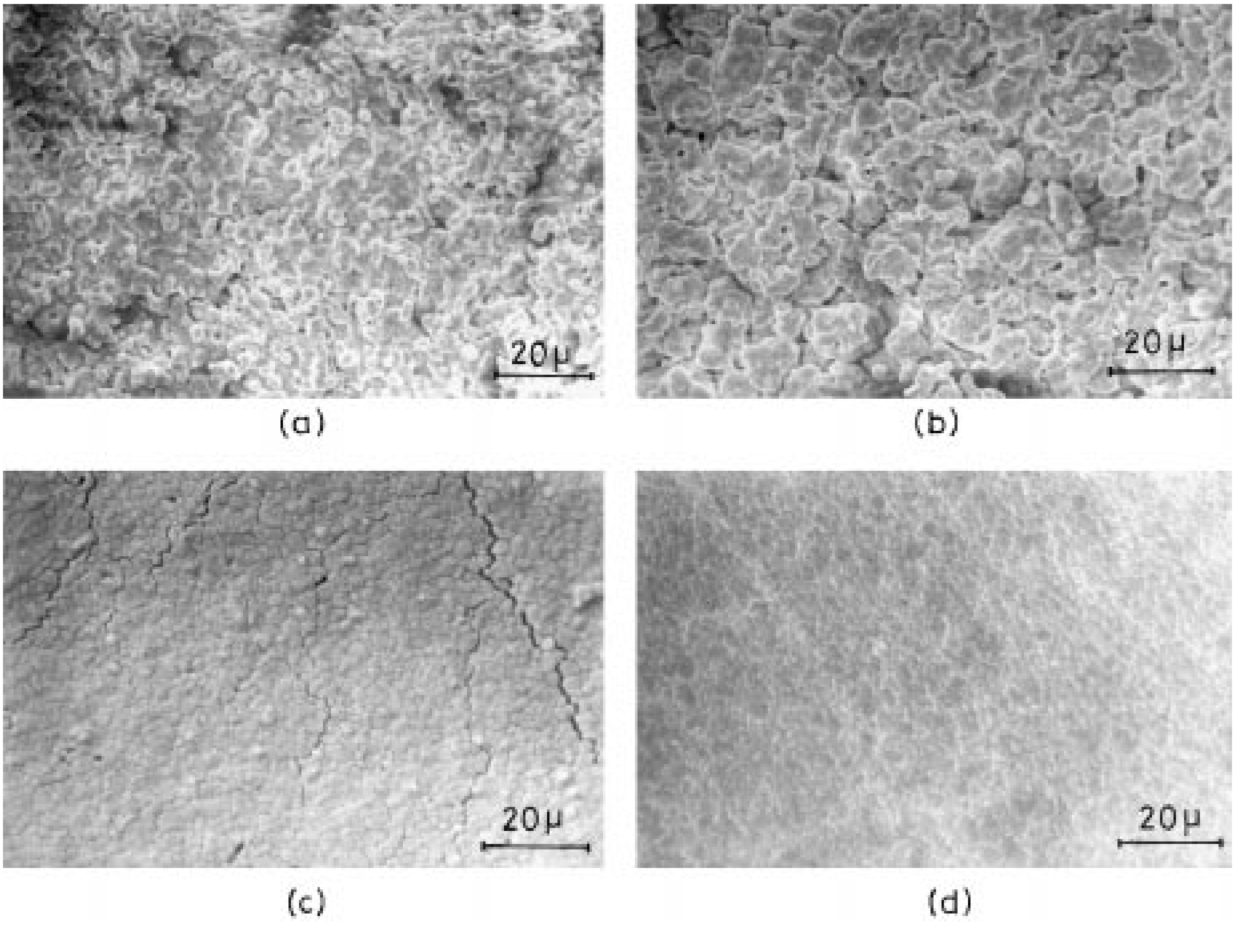

Fig. 7. Sintered (fired at 1400°C for 6 h) SEM micrographs of (a) PZ4, (b) PZ3, (c) PZ2, (d) PZ1.

Table 3
The shrinkage, weight loss and density characteristics of the films

Sample code	Green thickness (mm)	Decrease in thickness %	Loss of weight %	Densification
PA1	0.1651	15.4	21.0	98.75
PA2	0.1397	16.4	27.0	97.90
PA3	0.2159	13.6	38.0	97.64
PA4	0.2057	25.0	37.0	97.04
PA5	0.1702	31.4	42.0	80.80
PZ1	0.0659	20.9	20.0	97.98
PZ2	0.0762	18.0	22.0	97.64
PZ3	0.0813	17.0	28.0	97.09
PZ4	0.1397	16.0	30.0	93.38
PZ5	0.0736	29.0	34.0	86.82
AZ1	0.0787	3.2	14.0	76.70
AZ2	0.2209	2.0	7.0	76.90
AZ3	0.2768	9.1	8.0	81.35
AZ4	0.2286	6.1	23.0	88.64
AZ5	0.3683	4.0	29.0	92.82

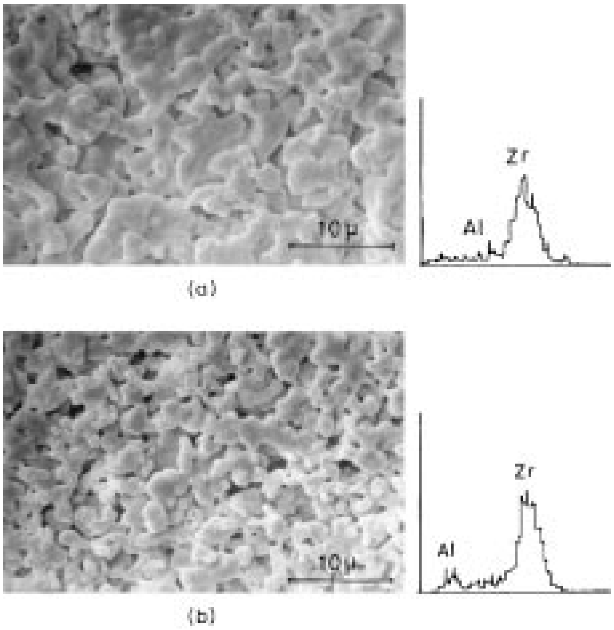

Fig. 8. Sintered (fired at 1400°C for 4 h) SEM micrographs of (a) AZ1, (b) AZ2.

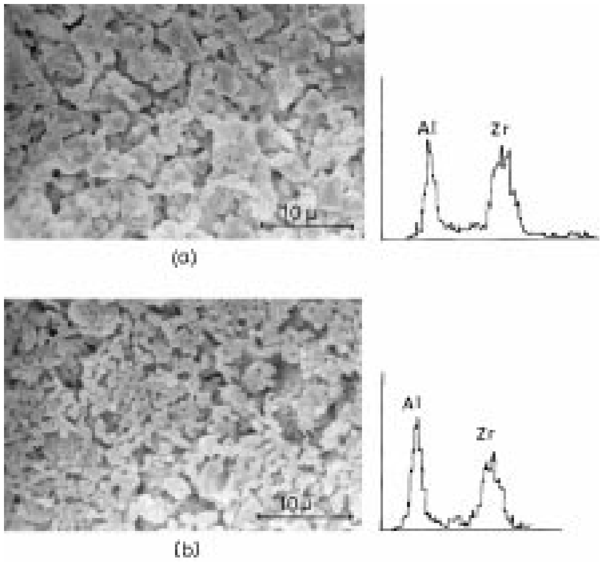

Fig. 9. Sintered (fired at 1400°C for 4 h) SEM micrographs of (a) AZ3, (b) AZ4.

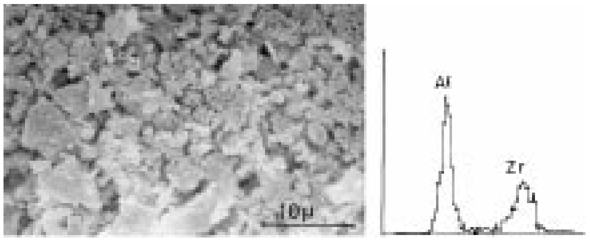

Fig. 10. Sintered (fired at 1400°C for 4 h) SEM micrographs of AZ5.

of pores. X-ray diffraction patterns of two sintered products consisting of Al_2O_3 and ZrO_2 are shown in Fig. 11. They are respectively in α- Al_2O_3 and m-ZrO_2 structures in the composites which is as expected. From Table 3 the final density seems to be significantly lower than in the sintered single components namely Al_2O_3 or ZrO_2. Since Al_2O_3 and ZrO_2 do not form any known compounds and their mutual solubilities are also not significant. There is restrictive sintering and grain growth (since Al_2O_3 particles are well separated from ZrO_2 particles when ZrO_2 percentage is higher and ZrO_2 particles themselves do not sinter as well as Al_2O_3 particles at this temperature). The phase diagram for Al_2O_3-ZrO_2 system [16] support this finding. Since the ceramic particles sinter to a very limited extent at the contacts the pores left behind after burning out the PVA, remain essentially intact. Such connected and channel like porosity may be of use in applications like catalyst supports and filters.

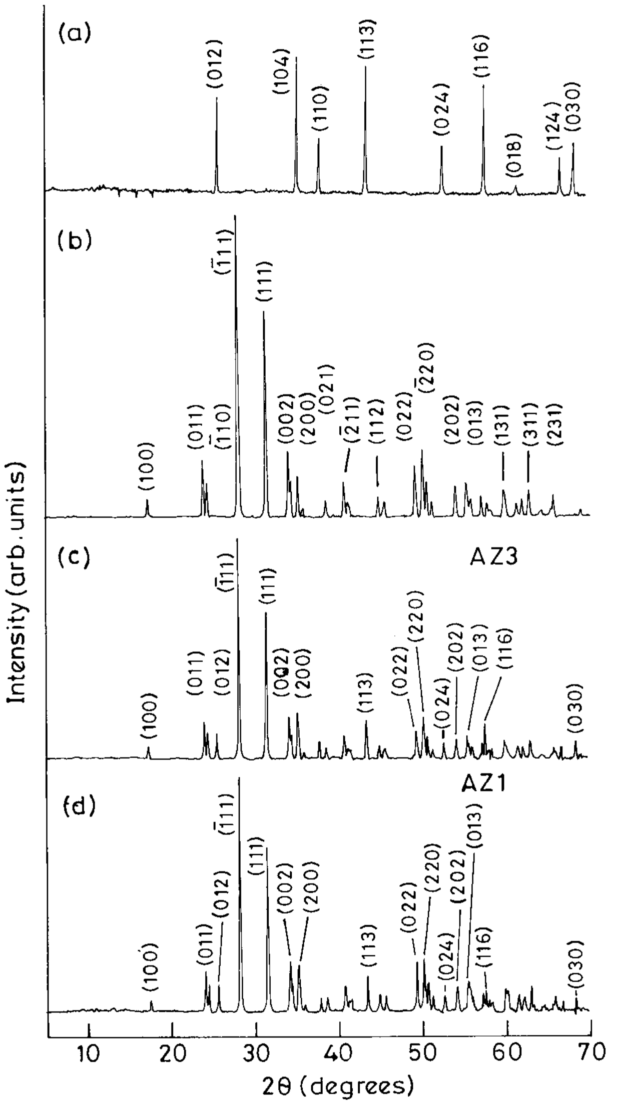

Fig. 11. X-ray diffraction pattern of powdered composites (a) alumina, (b) zirconia, (c) AZ3, (d) AZ1.

4. Conclusions

Ceramic rich PVA-ceramic composites can be made into films. Polymer can decompose and the ceramic oxide sinter into thin wafers whose microstructure and porosity appear to be controllable by initial composition. This method can enable preparation of ceramic composites of potential applications as catalyst supports and filters.

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