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Relaxation Effects in Large Injection Moulded Ceramic Bodies

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Abstract

Small cubic samples were cut from various positions within large unfired injection moulded ceramic bodies and thermal expansion in different directions was measured by dilatometry. Dramatic heterogeneities and anisotropies in apparent thermal expansion were observed. Negative apparent expansions were noted in some cases. The results have implications for the way in which local deformation occurs during reheating such mouldings to remove the organic vehicle. Small organised displacements of particles resulting from the relaxation of the organic phase during binder removal may contribute to the defects which appear at that stage.

Kleine, kubusförmige Proben wurden aus verschiedenen Bereichen großer, ungebrannter Spritzguß-keramiken herauspräpariert und die thermische Ausdehnung in verschiedene Richtungen mit Hilfe der Dilatometrie untersucht. Dabei wurden dramatische Heterogenitäten und Anisotropien in der scheinbaren thermischen Ausdehnung beobachtet. In einigen Fällen konnte eine negative, scheinbare Ausdehnung gemessen werden. Aus den Ergebnissen läßt sich folgern, in welcher Weise lokale Deformationen während des Erwärmens der Formen zur Entfernung des organischen Lösungsmittels auftreten. Kleine, koordinierte Verrückungen von Partikeln, resultierend aus der Relaxation der organischen Phase während des Entfernens des Binders, tragen möglicherweise zu den in diesem Stadium auftretenden Defekten bei.

De petits échantillons cubiques ont été découpés à divers endroits d'un objet moulé par injection et non cuit. La dilatation thermique de ces échantillons a été suivie par dilatométrie. Des hétérogénéités importantes et des anisotropies ont été observées pour ce qui concerne la dilatation thermique. Des coefficients de dilatation négatifs ont été relevés dans certains cas. Les résultats permettent de comprendre comment des déformations se produisent durant le traitement thermique de telles pièces crues, effectué pour en extraire le liant organique. Des petits déplacements de particules résultant de la relaxation de la phase organique durant l'élimination du liant peuvent contribuer à la formation des défauts à ce stade de la fabrication.

1 Introduction

During the course of studying ways to predict the thermal properties of ceramic injection moulding suspensions to assist computer modelling[1] it was noticed that quite dramatic anisotropy could be discerned in the thermal expansion coefficient of small pieces of highly loaded polymer cut from a moulded disc.[2] The practical implication was that annealing is an essential prerequisite for accurate measurement of thermal expansion. The anisotropy appeared to be related to residual stresses in the moulding but the effects of molecular orientation induced during mould filling were also considered.

The full implications of these internal relaxations in the suspension were not fully addressed. The work of Thomas & Evans[3] showed how an array of gross internal defects could appear in a moulding after pyrolysis of the binder, yet the defects appeared to have a genesis in the solidification stage of the injection moulding operation. An explanation of why these defects become apparent only after binder removal was not given but the thermal expansion anisotropy effect seems to shed more light on this matter now. Of course, it is not claimed that thermal expansion of the material has changed; rather that additional anisotropic strains associated with relaxation phenomena are superimposed on the thermal strain on the first occasion that dilatometry is used.

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In the highly loaded polymer, the relaxation of residual stresses or of polymer orientation is expected to result in strains and therefore in small displacements in interparticle distance. The objective of ceramic injection moulding is to create an assembly in which particles are in contact with their neighbours immediately prior to sintering. Although the success of ceramic injection moulding depends critically on the physical and chemical properties of the organic phase, the role of the latter is usually transient. Very few polymers have been developed which will yield the desired ceramic during pyrolysis, although this is a promising approach.[4] If molecular relaxation during reheating displaces the conveyed particles they will not all present the same co-ordination number at the start of sintering. If the displacement is locally organised in some way, then the large defects seen after debinding can be better understood. Defects originating from the solidification stage will of course present themselves irrespective of the binder removal conditions.

In the present work, mouldings prepared in various ways were sectioned to produce small cubic samples for dilatometry. The apparent expansion curve was studied at several positions and in different directions to establish the pattern of heterogeneity and anisotropy respectively.

2 Experimental Details

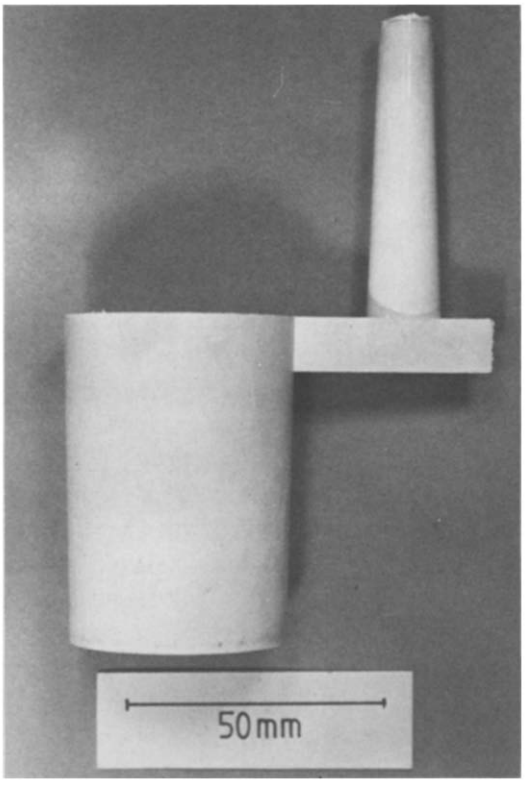
2.1 Materials

The ceramic powder was RA6 alumina kindly donated by Alcan Chemicals, UK. The organic vehicle was atactic polypropylene (Grade MF70, APP Chemicals, Salop, UK), isotactic polypropylene (Grade GY545M, BP Chemicals, Grangemouth, UK) and stearic acid (GPR, BDH Chemicals, Poole, UK) in weight ratios 4:4:1. Mixing was done on a corotating intermeshing twin screw extruder (TS40, Betol Machinery, Luton, UK) with barrel temperature 190–200–220–210°C feed to die. The mixture was prepared with ceramic loading of 56 vol.%.

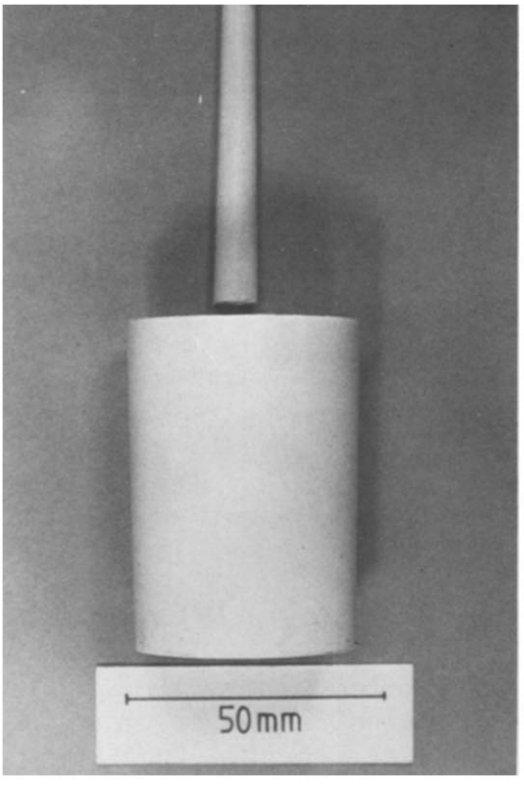
2.2 Injection moulding

A Negri Bossi NB90-SM290 machine, modified for ceramics use and with barrel temperatures 190–200–210–210°C feed to nozzle was used to make 40 mm diameter cylinders, 60 mm in length. The cylinders had a 1·5° taper to ease ejection. Cavity pressure was recorded on a 2000 lb fsd force transducer (GT81-F2-2000 from Terwin Instruments, UK) activated by a 5 mm diameter pin for conventional moulding and modulated pressure moulding and by an 8 mm diameter pin for heated sprue moulding. Injection speed was $4 \times 10^{-5}\,m^2\,s^{-1}$ and pressure trip to constant hold pressure was set at 140 MPa.

For conventional moulding and modulated pressure moulding, the cylinder was side-gated at one end (Fig. 1(a)). For the heated sprue work the cylinder was axially centre gated (Fig. 1(b)). The latter configuration is very likely to produce weld



(a)



(b)

Fig. 1. (a) The side gated cavity for conventional and modulated pressure and (b) the axial centre gated cavity for heated sprue moulding.

lines but was necessary in this case to get the benefits of heated sprue moulding. Mould temperature was controlled at 20°C and 80°C by a Conair Churchill (Uxbridge, UK) type 3/100 water circulator. The procedure for heated sprue moulding has been described before.[5] The sprue was heated to 210°C before injection and held for 250s, which exceeds the time for solidification of the centre of the cylinder.[6] Hold pressure was held static for this duration. Modulated pressure moulding has also been described before.[7] One second after injection pressure trip, the barrel pressure was reduced to 5 MPa and the oscillating valve was activated at 1 Hz and with various pressure amplitudes which were constant throughout the solidification stage.

2.3 Measurement of thermal expansion

The samples were cut from moulded cylinders in the configuration shown in Fig. 2 and abraded to approximately 5 × 5 × 5 mm. The radial direction was described as R. The direction in the length of the cylinder was labelled Z and θ was the circumferential direction. Thermal expansion was measured using a Perkin-Elmer TMS-1 thermomechanical analyser with a flat ended silica rod with a loading of 4 g. A heating rate of 4°C min^{-1} was used. The dilatometer was first calibrated by measuring the thermal expansion of a pure aluminium standard.

The deformation of polished sections was observed by cutting axially and polishing the flat sections on 600 grade SiC paper before annealing at 120°C for 1 h. A temperature below the softening point was selected to avoid deformation caused by sagging. The relaxation was then measured using a point contact transducer survey. The surface was scribed with a grid before annealing. A modified Talysurf 4 (Rank-Taylor-Hobson, Leicestershire, UK) surface roughness measurement device was used to measure the height of the sample supported on V blocks using a LVDT displacement transducer (Penny and Giles, Dorset, UK) at each intersection before and after annealing.Three factors influence the apparent deformation: (i) since the sample is large it is not perfectly flat after polishing; (ii) the sample cannot be mounted in the V blocks perfectly parallel to the horizontal plate; (iii) the longitudinal position in the V block cannot be exactly the same before and after annealing. These factors were corrected using a computer program which treats the edges in the longitudinal direction as coincident before and after annealing and then calculates the displacement of all other points.

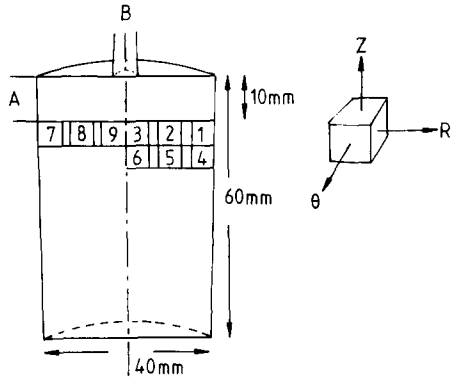


Fig. 2. The positions from which dilatometer samples were cut. A, Gate position for conventional and modulated pressure moulding; B, gate position for heated sprue moulding.

3 Results and Discussion

The results presented are important for ceramic injection moulding because they imply differential strains will occur throughout the body during the process of reheating to remove the organic phase by pyrolysis. The results, however, present a number of paradoxes and their interpretation is complex. Sections 3.1 to 3.3 will discuss the phenomena observed under different moulding conditions and Section 3.4 will examine possible causes.

3.1 Conventional moulding

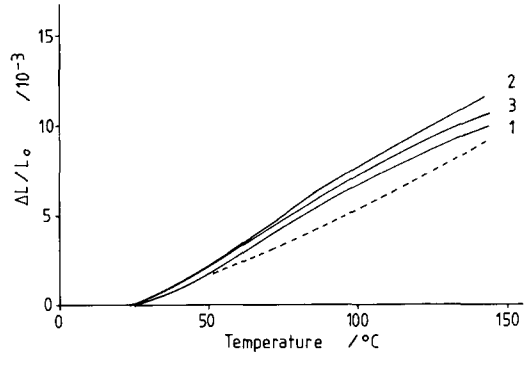
Cubes cut from positions 1, 2 and 3 (Fig. 2) and tested in the θ direction show apparent thermal expansion traces which differ from the expansion coefficient obtained from samples that had been annealed at 150°C after cutting and tested in the same direction (dashed curve). This temperature is slightly above the dilatometric softening point for the suspension obtained with a 10 g load on the push rod, which was approximately 145°C. It is reasonable to suppose that annealing of the small cubic samples had allowed extensive relaxation to occur and the dashed curve is close to the 'true' expansion curve for the material.[2] This is supported by the consistency presented in Table 1.

The deviations shown in Fig. 3 are not very great compared to those reported later for other moulding conditions. One reason for this is that it is not possible to injection mould this suspension in this cavity by conventional moulding without the appearance of either voids when low hold pressures are used or cracks at high hold pressure. This is the case even for a wide range of mould temperatures.[8] The moulding referred to in Fig. 3 contained internal cracks resulting from the solidification process. Of course, the samples for dilatometry were cut from uncracked regions, but the internal cracking is expected to perturb the relaxation of the body during cooling in the cavity. In the results that follow it will be shown that conditions favourable for relaxation to occur are more strongly brought about by the removal of restraint by cutting than by long cooling periods.

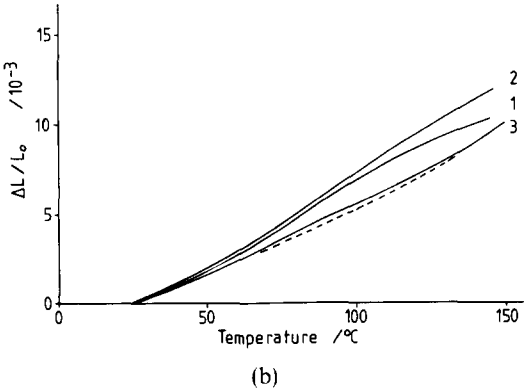
Table 1. Reproducibility and cross-referencing of expansion curves

Fig.	*Curve*	*Corresponding curves*
3, 4, 6	Annealed sample	Two coincident measurements; mean value in Fig. 7(a), (b), (c)
4(b)	Position 1	Fig. 4(b) position 4
	Position 2	Fig. 4(b) position 5
	Position 3	Fig. 4(b) position 6
		Correspondence between adjacent positions
6(c)	Positions 1, 2, 3	Two measurements for each
7(a)	θ direction	Fig. 6(c) position 1
7(b)	θ direction	Fig. 6(c) position 2
7(c)	θ direction	Fig. 6(c) position 3
		Also note consistency of mean curves for each position

Most of the samples in Fig. 3 show higher apparent expansion in the θ direction than the value for the annealed material. Current theories and measurements of residual stresses in flat mouldings[9-11] all suggest that in conventional moulding, the outer regions are in compression in the plane parallel to the wall. The residual stress distribution in the short cylindrical moulding is, of course, more complex. It is pertinent to the discussion which follows to note that Samples 2 and 3, which are near the centre of the moulding, have experienced a very long cooling time[6] and this is particularly so for samples in Fig. 3(b) with a mould temperature of 80°C. This should allow relaxation processes to take place. It is normal practice to open the mould after the centre



(a)



(b)

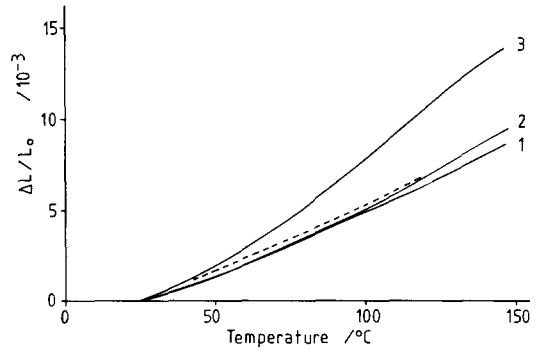
Fig. 3. Apparent thermal expansion curves for conventional mouldings in the θ direction with (a) hold pressure 141 MPa, mould temperature 20°C; (b) hold pressure 141 MPa, mould temperature 80°C; dashed curve shows expansion of material annealed after cutting.

temperature has fallen below the softening point (145°C). After the mould is opened and the sample is ejected, the heat transfer coefficient changes from 500–1000 $Wm^{-2}K^{-1}$ to about 13 $Wm^{-2}K^{-1}$ for free convection in air. So the time needed for the centre of the moulding to reach 20°C is up to 30 min. Despite this long period, heterogeneity of apparent thermal expansion persists. It is relieved after cutting the moulding to small pieces and heating in the dilatometer.

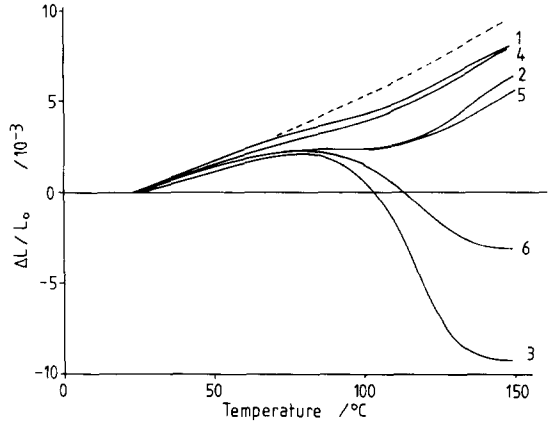
3.2 Modulated pressure moulding

The principal advantage of modulated hold pressure is that it prolongs the solidification of the sprue, allowing entry of material to compensate for shrinkage and prevent void formation in the moulding without the large pressure decay which is characteristic of conventional moulding.[7] This is achieved by oscillatory flow in the centre of the sprue arising from alternate compression and decompression of the fluid in the cavity. A minimum pressure amplitude is needed to prevent voids but at very high amplitudes the solidification time is extended well beyond the natural time for the moulding itself to solidify. It follows that heat is also dissipated in the bulk of the moulding as a result of compression and decompression of the liquid in the core. For a mould temperature of 80°C, a pressure amplitude of 98 MPa is just sufficient to keep the sprue open for the duration of solidification of the 40 mm cylinder[7] and mouldings are free from macroscopic voids or cracks. Figure 4(a) shows the θ direction curves for such mouldings. Although the central sample (position 3) shows an additional dilation, the curves for other samples are close to those for the annealed material. Position 3 is close to the centre but opposite the gate (Fig. 2).

When the pressure amplitude is increased, previous work has shown that mouldings crack during storage or during reheating.[12] Such mouldings are sometimes referred to as 'overpacked'; a term whose meaning is far from transparent. Dilatometry on samples cut from such a moulding made with a modulated pressure amplitude of 120 MPa (Fig. 4(b)



(a)



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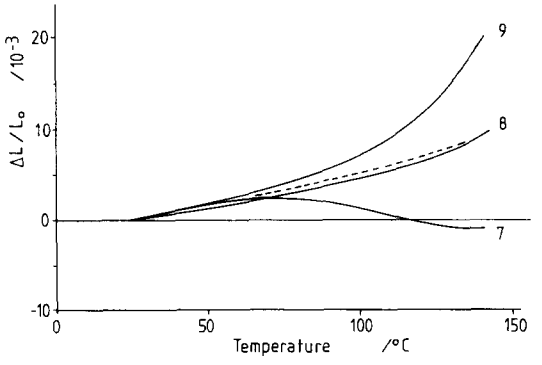


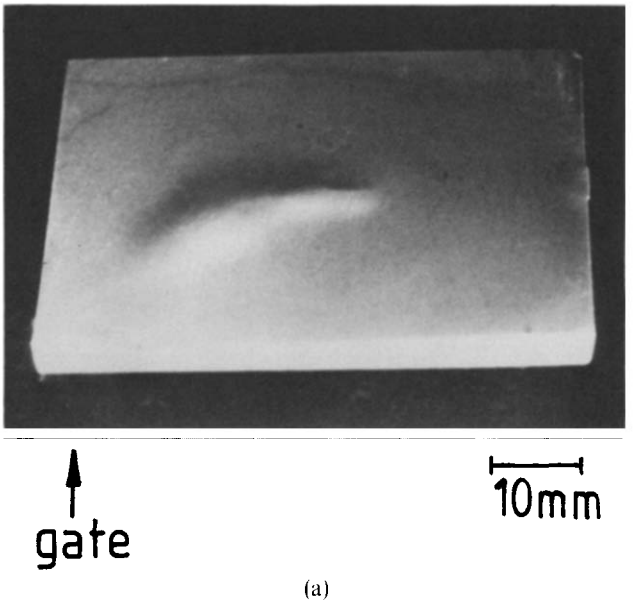
(c)

Fig. 4. Apparent thermal expansion curves for modulated pressure mouldings in the θ direction with (a) pressure amplitude 98 MPa, mould temperature 80°C; (b), (c) pressure amplitude 120 MPa, mould temperature 80°C; dashed curve shows expansion of material annealed after cutting.

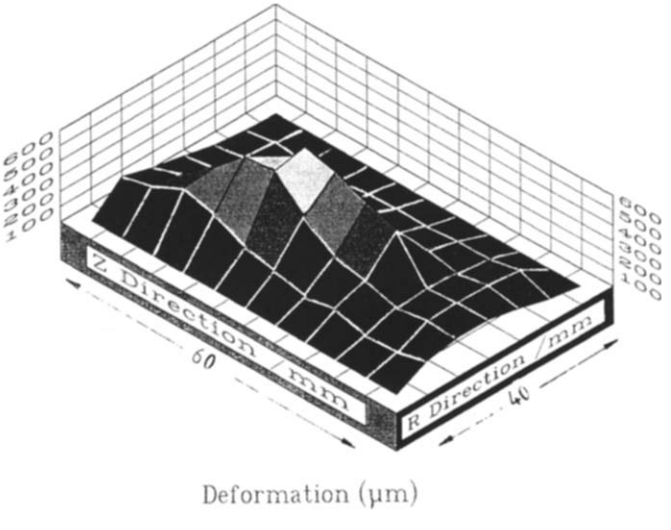
and (c)) reveals remarkable and disturbing behaviour. In samples close to the centre but opposite the gate (positions 3 and 6) a negative apparent thermal expansion is observed as contraction in the θ direction outruns the normal thermal expansion. Sample pairs 1 and 4, 2 and 5, 3 and 6 are adjacent to each other in the axial direction of the cylinder and their behaviour shows pairwise correspondence. The situation on the gate side is the reverse. Sample 9, near the centre, shows a massive expansion, while sample 7 contracts. This moulding was also made with a mould temperature of 80°C, giving rise to a long cooling time.

The relaxation strains can be revealed by a different method which makes them visible to the unaided eye. Sectioning of cylinders followed by heating to the softening point shows a dilated region in the centre of the moulding which appears as a bulge in the polished sections and is shown in Fig. 5(a). Annealing allows relaxation adjacent to the cut face which was apparently forbidden in the uncut moulding as it slowly cooled in the cavity.

Using the contact LVDT transducer the profile of the annealed moulding can be surveyed and is shown in Fig. 5(b). The dilated region appears to include the last pocket of liquid to solidify in the core, together with a path or channel to the gate which was kept molten by modulated pressure beyond the natural cooling time for the moulding. The sinking region predicted by individual dilatometric curves at positions 3 and 6 in Fig. 4(b) does not appear in the



(a)



(b)

Fig. 5. (a) Swelling of the central region of a polished section following annealing at 120°C. The sample was moulded with oscillating pressure at 120 MPa amplitude and mould temperature 80°C. The relevant expansion curves are in Fig. 4(b) and (c). (b) Profile of the cut and annealed moulding in (a) obtained by a contact LVDT transducer survey.

deformation of the polished section, apparently because such regions remain connected to the core which undergoes substantial expansion; a connection which is removed in dilatometric measurement.

3.3 Heated sprue moulding

The effect of an externally heated sprue is, in respect of sprue solidification time, comparable to modulated pressure moulding. However, the pressure history experienced by the material in the cavity is quite different. As a method of prolonging access to thick sections, the heated sprue is successful only if it enters the largest section directly, unlike modulated pressure moulding. Previous work has shown how residual stresses measured by the layer removal method were extremely low for a centre gated rectangular plaque made with a heated sprue.[11]

Figure 6(a) and (b) show the effect of mould temperature for a heated sprue moulding made at very low hold pressure (7 MPa). Increasing the mould temperature appears to enhance slightly the difference in expansion behaviour between the inner and outer regions but the pattern of dilation remains the same. Increasing the hold pressure has a dramatic effect on apparent expansion coefficient at position 3, as shown in Fig. 6(c). In each case the sample adjacent to the centre shows enhanced dilation in the θ direction.

Samples cut from a heated sprue moulding made with 54 MPa hold pressure and 20°C mould temperature were held at ~150°C after dilatometry and then cooled in the thermomechanical analyser. They were tested again under the same conditions and on this occasion gave thermal expansion curves close to those of annealed samples.

In Fig. 7 the expansion curves for the sample moulded at a hold pressure of 54 MPa and mould temperature 20°C in the θ, Z and R directions are compared at each sample position. The Z direction curves display a clear trend on moving from the perimeter to the centre of the cylinder. The apparent expansion decreases, becoming negative at the centre. The expansion in the θ direction shows the reverse trend on going from the perimeter to the centre. It is less than average near the surface and becomes extremely high at the centre. The radial direction expansions are all greater than average and increase systematically towards the surface region.

In each case Fig. 7 shows that the average curves for the three directions are coincident and correspond to the average expansion for samples annealed after cutting. It follows that there is no anomalous volumetric change associated with the anomalous linear expansions. It should be noted that annealed samples show isotropic thermal expansion behaviour.

Figure 8 shows the results of the expansion survey

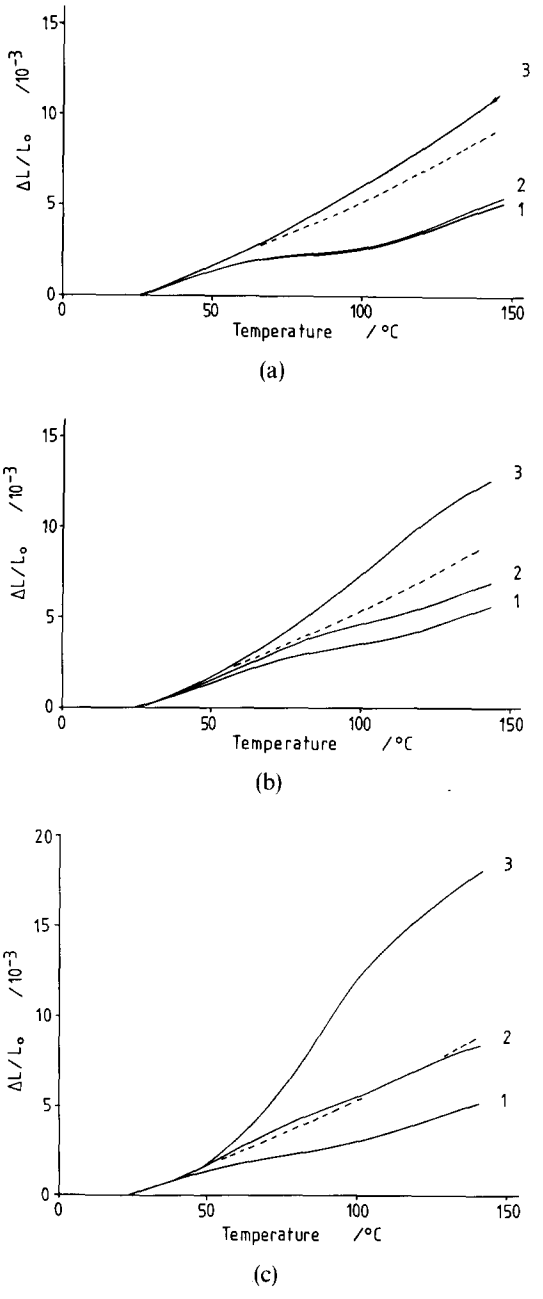


Fig. 6. Apparent thermal expansion curves for heated sprue mouldings in the θ direction with (a) hold pressure 7 MPa, mould temperature 20°C; (b) hold pressure 7 MPa, mould temperature 80°C; (c) hold pressure 54 MPa, mould temperature 20°C.

on a polished and annealed section for the sample in Fig. 7. The dilation of the central region is symmetrical about the axis because the moulding was centre-gated. The expansion is again most pronounced in the region which was the last to solidify. The expansion in the θ direction was greatest for the sample cut from this region (Fig. 6).

3.4 Causes of anomalous expansion curves

In order to interpret the results, the assumption is made that each dilatometric curve is the sum of two curves; a thermal expansion curve for the polymer–ceramic composite equivalent to that obtained from annealed samples and a superimposed relaxation strain versus temperature curve. The latter arises

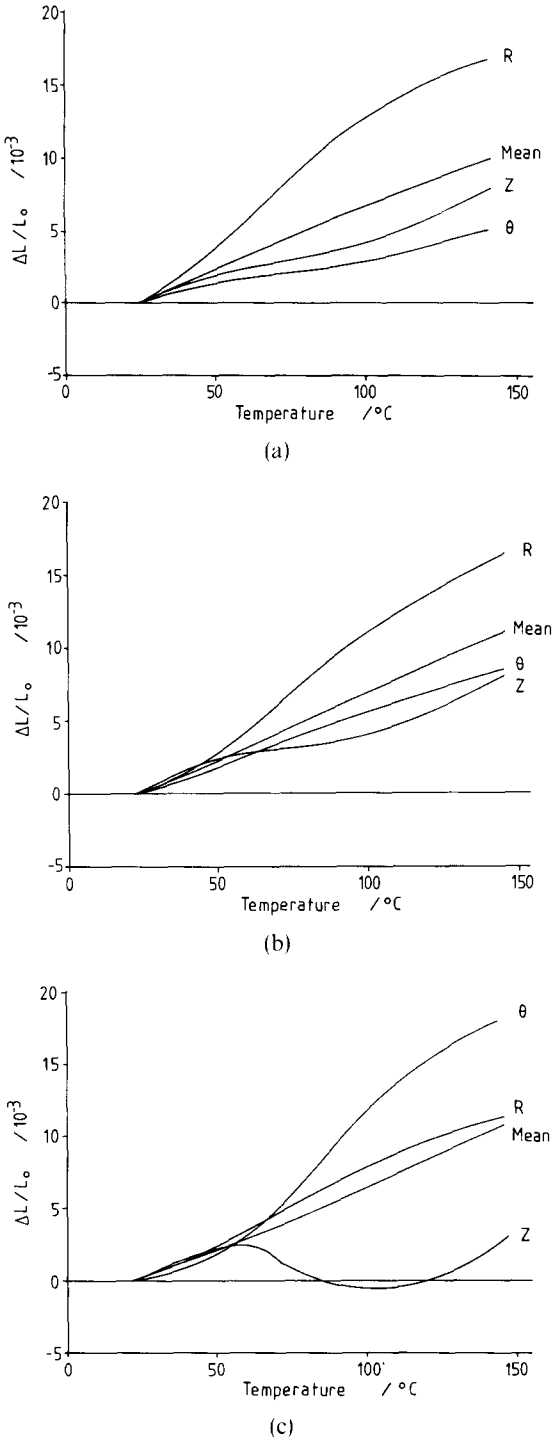


Fig. 7. Apparent thermal expansion curves in the θ, R and Z directions for samples taken from the three positions defined in Fig. 2 for a heated sprue moulding with hold pressure 54 MPa and mould temperature 20°C. (a) position 1; (b) position 2; (c) position 3.

from dilations or contractions caused by anisotropic heterogeneities in the solidified suspension. The reproducibility of the results reported in this paper is established in part by duplicated runs and partly by the cross-referencing described in Table 1.

Previous work showed that there was no significant difference in crystallinity between samples cut from moulded plaques which have been subject to fast cooling and annealed samples.[2] It also showed no significant difference in density between moulded

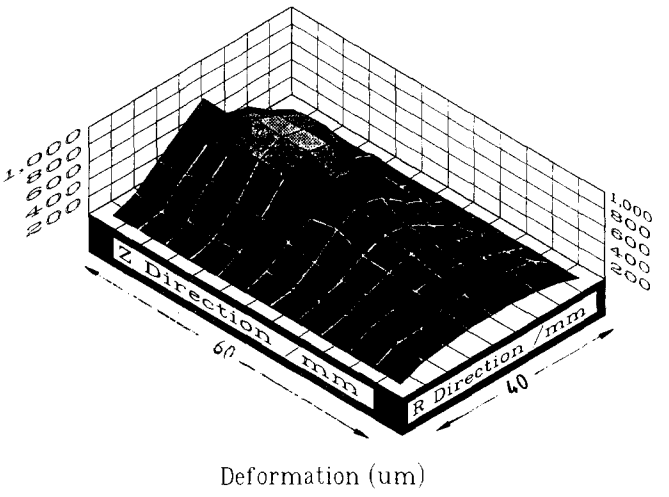


Fig. 8. The profile of the cut and annealed moulding shown in Fig. 6(c) obtained by the contact LVDT transducer survey.

or annealed samples. The density and loss on ignition for samples taken at each position for samples in Fig. 7 were also measured (Table 2). Within the ranges of experimental error, no difference in either quantity can be detected.

The absence of a specific volume difference is compatible with the observation that the average linear expansion in the θ, R and Z directions corresponds with the curve for annealed samples. The fact that the average expansion curves, densities and powder loading are the same in each position of the moulding (Fig. 7 and Table 2) shows that there is no difference in ceramic volume loading with position. Such a difference would have a dramatic influence on thermal expansion[1] because of the difference in expansion coefficients of continuous and dispersed phases but could not, of course, produce a negative apparent coefficient. The absence of a disparity in density also relieves the discussion of the need to consider microvoid effects at the polymer–filler interface under the influence of restrained shrinkage in the cavity. The fact that annealing brings the expansion behaviour back to a consistent value implies that particle orientation is not a cause of anomalous expansion. The anomaly

Table 2. Density and loss on ignition for samples cut from positions 1, 2 and 3 for a heated sprue moulding with hold pressure 54 MPa and mould temperature 20°C

Position	*Density*			*Loss in ignition (%)*[c]
	Mean	*95% CL*[a]	n[b]	
1	2·685	0·015	4	13·93
2	2·683	0·001	4	14·02
3	2·677	0·014	4	14·08

[a] 95% Confidence limits from 't' distribution for small populations.
[b] Number of samples tested.
[c] Maximum error ±0·5%.

would persist until extensive particle reorientation to a random state was obtained.

Eliminating from the discussions therefore, density, composition, particle orientation and fractional crystallinity effects, explanations in terms of residual stresses, orientation either in the amorphous or crystalline regions or anisotropies and heterogeneities in crystalline morphology in the organic phase remain.

Residual stresses are expected to relax in the region 60–140°C because the stearic acid fraction of the blend becomes molten independently at ~60°C and the polypropylene is substantially atactic with only 30% crystallinity overall. If the observed strains are solely attributed to residual stresses, however, the resulting stresses would be exceedingly large. For the Z direction in Fig. 7(c), for example, the overall thermal expansion is the sum of the expansion and a negative strain resulting from a residual tensile stress. The Young's modulus of the composition at room temperature is ~7 GPa,[13] giving rise to an apparent tensile stress of 70 MPa. The sample clearly should have fractured. The act of cutting the 5 mm cube samples should itself largely have released residual stresses. Furthermore, direct measurement of in-plane residual stresses in plaque mouldings of the same material, employing the layer removal technique, suggests that heated sprue mouldings present very low residual stresses.[11] This is in agreement with the theoretical work of Mills[10] who states 'The level of residual stress can be reduced by any method that minimizes the variation in the cavity pressure during solidification.'

It is well known that shear flow, especially during mould filling, can introduce orientation in macromolecules. In its simplest form, molecules which are fixed by the solidification front are extended by flow adjacent to the solidified layer. However, it is generally held that recovery takes place during the slow process of solidification in a large section. Thus orientation tends to be more pronounced at the surface of mouldings, yet some of the most dramatic anomalies in thermal expansion in these ceramic mouldings are seen in samples cut from the centre of 40 mm diameter sections which have experienced long cooling times.

Nevertheless, the 5 mm cubic samples used for dilatometry commence relaxation at 60°C under heating rates of 4°C min^{-1}, as indicated by departure of the data from the path followed by the annealed reference. Furthermore, the material adjacent to the polished section (Fig. 5) undergoes relaxation on heating to 120°C. The implication is that in a heavily filled system relaxation phenomena are constrained by the particle network. Two operations appear to be necessary for recovery to take place; removal of restraint by cutting and molecular mobility resulting from heating. Loss of polymer during pyrolysis would meet both requirements.

Thus a molecule which is attached by adsorption, perhaps at sites which have become oxidised during processing, to more than one particle can only change its conformation if particles move with respect to each other throughout the network.

The crystalline morphology of polymers is also influenced strongly by pressure and flow history and such effects can be detected in unfilled polymer mouldings by X-ray diffraction studies.[14] Such studies are presently impeded in samples of the type considered here by the high ceramic loading. Furthermore, crystallisation of oriented macromolecules can give rise to very high levels of contractility in the direction of orientation during subsequent melting.[15] The strains are comparable to or greater than those reported here. Oriented crystallinity can develop in a system which is cooled under conditions where the length is held constant,[15] which may be the case in ceramic mouldings where the solidified layers have low compliance. The observations reported here show that contractility is observed in mouldings made with very low static hold pressures (heated sprue) and in with very high oscillating hold pressures. It is easy to see how dramatic flow-induced orientation occurs as the temperature falls into the solidification range in the latter case. In the former case, the pressure is low and constant, although the heated sprue allows sufficient flow to compensate for shrinkage. The full explanation for the observed anisotropic and heterogeneous strains must accommodate both these situations, together with the impediment to recovery during slow cooling of mouldings. At present the authors cannot offer an unequivocal explanation for these phenomena but they draw attention to their very considerable importance for ceramic fabrication in which the aim is to place particles in contact ready for sintering.

4 Conclusions

Dilatometry on small samples cut from an injection moulded ceramic–polymer body reveals gross anisotropy and heterogeneity. The relaxation strains are also visible to the naked eye when the body is sectioned, polished and annealed. Removal of restraint, together with thermal treatment are necessary for relaxation to take place. Thus the particle network appears to prevent relaxation during cooling after moulding. The effects are too large to be caused by residual stress and appear to be related to flow-induced orientation or to orientation set up during restrained shrinkage. The recovery strains

are so large that they must be given serious attention as potential sources of defects in large ceramic mouldings which may arise during removal of the organic vehicle. The recovery strains are expected to influence particle positions and, if particle movements are locally organised during pyrolysis, may give rise to cracks independently of the pyrolysis conditions.

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