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Joining Ceramics before Firing by Solvent Welding

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Abstract

A procedure is described which allows ceramic bodies to be joined before firing in order to achieve a high level of complexity of form incorporating, for example, re-entrant chambers. Suspensions of fine ceramic powder in an organic vehicle which can be shaped initially by extrusion, injection moulding or other plastic forming operations were subsequently joined by solvent welding. The organic vehicle was removed by pyrolysis and the arrangement of particles at the interface was explored by scanning electron microscopy after partial and nearly complete sintering.

Es wird ein Verfahren beschrieben, das es ermöglicht, keramische Teile vor dem Brennen zu fügen, um Körper mit komplexer Form wie z.B. Bauteile mit hinterschnittenen Hohlräumen herzustellen. Formteile aus mit organischen Bindemitteln versetzten keramischen Pulvern, die durch Strangpressen, Spritzgießen oder andere plastische Formgebungsverfahren gefertigt werden können, wurden durch ein entsprechendes Lösungsmittel zusammengefügt. Das Bindemittel wurde durch Pyrolyse entfernt und das Gefüge an der Nahtstelle wurde mittels Rasterelektronenmikroskopie nach teilweisem und nach vollständigem Sintern untersucht.

On décrit ici une méthode permettant de joindre des pièces céramiques avant leur chauffage, dans le but d'élaborer des matériaux ayant des géométries complexes. Des suspensions de poudres céramiques fines en milieu organique qui pouvaient être initialement mises en forme par extrusion, moulage par injection ou autres techniques de formage plastique étaient ultérieurement jointes par soudure par solvant. Le milieu organique était éliminé par pyrolyse et l'arrangement des particules à l'interface était étudié par microscopie à balayage après frittage partiel ou presque total.

1 Introduction

Procedures for the arrangement of fine ceramic particles into complex shapes prior to firing must be perfected if full benefit is to be obtained from the high-temperature, mechanical, tribological, electrical and magnetic properties of ceramic materials. Previous work in this laboratory has explored the systematic application of techniques drawn from the polymer processing industries to ceramic suspensions. Thus injection moulding,[1,2] post-extrusion forming,[3] vacuum forming[4] and blow moulding[5] of ceramics have been made possible by understanding the rheological, thermomechanical and pyrolytic properties of ceramic suspensions conferred by organic polymer and wax blends. It is a creative challenge to the ceramist to explore the full potential of the transfer of technologies from plastics processing to ceramics fabrication.

The problems associated with the manufacture of large sections such as the hub of a ceramic rotor[6,7] have been successfully side-stepped by joining a hollow injection-moulded rotor to an isostatically pressed hub by warm pressing before removing the organic binders and sintering.[8] No details of the organic materials or experimental procedures were given but the joints were claimed to have comparable strength to the bulk of the fired body. Similarly, it has for millenia been the practice to join water-based clay ceramic bodies before firing with a low viscosity suspension. It is therefore pertinent and timely to explore the techniques whereby modern ceramic powders, in wax or polymer suspensions,

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may be joined prior to firing in order to achieve a higher level of complexity of form than that offered by existing operations.

A wide range of welding methods for polymeric materials is available[9] and they have in common the introduction of temporary molecular segment mobility in the interfacial region in order that diffusion of polymer end groups across the interface, under the influence of Brownian motion, can occur.[10,11] Joint strength can then be related to the number and depth of diffusing species.

The initiation of molecular mobility is achieved by two distinct techniques: (i) the application of heat to the interfaces by conduction, ultrasonic absorption, radio frequency absorption or friction,[9] or (ii) the transient application at room temperature of a solvent with sufficiently strong interaction with the polymer to form a local concentrated polymer solution near the interface. The solvent must then diffuse away from the joint region in order to raise the glass transition temperature above the joint operating temperature and hence increase strength and modulus.

The present work attempts to apply the latter technique to suspensions of a fine alumina powder in an amorphous polymer at loadings of 54 and 60 vol.% alumina. The objective of polymer welding operations is to achieve intimate molecular contact at the interface and it can be hypothesised that if the organic vehicle conveys well-dispersed powder, intimate molecular contact of the organic vehicle will be accompanied by close particle positioning across the interface. Inherent in the solvent welding operation is the transient dilution of the suspensions and hence the possible reduction in ceramic volume loading in the interfacial region. It is therefore of great importance to observe how the suspension reasserts its true specific volume as solvent diffuses out of the system. If a lower prefired density of ceramic at the interface results from solvent welding then a series of differential sintering defects are possible. The importance of differential sintering is now well recognised and continues to be investigated.[12-14] Rather than explore the strength of such joints, which reveals only a critical defect size, it is prudent to explore the microstructure of interfaces in the partially and fully sintered states in order to observe the arrangement of particles and to deduce the cause of defects which appear in the joined sintered body.

2 Experimental Details

2.1 Materials and mixing procedures

Details of the materials are given in Table 1. The compositions of the mixtures are given in Table 2 and are based on the mean of four ashing experiments after mixing with the exception of the adhesive paste which was not ashed. The volume fraction of ceramic was calculated from the densities in Table 1.

Composition 2 was prepared by mixing on a twin-roll mill (Joseph Robinson & Co. Ltd, Manchester, UK), fitted with oil heating, at 190°C. The hide was folded four times to effect lateral mixing and the total mixing time was 15 min.

In composition 1, alumina powder, polystyrene, stearic acid and plasticiser were mixed in a Henschel FM 101L high-speed mixer at 3000 rpm for 2 min. The mixture was then compounded in a co-rotating Betol TS-40 twin-screw extruder, the operation of which has been described previously.[15] A screw speed of 60 rpm was used throughout and the temperatures were 140–160–180–190–210°C feed to die. On leaving the extruder, the mixture was cooled in a water bath and subsequently dried in a vacuum furnace at 70°C for 24 h. Four samples of each mixture were ashed to 600°C to obtain the exact weight fraction of ceramic. A Perkin-Elmer DSC-2 was used to determine the glass transition temperature of composition 1 and a Perkin-Elmer TMS-1 thermomechanical analyser was used to record the softening point of composition 2.

2.2 Sample preparation

Discs of compounded material were compression moulded in an Apex M114 press at 12 MPa. Approximately 2·8 g of the powdered extrudate was

Table 1. Details of materials

Material	*Grade*	*Manufacturer*	*Density* (kg/m^3)
Alumina	RA6	Alcan Chemicals Ltd	3 987
Polystyrene	HF555	BP Chemicals Ltd	1 060
Ditridecyl phthalate	Hexaplas DTDP	ICI Chemicals and Polymers Ltd	950
Trimellitate ester	Hexaplas OTM	ICI Chemicals and Polymers Ltd	989
Stearic acid	GPR	BDH Chemicals Ltd	941
Cyclohexanone	GPR	BDH Chemicals Ltd	998
Ethyl acetate	GPR	BDH Chemicals Ltd	902

Table 2. Compositions of ceramic suspensions

Constituent	*Composition 1 (wt%)*	*Composition 2 (wt%)*	*Solvent based 'adhesive' paste*
Alumina	85·71	81·96	48·21
Polystyrene	10·00	12·63	7·43
DTDP	2·86	—	—
OTM	—	3·61	2·12
Stearic acid	1·43	1·80	1·06
Cyclohexanone	—	—	41·18
Alumina, vol.%	60·6	54·0	19·0

weighed and introduced into a preheated 25-mm diameter die giving discs measuring approximately 2 mm in thickness.

2.3 Solvent welding operations

The surface of discs to be joined was either as-pressed or abraded on 600 grade SiC paper. The pairs of discs were weighed before and after applying solvent using a four-place R300S Sartorius balance. Six drops of solvent were applied to the face of one disc and the discs were then pressed together under various pressures at room temperature. The samples were allowed to dry at ambient temperature to constant weight. In some experiments the discs were preheated to 64°C before joining.

A 10:7 (w/w) solution of composition 2 in cyclohexanone was prepared and discs of composition 2 were joined in a similar way with the pure solvent replaced with the solvent-based 'adhesive paste'. The composition of this suspension is given in Table 2.

2.4 Scanning electron microscopy

In order to view the arrangement of particles at the interface the organic vehicle was removed by heating in nitrogen at 60°C/h to 60°C and thereafter at 2°C/h to 450°C followed by cooling to room temperature at 75°C/h. Partial sintering was carried out in air at 1250°C for 40 min. When cold, the porous samples were mounted in resin (Araldite MY753 resin and Araldite HY951 hardener mixed 10:1 parts by weight). These were cured at room temperature for 12 h and post-cured at 80°C for 2 h before polishing to 1 μm on a diamond lap. Samples were then cut from the mounts and heated at 1°C/min to 600°C in flowing air to remove the resin. The polished sections were sputter-coated with gold and viewed in a Cambridge Stereoscan S250. Samples were also viewed before and after joining before pyrolysis of the organic vehicle.

3 Results and Discussion

3.1 Solvent selection

There is a wide range of solvents for polystyrene. In the present work chlorinated solvents were excluded. During pyrolysis of the organic vehicle residual chlorinated solvents would be expected to decompose, liberating acids, and, with some ceramics this could result in the fixation of chlorine by salt formation, which would add a grain boundary contaminant.

The simplest approach to the solubility of polymers is to apply Hildebrand's solubility parameter δ, to a regular solution model[16] whereupon the enthalpy of mixing ΔH^{m} is given by

$$\frac{\Delta H^{\mathrm{m}}}{V} = (\delta_{\mathrm{p}} - \delta_{\mathrm{s}})^2 \phi_{\mathrm{s}}\phi_{\mathrm{p}} \qquad (1)$$

where ϕ is the volume fraction and V is the total volume. Subscripts s and p represent solvent and polymer respectively. Since the change in entropy on mixing is usually very large, the free energy of mixing is largely influenced by the enthalpy term.[17] It follows that solubility is favoured if solvent and polymer present similar solubility parameters.

The solubility parameter is given by

$$\delta = \sqrt{\frac{\Delta H_{\mathrm{v}} - RT}{V_{\mathrm{m}}}} \qquad (2)$$

where ΔH_{v} is the molar latent heat of vaporisation and V_{m} is molar volume. If the solubility parameter of polymer and solvent are close, mutual solubility is likely. This approach suffers from a failure to distinguish dispersion interactions and polar or hydrogen-bonding interactions between solvent and polymer and a remedy is to treat the dispersion and polar interactions as separate terms in eqn (1).[16] This approach has been criticised by Fowkes *et al.*[18] who argue that polarity should be treated by the theory of acid–base interactions.

In the present work, two solvents were selected with solubility parameters close to polystyrene (Table 3), namely cyclohexanone and ethyl acetate, having a high and a low boiling point respectively. For reasons discussed later, most applied solvent

Table 3. Properties of solvents for polystyrene

Solvent	*Solubility parameter[20] × 10^3 (J/m^3)$^{1/2}$*	*Boiling point (°C)*	*Molecular weight (g/mol)*
Cyclohexanone	20·3	156	98·15
Ethyl acetate	18·6	77	88·12

The solubility parameter for polystyrene is 18·4–19·2.

Table 4A. Summary of solvent joining operations for composition 1

Sample number	*Surface finish*	*Joining temperature*[a] (°*C*)	*Applied pressure* (*kPa*)	*Pressing time* (*min*)	*Drying time* (*h*)	*Observed defect types*[b]	
						Cyclohexanone	*Ethyl acetate*
1	Abraded	64	6	5	112	I, II	I, III
2	Abraded	64	6	30	142	I	I, II
3	Abraded	64[c]	6	5	112	I	I, II, III
4	Abraded	64	6	30	48	III	III
5	Abraded	64	16	5	142	I	III
6	Abraded	64	16	30	142	none	I, II
7	Abraded	64[c]	16	5	48	III	I, II
8	Abraded	64	16	30	48	I	I
9	Abraded	20	16	30	312	NT	I
10	Pressed	20	16	30	39	NT	I, III

[a] Removed from oven and joined immediately at room temperature unless otherwise indicated.

[b] I, Macroscopic regions which failed to weld; II, regions where the interface is visible as a reduced number of particle contacts; III, transverse cracks; IV, porisity in the SAZ; NT, not tested.

[c] Held at 64°C for 72 h.

remains 'locked in' after solvent welding and may only emerge during pyrolysis of the organic vehicle. The question is therefore whether the boiling of the solvent causes defects during pyrolysis of the organic vehicle.

Comparison of the microstructures resulting from the joining conditions in Table 4A showed no systematic difference attributable to the solvent. Since ethyl acetate has somewhat higher volatility it could be argued that the operator has less time for joint assembly. In further work (Table 4B) cyclohexanone was used throughout.

3.2 Effect of solvent on the surface of mouldings

The surfaces before joining were first examined by scanning electron microscopy. The welding operation must be capable of removing surface roughness (Fig. 1) and it is therefore interesting to see if defects in the fired body can be traced back to initial scratches. The as-pressed surface (Fig. 2) was

Table 4B. Summary of solvent joining experiments for composition 2

Sample number	*Adhesive*	*Applied pressure* (*kPa*)	*Pressing time* (*min*)	*Observed defect types*
11	Paste	16	90	I, II
12	Paste	26	90	II
13	Paste	48	90	none
14	Cyclohexanone	16	120	I, II
15	Cyclohexanone	26	120	I, II
16	Cyclohexanone	48	120	none
17	Paste	0	NA	IV
18	Cyclohexanone	0	NA	I
19	Cyclohexanone	0	NA[a]	IV
20	Paste	48	90	none

All discs were joined in the as-pressed condition at room temperature. The drying time was 168 h in each case.

[a] 30 min open time was allowed before joining.

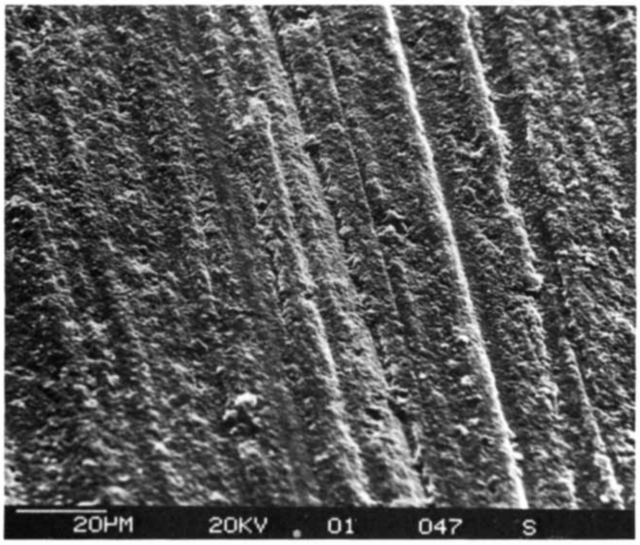

Fig. 1. Abraded surface of a disc of composition 1 before welding.

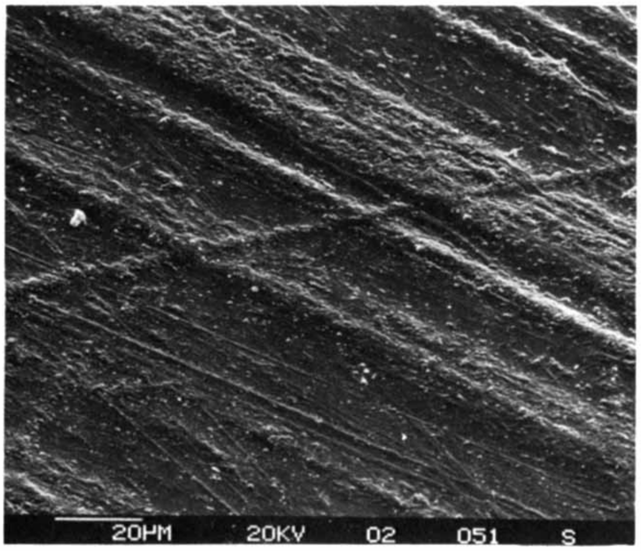

Fig. 2. As-pressed surface of a disc of composition 1 before welding.

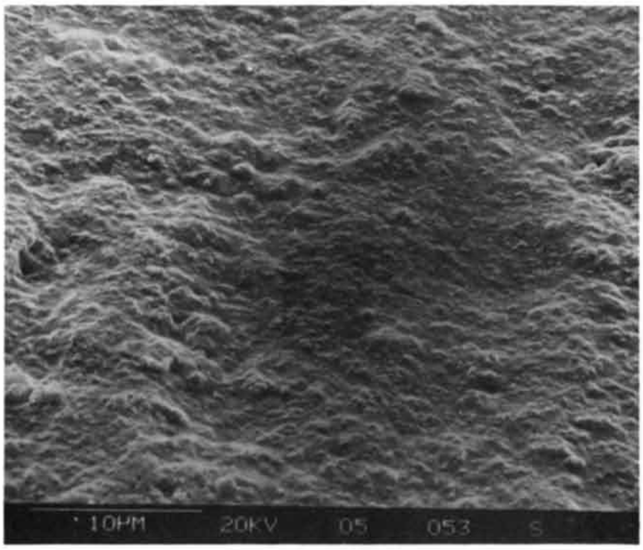

Fig. 3. Abraded disc of composition 1 after evaporation of ethyl acetate.

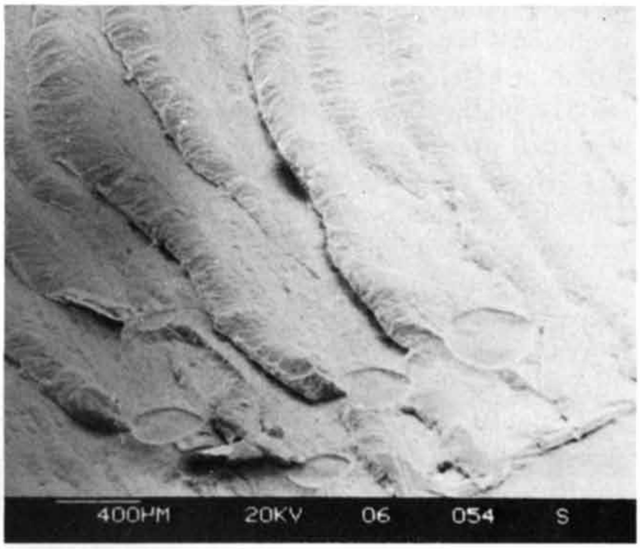

Fig. 5. Fracture surface of sample 9 before pyrolysis of the organic phase, showing unbonded regions.

smoother, showing only the replicas of scratches on the die.

The effect of solvent on these surfaces was examined by depositing drops of solvent and allowing them to evaporate. Figure 3 shows that although undulations resulting from abrasion remain, there is considerable smoothing which is emphasised in Fig. 4 where individual submicron ceramic particles can be seen close to the surface. Thus, the diluted suspension possessed transient low viscosity allowing mass transport under the influence of surface energy. Such flow properties are necessary for the achievement of intimate molecular contact in the joining operation.

Despite the surface smoothing action of the solvent, problems of joining an area of 490 mm^2 occur at macroscopic level. Figure 5 shows local regions of imperfect contact. This fracture surface was produced by splitting discs which had been joined with ethyl acetate at a pressure of 15·6 kPa (sample 9 in Table 4A). The rough regions show cohesive fracture in the bulk of the disc while the smooth areas have been wetted by solvent but have not joined.

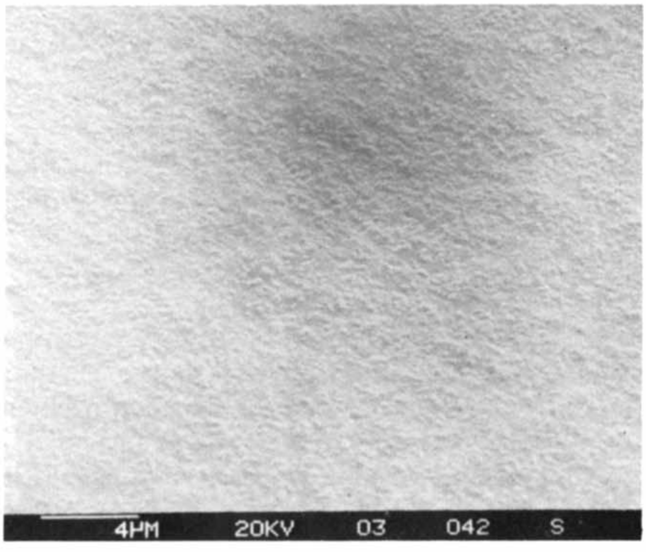

Fig. 4. As-pressed surface of a disc of composition 1 after evaporation of cyclohexanone showing ceramic particles in smooth polymer matrix.

3.3 Defects associated with the joining process

Regions which were unbonded at the joining stage can be identified by their rounded edges in section and a typical example is seen in Fig. 6 (Type I). These were seen in samples 1–3 prepared using either solvent and can be attributed in part to low applied

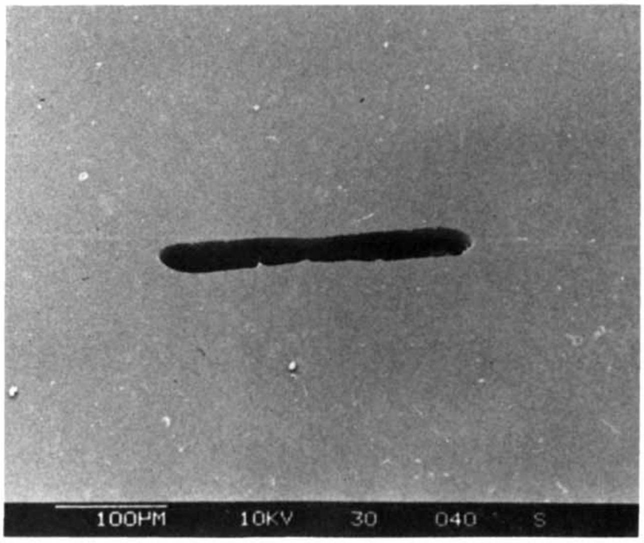

Fig. 6. Unbonded region in the polished section after partial sintering (sample 6 joined with ethyl acetate).

pressure during joining. They were not seen under condition 4 because these samples were pressed for 30 min at 64°C, a temperature just above T_g. This implies that the effects of low applied pressure can be alleviated by heating the sample into the softened state. However, this is not a practical solution, since some deformation of the body is likely. Neither is it necessary, since joints free from these defects were produced without heating (discussed later). Samples prepared under condition 5 also showed these defects despite the higher pressure and this can be attributed to the short time for which the pressure was applied. The defects were also noticed in samples 11 and 14 (Table 4B) which used a pressure of 16 kPa which appears to be a lower limit for these materials. Their appearance in sample 8 is somewhat misleading in that one very small unboned region was noted in each section.

The joining operation requires the flow of the suspension which has been plasticised by solvent at the interface in order that asperities are removed and valleys filled. Such flow is dependent on applied pressure and 16 KPa appears to be a minimum pressure for these materials. Similarly, a minimum pressing time of 30 min is required.

Another characteristic defect is shown in Fig. 7 (Type III). This consists of cracks perpendicular to the interface but central to the joint. There are two possible related causes for this:

(a) It is due to rapid liberation of solvent from the solvent affected zone (SAZ) during pyrolysis of the organic matter or
(b) it is due to differential sintering of the SAZ and the parent plate.

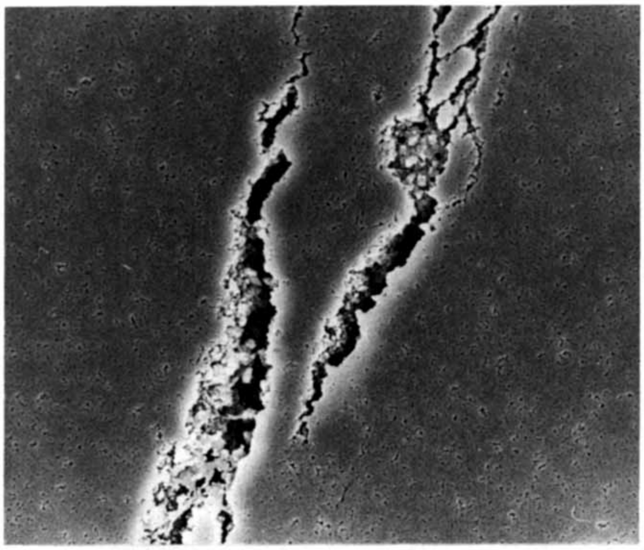

Fig. 7. Transverse cracks near the interface in the partially sintered joint (sample 4). The original interface is horizontal and central.

The fact that sharp cracks are seen implies that failure occurred late in the binder removal stage when fluid properties of the molten suspension had been lost.[21]

Most residual solvent remains in the SAZ at room temperature[22] so that the ceramic volume fraction in the SAZ is reduced. Residual cyclohexanone, estimated from weighing the joints, was in the region of 40 g/m^2 for samples joined with pure solvent after drying for 168 h. Titow[22] argues that the SAZ has a sharp boundary because of the large dependence of binary diffusion coefficient on concentration of solvent. He found SAZ thickness values of 50–100 μm for polycarbonate sheet. If these values were true in the present work the ceramic volume fraction in the SAZ would be reduced to 43–50 vol.% for composition 1. Since the relative density at the end of binder removal is dependent on initial volume fraction,[21] the resulting differential sintering stresses could account for the transverse cracks. These cracks are most prevalent in samples which have short drying times. A minimum drying time of 1 week is therefore added to the list of conditions for solvent welding of this system, but this could be shortened by prolonged heating of the joint as for solvent welded polymers,[23] which could be combined with the early stages of binder removal.

This explanation for transverse cracks neglects the fact that the geometry appears to allow unrestrained shrinkage in the direction perpendicular to the interface. In reality, however, solvent is removed from the edges of the disc by radial diffusion and evaporation[22] and this restrains the system.

To be distinguished from the unbonded regions are the defects seen in Fig. 8 (Type II). Such low density regions do not constitute a conventional crack but the number of particle contacts across the interface is significantly less than in the bulk. This defect generally appears in conjunction with Type I and may therefore be attributable to imperfect contact at the pressing stage or even to some form of elastic recovery when pressure is released.

3.4 Joining with a ceramic paste

The paste consisted of the bulk mixture (composition 2) diluted with cyclohexanone. There is considerable scope for tailoring the ternary system ceramic–polymer–solvent to suit the joining process, but the volume fraction of ceramic based on the binary system ceramic–binder must never be less than that in the bulk. The effect of the paste is similar to that of the pure solvent; the main difference is that more solvent is introduced into the joint and must

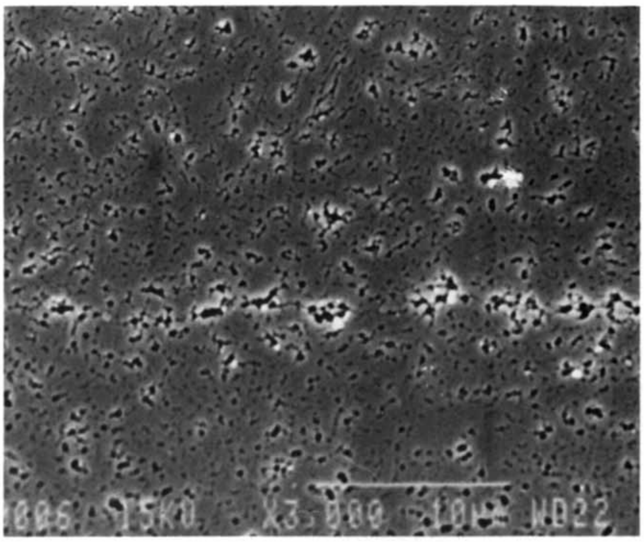

Fig. 8. A region of reduced particle contact at the interface (sample 5 joined with ethyl acetate).

therefore be removed subsequently by diffusion into the parent material. One advantage of using a paste is that the volatility of the solvent is reduced by the polymer solute so that the operator has more time to assemble the joint. In addition, more solvent can be absorbed into the parent plate before the weld is assembled. Although the paste should offer better gap-filling ability, the conditions which favoured unbonded regions are the same as those for pure solvent. Thus samples 11, 14, 15 and 18 (Table 4B) showed unbonded regions attributable to low applied pressure.

The paste has a low ceramic volume fraction (19 vol.%) and as solvent is removed this must rise to a maximum of 54 vol.% for composition 2. This in turn involves a volume shrinkage of 65%. From Titow's argument,[22] the SAZ continues to expand by diffusion of solvent until the solvent concentration is sufficiently low that the glass transition temperature of the solution rises to the ambient temperature.

Significant diffusion can only take place thereafter if the temperature is raised. In the present work the large concentration of plasticiser in the polystyrene reduces the glass transition temperature to 63°C and the amount of solvent needed to reduce this further to 20°C is correspondingly reduced.

The residual solvent in joints was recorded by weighing the discs before and after pressing and again after the drying stage. In joints which were subject to pressure, the average initial mass of solvent was 59 g/m^2 for solvent welding and 124 g/m^2 for paste welded joints after correcting for the composition of the paste. Of this, only 30% was removed after drying in both cases. The concentration established by this residue in the SAZ defines the boiling point of the solvent–polymer solution on subsequent reheating as discussed later.

The effect of application of paste can be simulated by using a long open time with pure solvent application and this was the procedure followed in sample 19. The 30-min open time allowed solvent to swell the surface region and much solvent (540 g/m^2), which would otherwise be displaced by pressing, was taken up. Of this 26% was lost on drying. The microstructure of the resulting weld was identical to the paste welded sample with no applied pressure (sample 17).

In general, the paste welded samples all showed a characteristic low density region adjacent to the interface which was susceptible to polishing damage, which produced grooves or recesses, as shown in Fig. 9. They also tended to show porosity at the 10–20 μm scale which may be associated with shrinkage effects. For these reasons the direct application of the solvent followed by a short open time appears to be the preferable approach.

3.5 The migration of solvent and its effect on ceramic volume fraction

The concentration dependence of diffusion coefficient for small molecules in molten polymers has been ordered by using the free volume theory of Vrentas & Duda[24,25] and diffusivities can vary by four orders of magnitude for solvent concentrations in the range 0–10 wt%. In the region of the glass transition temperature the situation is less well understood and is further complicated by the fact that compositions 1 and 2 incorporate 22 wt% diluent based on polystyrene. This both lowers T_g

Fig. 9. Low density region in sample 11 joined with paste. The groove is attributed to polishing damage after partial sintering.

and also reduces the concentration dependence, making quantitative evaluation superficial in the absence of accurate diffusion data for this system. Titow[22] has calculated desorption of dichloroethane from welded polycarbonate and the time for the concentration in the SAZ to fall to half its original value is 3000 years for 1-mm thick films. The presence of diluent in the polystyrene will increase diffusion through the welded plates and along the weld line and the sharp SAZ boundary predicted by Titow may be less relevant to the compositions used here. The ceramic volume fraction influences diffusion according to a series of models reviewed by Barrer[26] and these predict that 60 vol.% ceramic powder would reduce the diffusivity in the continuous polymer phase by a factor of 0·25–0·36; an effect considerably less than the influence of solvent concentration.

A weight fraction W of solvent in a ceramic suspension of initial volume fraction V_0 reduces the volume fraction to V_1 given by

$$V_1 = \frac{V_0\rho_s(1-W)}{\rho_s(1-W) + W[V_0\rho_c + (1-V_0)\rho_p]} \tag{3}$$

where ρ_s, ρ_c and ρ_p are the densities of solvent, ceramic and organic vehicle respectively. The sensitivity of ceramic volume fraction to solvent content is plotted in Fig. 10 for the compositions used here and shows how small additions of solvent have a pronounced effect on ceramic volume fraction.

Residual solvent also influences the temperature at which voids are formed during pyrolysis of the binder. The vapour pressure P^0 of the polymer solvent system is given by the Clausius–Clapeyron relationship:

$$\ln P^0 = \frac{-\Delta H}{RT} + i \tag{4}$$

where ΔH is the enthalpy of vaporisation and i is a constant. Values of ΔH are 41·9 kJ/mol and 36·5 kJ/mol and values of i are 23·32 Pa and 24·04 Pa for cyclohexanone and ethyl acetate respectively deduced from vapour pressure data.[27]

The activity of solvent in the polymer is given by the Flory–Huggins equation:[28]

$$a_1 = \theta_1 \exp[(1-\theta_1) + \chi(1-\theta_1)^2] \tag{5}$$

where θ_1 is the volume fraction of solvent based on the solvent–polymer system and χ is the Flory–Huggins interaction parameter ($\chi < 0{\cdot}5$ for solubility). χ lies in the region 0·3–0·4 for polystyrene in toluene solutions (Ref. 28, p. 515) and was taken as 0·4 for the slightly more polar solvents used here.

From eqns (4) and (5) the boiling point at atmospheric pressure of both solvents as a function of concentration in the polymer is plotted in Fig. 11. It can be seen that solvent dilution, i.e. diffusion into the bulk and enlargement of the SAZ, is an essential prerequisite to the avoidance of defects caused by heterogeneous bubble nucleation during reheating to remove the binder, and this is analagous to the diffusion of low molecular weight polymer degradation products out of moulded ceramic bodies.[29,30]

3.6 Successfully welded interfaces

Samples 13, 16 and 20 present interfaces free from the defects described in Section 3.3 while samples 4, 5 and 16 present defect-free interfaces but show some transverse cracks. These successes can be attributed to high joint pressure, long pressing times and long drying times, although clearly drying times may be shortened by heat treatment. Figures 12 and 13 show

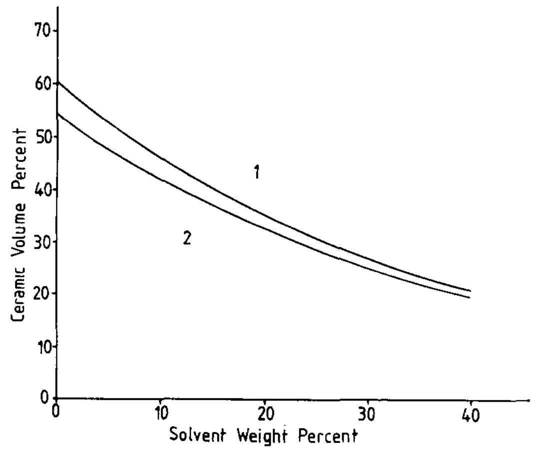

Fig. 10. The ceramic volume fraction as a function of the weight fraction of included solvent.

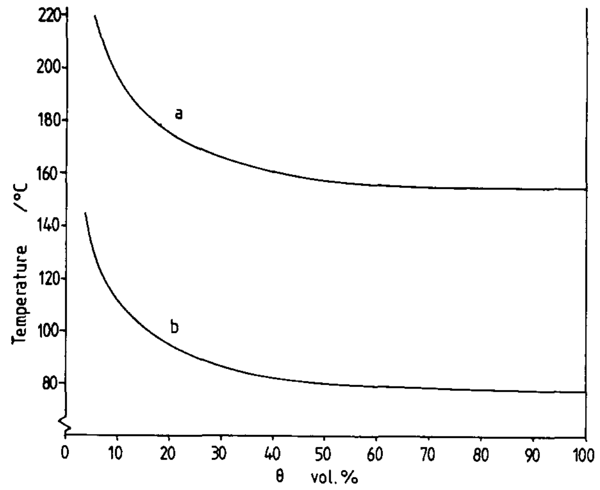

Fig. 11. The effect of solvent on the boiling point of polystyrene–solvent systems as a function of solvent volume fraction θ for (a) cyclohexanone and (b) ethyl acetate.

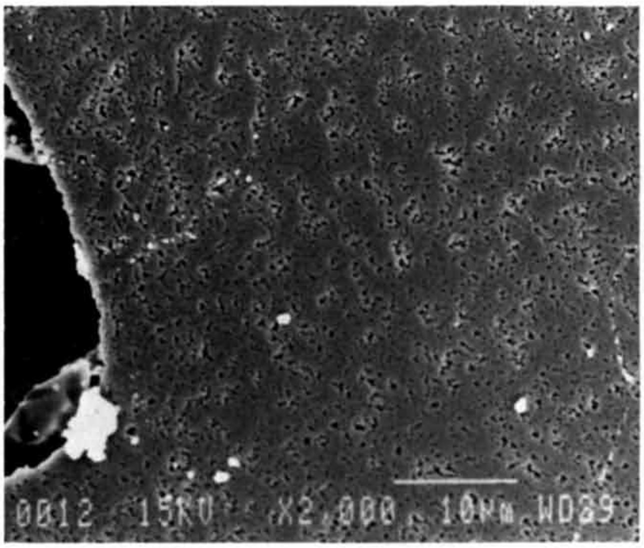

Fig. 12. Interface which is indistinguishable from the bulk (sample 4 joined with ethyl acetate).

that there is no detectable difference in the microstructure of the interfacial region and the bulk after partial sintering and hence that solvent welding is a viable joining operation for technical ceramics. Although the microstructure generally cannot reveal small differences in relative density, the implication is that during drying and subsequent binder removal the volume fraction of ceramic reasserted its initial value based on the ceramic–polymer system by exclusion of solvent entrapped in the SAZ. At low magnification on some samples it was possible to see the interface region, and this is shown in sample 15 as a faint horizontal line (Fig. 14). The sintering system appears able to accommodate the small changes in volume fraction that may exist. This was confirmed by sintering samples pressed at 50 kPA with a pressing time of 120 min and drying time of 168 h to near full density. Figure 15 shows the interfacial region.

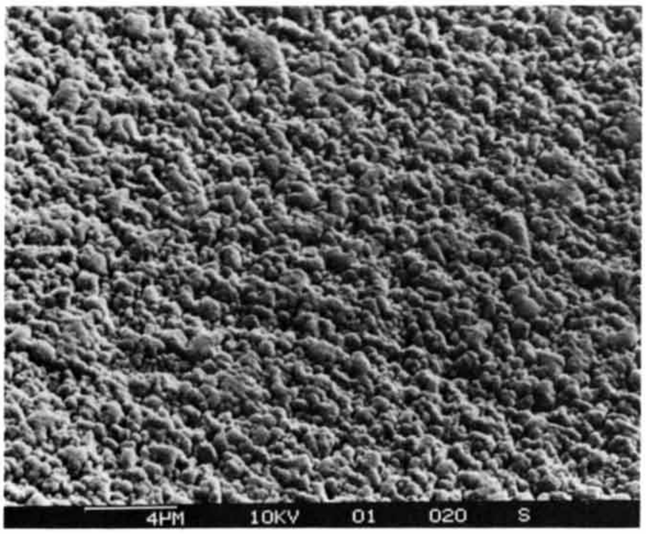

Fig. 13. Interface in sample 14 at the edge of a type II defect; beyond the crack tip the interface cannot be distinguished from the bulk.

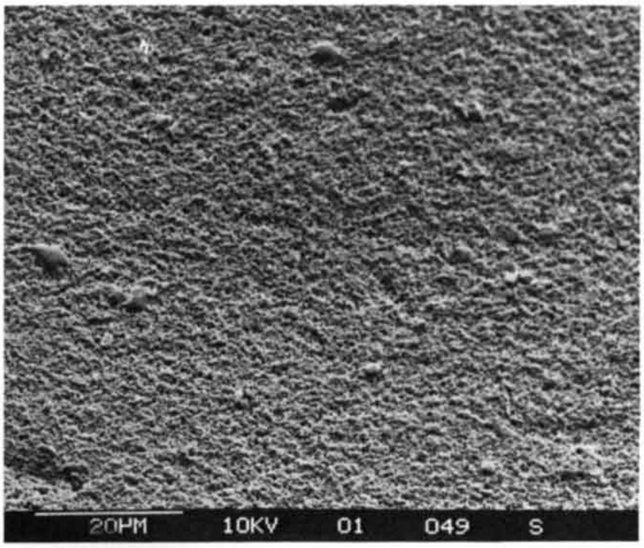

Fig. 14. Interfacial region in solvent welded sample 15 at low magnification seen as a faint horizontal line.

In order to demonstrate the complexity of form the process allows, the artefacts shown in Fig. 16 were prepared from 2·1-mm compression moulded plates. The internal re-entrant cavities are revealed by contact radiography. Clearly considerable extension to complexity of form is possible.

4 Conclusions

The experimental requirements for solvent welding of ceramics before firing have been delineated and it

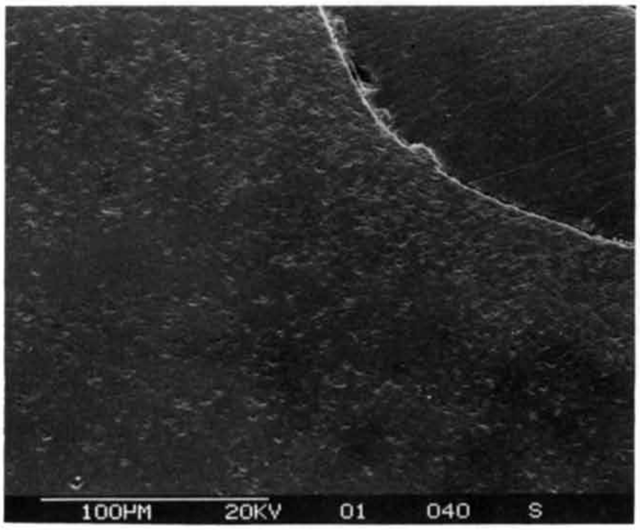

Fig. 15. A sintered laminate prepared using cyclohexanone and 50 kPa pressure applied for 120 min (the original interface was at half thickness).

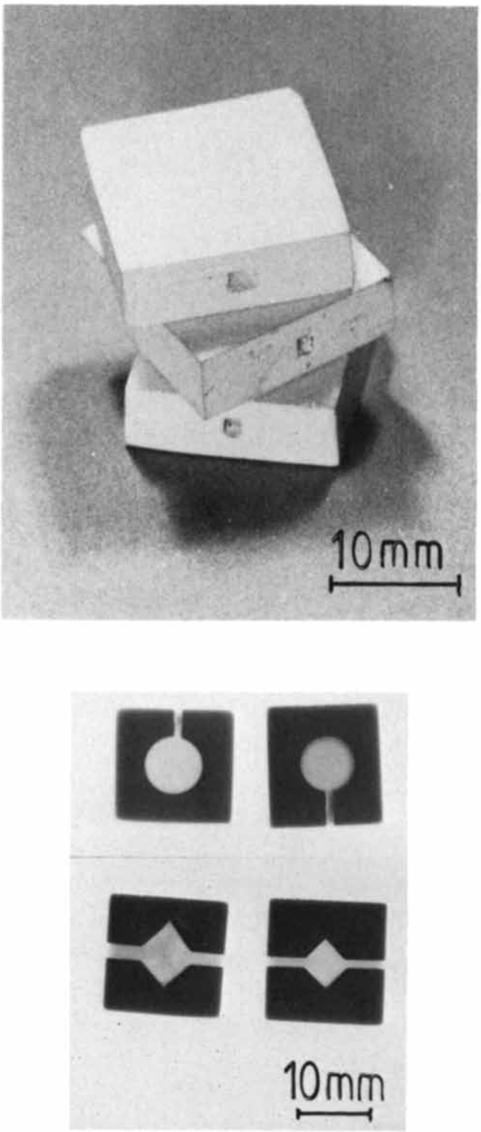

Fig. 16. Ceramic artefacts prepared by solvent welding containing interval cavities revealed by contact radiography.

is possible to obtain microstructures in which interfaces are indistinguishable from the bulk. The amount of solvent uptake can be reduced by applying pure solvent rather than a ceramic–polymer–solvent paste and by employing short open times. The use of paste or long open times produced a low-density interfacial region. High pressures are needed to achieve intimate contact at the interface and to compensate for the use of minimal solvent. Similarly, long pressing times are preferred. The migration of solvent into the bulk during pyrolysis allows boiling points to be increased and ceramic volume fraction to be reasserted. Complexity of the form of ceramic artefacts prepared by solvent welding has been demonstrated and the procedure is open for considerable development.

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