Int. J. High Technology Ceramics **2** (1986) 1–31

Review: Fabrication of Engineering Ceramics by Injection Moulding. I. Materials Selection

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SUMMARY

The present article, Part I, reviews the literature on ceramic powders and organic polymers used to compound ceramic injection moulding mixtures. The intention is to distil, from a somewhat diverse literature, guidelines for the proper selection of materials, with the aim of facilitating the development of the defect-free moulding of ceramic components. Part II will examine mixing methods, moulding techniques and procedures for removal of the organic vehicle prior to sintering.

1. INTRODUCTION

Recent surveys of the world market for ceramics[1–5] show that, while ceramics in electrical and electronic engineering are well established with a high growth rate,[6] the structural ceramics market is at an earlier stage of development but that the demand for ceramic components in heat engines is poised to reach high levels by the turn of the century.[5]

One of the principal difficulties to be overcome before structural engineering ceramics can be fully exploited, especially in heat engine components, concerns fabrication of shapes from powders. At present the ability to produce complex shapes of high dimensional accuracy, high strength and uniformity with low scrap rates and at reasonable cost eludes the industry. Two techniques, i.e. slip casting and injection moulding, offer versatility. In addition injection moulding offers automated production at high rates.

Int. J. High Technology Ceramics 0267-3762/86/$03·50

In the injection moulding route the following stages in the fabrication process are necessary[7] and need to be developed to a level that precludes the introduction of strength-limiting defects:

1. Compounding, which involves the mixing of ceramic powder with an organic vehicle to confer sufficient fluidity to fill the mould under available machine pressures.
2. Injection of the mould cavity without introducing moulding defects.
3. Removal of the organic vehicle without disrupting the powder body.
4. Sintering of the body to near full density.
5. Final machining.

It is generally considered that for most reciprocating engine components moulding accuracy should be sufficient to dispense with expensive machining. However, the sensitivity of gas turbine efficiency to blade profile and the importance of surface finish suggest the need for a slight final machining for some components.

Only stages 1–3 are novel to the ceramics industry. The present review confines itself to the selection of materials, principally the powder properties and the components of the organic vehicle. A subsequent publication[8] will review machinery development and binder removal methods.

Although injection moulding has been used for natural polymers since the 19th century, in its present form it was first used for fabrication of spark plug insulators in 1937,[9] only to be replaced later by isostatic pressing. There are, however, patented moulding techniques which are conceptual precursors of injection moulding for ceramics. A patent by Miller[10] describes a device in which an extruder is registered with an open mould. Later patents[11] describe a device in which air is used to confer fluidity to a dry powder and to force it into a mould. There is an uninterrupted record of the development of ceramic injection moulding in the patent literature since the 1930s as listed by Hennicke and Neuenfeld.[12] Nevertheless, reports on this technique began to appear in the scientific literature only recently, probably for two major reasons. First, the pressureless sintering to near full density of fine powders of covalently bonded silicon-based ceramics became realistic in the 1970s,[13–17] opening up the possibility of producing complex shapes without expensive high pressure processes or machining. Secondly, the revolution in materials selection for critical engine parts has focussed on ceramics for the reciprocating engines, gas turbine[18,19] and rocket[20] engines. Although ceramic injection moulding techniques are not yet sufficiently developed to qualify as a significant fabrication process, it is clear that many organisations are developing this technique for the net shape fabrication of complex structural ceramic components.[21–38] Component complexity and the need for large-scale production suggests that the most feasible manufacturing technique is injection moulding.[38]

According to Strivens[39] components with dimensions from 2·5 to 25 mm can be made to a tolerance of 1%. In addition the components produced would have the surface finish demanded for thread guides and wire drawing dies.[40] The only disadvantages are the rather complicated binder removal process and high tooling costs.[41]

A characteristic of published work on ceramic injection moulding is that the literature is frequently silent on crucial experimental detail. This arises from the difficulty of defending proprietry knowledge of optimum organic vehicle components. Neither is there a logical theme to the development of this technology; much work is haphazard in its empirical approach. It is only in recent years that systematic studies[30,35–38] have begun in earnest.

2. CERAMIC POWDER

2.1. Shrinkage considerations

Most of the candidate materials for engineering ceramics applications have been subject to injection moulding studies, principally silica,[42] silicon for the fabrication of reaction-bonded silicon nitride,[43] silicon nitride itself,[44] silicon carbide,[45,46] alumina and zirconia.[47] The powder characteristics have a strong influence on the green density and mechanical strength of the body after binder removal and on the viscosity of the moulding mixture. It is important to achieve a high green density for a given powder not just because the error in firing shrinkage increases as the overall shrinkage increases[39] but because failure to achieve a near-maximum powder volume fraction in a polymer may result in the body slumping or distorting during removal of the organic vehicle. What is perhaps more important than the net green density is the uniformity of powder packing throughout the moulded body. Non-uniform shrinkage during sintering resulting from poor mixing of polymer and ceramic may result in a type of distortion which, as for example in thin aerofoil sections, cannot be corrected by subsequent machining.

There are several contributions to shrinkage in the injection moulding process which must be taken into account in die design. In the first place there is a shrinkage of the moulded body by thermal contraction during cooling in the cavity. Typical coefficients of expansion for polymers used in ceramic moulding, together with shrinkage to be expected by cooling from the melting point to room temperature (20°C) for a typical 35 vol%

TABLE 1
Typical Melting Points and Coefficients of Thermal Expansion for Polymers used in Ceramic Moulding Together with Shrinkage to be Expected for a 35 vol% Formulation with Silicon Nitride[a] on Cooling from Melting Point to Room Temperature

Polymer	*Melting point/°C*	*Thermal expansion coefficient/ MK^{-1}*	*Thermal expansion coefficient of formulation/ MK^{-1}*	*Shrinkage on cooling from melting point to 20°C/%*
Polypropylene	171	80	31	0·5
Low density polyethylene	132	190	69	0·8
Polystyrene	240	70	27	0·6

[a] Thermal expansion coefficient, 3·8 MK^{-1}.

polymer blend with silicon nitride, are given in Table 1.[48,49] If the polymer is partially crystalline there is a shrinkage associated with solidification. Specific volumes for amorphous and crystalline components of typical polymers are given in Table 2.[50] When the organic vehicle is removed there is a further slight shrinkage associated with the drawing together of particles by capillary action. In a moulding composition there must be excess vehicle to prevent the particles contacting or the composition would be too viscous to enter the mould. Finally, the largest shrinkage contribution is caused by pore removal during sintering.

In practice, using conventional metrology equipment the moulding shrinkage (S_m) can be found from the dimensions of the moulded body L_1 and the mould itself L_0:

$$S_m = \frac{L_0 - L_1}{L_0} \tag{1}$$

The small shrinkage due to polymer removal involves accurate measurements on an extremely fragile body and is normally included in the sintering shrinkage S_s:

$$S_s = \frac{L_1 - L_2}{L_1} \tag{2}$$

where L_2 is the dimension of the as-sintered body.

Thus the final dimensions are related to the die dimensions by

$$S_s = 1 - \frac{L_2}{L_0(1 - S_m)} \tag{3}$$

and since $S_m < 0{\cdot}02\, S_m \approx -\ln(L_1/L_0)$.

TABLE 2
Specific Volumes for Amorphous and Crystalline Components of Polypropylene, Low Density Polyethylene and Polystyrene

Polymer	*Specific volume/m³ Mg⁻¹*	
	Amorphous	*Crystalline*
Polypropylene	1·128–1·233	0·986–1·032
Low density polyethylene	1·172–1·176	1·060–1·073
Polystyrene	0·950–0·977	0·888–0·898

If the final relative density ρ_s is known the volume fraction V of powder in the moulded body can be related to the sintering shrinkage S_s by

$$1-\frac{V}{\rho_s}=3S_s-3S_s^2+S_s^3 \tag{4}$$

(The common approximation $1-(V/\rho_s)=3S_s$ should be avoided as it introduces a large error: 17% for a linear shrinkage of 15%.)

This equation assumes that shrinkage is uniform in all directions and that there are no volume dilations associated with phase changes during sintering.

2.2. Effect of powder on viscosity

The volume fraction of powder in the injection moulding blend is limited by the viscosity of the powder–fluid mixture which increases steeply as $V>0{\cdot}5$. The derivation of the filler volume dependence of viscosity has an identical mathematical derivation to the filler volume dependence of the elastic constant for particle-reinforced composites.[51] The first theoretical treatment was due to Einstein[52] but was valid for very dilute systems of spherical particles at volume fractions less than 0·1:[53]

$$\frac{\eta}{\eta_0}=1+2{\cdot}5V \tag{5}$$

where η is the viscosity of the suspension and η_0 the viscosity of the fluid.

Subsequent treatments have attempted to extend the theory to concentrated suspensions and non-spherical particles; these have been reviewed by Rutgers[54] and Frisch and Simha.[55]

Eilers[56] used an equation of the type

$$\frac{\eta}{\eta_0}=\left(1+\frac{1{\cdot}25V}{1-(V/V_{\max})}\right)^2 \tag{6}$$

where $V_{\max}$ is the maximum space filling efficiency for uniform-sized spheres ($V_{\max}=0{\cdot}74$) and this gave a fit with results of experiments for emulsion systems where particle sizes ranged from 1·6 to 4·7 μm. In fact this particle size range is too large to use $V_{max} = 0{\cdot}74$ and this has been a source of criticism.[57] One important approach was to consider a general power-series equation in volume fraction:

$$\frac{\eta}{\eta_0} = 1 + k_1 V + k_2 V^2 + k_3 V^3 + \cdots \tag{7}$$

where k values are constants and $k_1 = 2{\cdot}5$ from Einstein's treatment.[52] Several workers have established different values for k_2 and k_3 and these attempts have been reviewed by Goodwin.[58] De Bruijn[59] assumed that eqn (7) was a quadratic and that the relative viscosity η/η_0 would become infinite when the volume fraction reached the value for the cubic close-packed spheres. The value of k_2 then becomes 4·7 but increases slowly as the packing fraction decreases. Vand[60] assumed that after collision two particles, considered as monosized spheres, would separate along rectilinear paths and this led to an equation of the form

$$\frac{\eta}{\eta_0} = 1 + 2{\cdot}5V + 7{\cdot}349V^2 \tag{8}$$

This was found[61] to fit experimental data for glass spheres in a glycerol solution up to a concentration of $V = 0{\cdot}5$. Subsequently, Manley and Mason[62] and Mooney[57] have shown that Vand's assumption[60] was not fully justified, as it can be proved that paths of recession of two colliding spheres are curvilinear and mirror images of their paths of approach.

At very high concentrations a large number of terms in eqn (7) would be required to calculate η/η_0 and the higher power terms would have an increasing influence on the value obtained.

Another more acceptable approach was to consider an infinite power-series in a general form of an exponential function:

$$\frac{\eta}{\eta_0} = \exp(2{\cdot}5V) \tag{9}$$

Equation (9) has been modified by including a factor h so that it satisfied disperse systems in general:[54]

$$\frac{\eta}{\eta_0} = \exp\left(\frac{2{\cdot}5hV}{1 - hV}\right) \tag{10}$$

Mooney[57] has developed an identical equation for monodisperse spheres, in which he took into account the crowding of particles in concentrated suspensions:

$$\frac{\eta}{\eta_0} = \exp\left(\frac{2{\cdot}5\,V}{1 - k\,V}\right) \tag{11}$$

where k was called the crowding factor; $k = 1/V_{\max}$ where $V_{\max}$ is the volume fraction for maximum packing. Spheres in a cubic close-packed lattice ($V_{\max} = 0{\cdot}74$) were considered to exhibit infinite viscosity because of mechanical interlocking. Simple cubic packing ($V_{\max} = \pi/6$) was taken to provide the greatest density which would permit continuous movement. Thus the lower and upper limits of k are

$$1{\cdot}35 < k < 1{\cdot}91$$

Mooney[57] has pointed out that Vand's theory[60] gives a k value of 0·61 which was well outside the limits of k. He points out that Vand's experimental observations[60] can be made to fit his equation if $k = 1{\cdot}43$.

Brodnyan[63] extended Mooney's equation, shown as eqn (11), to ellipsoidal particles:

$$\frac{\eta}{\eta_0} = \exp \frac{(2{\cdot}5\,V + 0{\cdot}399(p-1)^{1{\cdot}48}\,V)}{1 - k\,V} \tag{12}$$

where p is the axial ratio. This equation was found to fit experimental data up to $V = 0{\cdot}55$. This was extended on an empirical basis by Kitano *et al.*[64] to give a relationship for acicular particles:

$$\frac{\eta}{\eta_0} = 1 - \frac{V}{0{\cdot}54 - 0{\cdot}0125p} \tag{13}$$

Krieger and Dougherty[65] derived an equation by a modification of Mooney's analysis:[57]

$$\frac{\eta}{\eta_0} = (1 - kV)^{-2{\cdot}5} \tag{14}$$

and this has found experimental justification.[66]

The work of Chong *et al.*[67] has shown good fit between experimental results and an equation of the type

$$\frac{\eta}{\eta_0} = \left(1 + \frac{0{\cdot}75\,V/V_{\max}}{1 - (V/V_{\max})}\right)^2 \tag{15}$$

for $V/V_{\max}$ close to unity.

2.3. Effect of particle size distribution

Equations (5)–(15) are valid for particles of uniform diameter and near spherical shape and it is pertinent to note that modern developments in ceramic powders[68,69] are yielding materials which closely meet those conditions. In fact the requirement for uniform shrinkage without discontinuous grain growth during sintering imposes the requirement of near uniform particle size, for which, given sphericity, $V_{max} \simeq 0{\cdot}74$. The disadvantage of this approach is the low green density and consequent high sintering shrinkage compared to the more traditional approach of achieving high green density by blending of particle sizes.

Clearly if a range of particle sizes is present the value of the crowding factor *k* in Mooney's equation[57] changes. Unfortunately, fit with experiment has usually been obtained by choosing rather than deriving a suitable value of *k*. Theories on the viscosity of polydisperse systems have been developed by Lee[70] and by Farris.[71] Chong[67] has also developed his own equation to consider more complex particle size distributions. In general, the incorporation of more than one particle size leads to a decrease in viscosity for the same volume fraction of powder but it is generally insufficient to replace *k* with a new, higher packing efficiency.

There are cases in the fabrication of ceramics where a wide distribution of particle sizes can be accommodated without consequent grain growth during sintering. One such case is the fabrication of reaction-bonded silicon nitride where vapour phase reactions refine the grain size during nitriding[72] and Mangels[43,73] has made use of the reduced viscosity of wide size distribution powders to produce injection moulding blends of high powder loading (73·5 vol%).

Farris[71] attempted to predict the viscosity of multimodal suspensions from data for monomodal suspensions. For uniform spherical particles viscosity increased steeply after $V = 0{\cdot}5$, approaching infinity at $V = 0{\cdot}74$. However, if the total volume of particulate filler is split into 25% fines and 75% coarse, very high loading can be obtained without increase in viscosity; this is shown in Fig. 1. If the ratio of the coarse to fine particle diameters is 7:1 the volume of filler can be increased to $V = 0{\cdot}73$ from the monomodal loading of $V = 0{\cdot}59$ without increase in viscosity. Figure 2 shows the proportion of coarse and fine particles to give minimum viscosity for a range of total filler loading, indicating minima in the region of 30% fines.

Strivens[74] attempted to analyse the influence of particle size distributions on the packing characteristics and filler loading in an injection moulding mix. He observed that one intermediate milling time yielded a powder with improved flow behaviour during moulding but this material was not characterised. A patent by Waugh[75] states that better mixing was obtained if fines were added to the mix when using a bimodal powder distribution for investment casting cores. In 1978, Mangels[43] working with silicon powder obtained particle size distributions by dry ball milling and air classifying as shown in Fig. 3, and subsequently showed that a 140 h dry

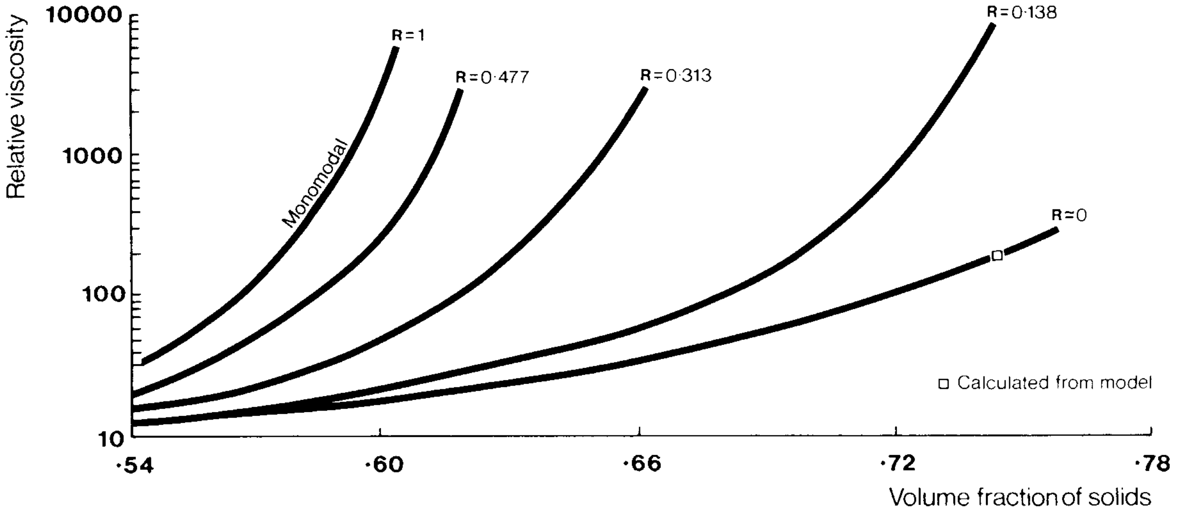

Fig. 1. Calculated and measured viscosities of monomodal and bimodal suspensions; after Farris.[71] R = (mean fine particle size)/(mean coarse particle size).

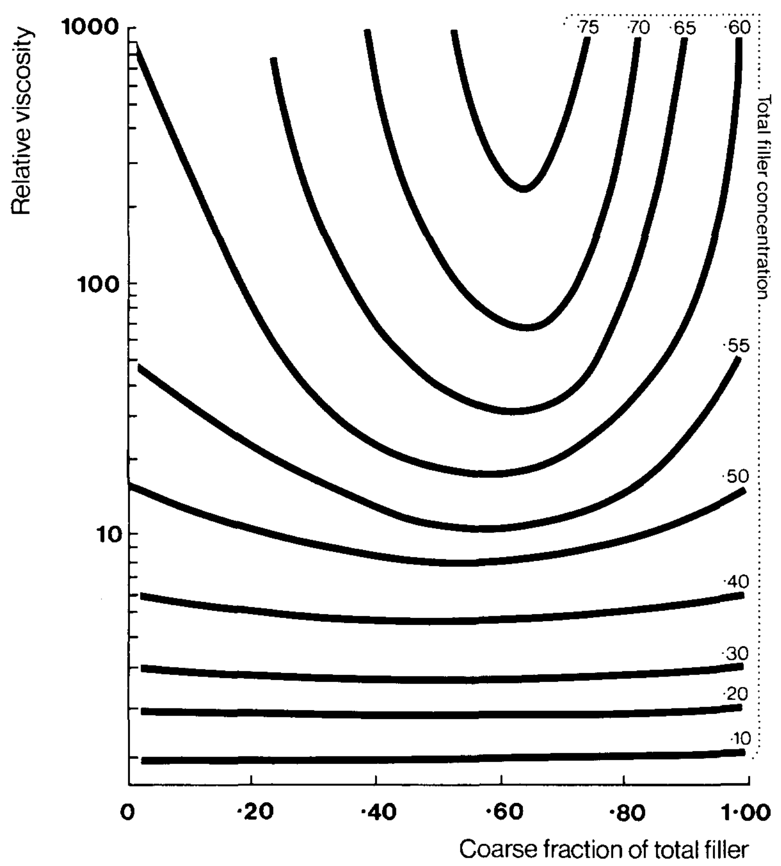

Fig. 2. Comparison of calculated viscosity for bimodal suspension for various blend ratios and concentrations; after Farris.[71]

ball-milled powder with the broadest particle size distribution yielded the best viscosity in a spiral flow mould test.[73] In general, by altering the particle size distribution from a sharp, monomodal type[76] distribution to a very broad distribution the solids content can be increased without increasing the viscosity of the system.[41] Similar requirements have been noted by Adams[77] for slip cast ceramics and there is a similarity with the requirements for achieving high green density in a pressed powder.[78–80]

2.4. Effect of particle size and shape

Matsumoto and Sherman[81] found k, the crowding factor defined by Mooney,[57] to be very sensitive to mean particle size. In contrast, Barsted *et al.*[82] found only a small variation in k over a broader particle size range than that employed by Matsumoto and Sherman.[81] Thus the value of k does not vary systematically with particle size.

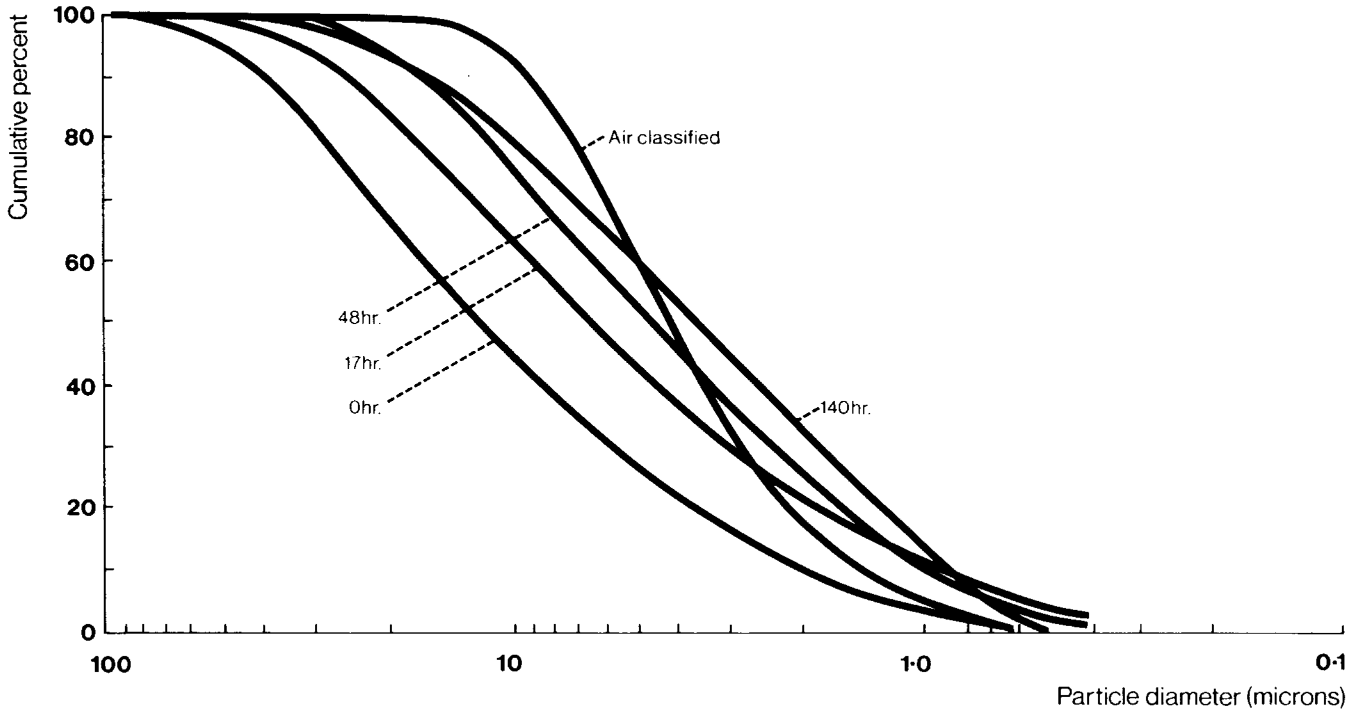

Fig. 3. Particle size distribution curves for silicon, dry ball-milled for various times; after Mangels.[43]

This is not surprising as eqns (5)–(15) do not allow for an effect of overall particle size on viscosity. Yet this effect has been noticed.[83,84] It was found that viscosity sometimes increased as particle diameter decreased and this has been attributed to an adsorbed immobile layer on fine particles which effectively increases particle diameter[83] and hence total filler loading. Willermet *et al.*[46] report a halving of spiral flow length during moulding, caused by a decrease in mean particle diameter from 28 to 10 μm. There does not appear to be a sound explanation for this but the respective particle size distributions were not given.

A further explanation of the effect of particle size on viscosity for a fixed volume loading may be sought from the combined effects of particle size and shape. The effect of non-spherical morphology on the viscosity of suspensions may influence both the packing efficiency of the powder V_{max} and the effective radius of rotating particles in shear. Mangels and Trela[41] therefore preferred a spherical particle morphology to obtain maximum prefired densities. The effect of shape on V_{max} is shown in a study of vibratory compaction of spheres and angular particles.[85] For spherical particles the packing efficiency is not influenced by particle diameter, but as the number of sides of the particle considered as a regular polyhedron decreases, i.e. as the particles become more angular, the effect of particle diameter on the packing efficiency becomes more pronounced and packing efficiency decreases with decreasing particle diameter. This may help to explain the results of Willermet *et al.*[46] mentioned above. An apparent contradiction to this effect was noted by Mutsuddy[47] who found that a higher proportion of angular alumina particles than spherical zirconia particles could be accommodated in injection moulding blends. However, since the particle size distribution of the two powders was different, this is inconclusive.

2.5. Effect of agglomerates

The viscosity of ceramic injection moulding blends is also influenced by the tendency of fine particles to agglomerate. The adhesion forces between particles have been discussed by Rumpf and Schubert.[86] In addition to electrostatic and van der Waals' forces the presence of liquid and solid bridges contribute to high agglomerate strength. The initial drying of powders and the heating associated with processing with a high molecular weight organic vehicle help to reduce the effect of liquid bridges. The presence of solid bridges when a small amount of additive has been incorporated in the powder via a salt by spray drying, such as magnesia in alumina or yttria in zirconia, gives rise to more serious problems. Such agglomerates can only be broken down by milling of the powder or by using mixing devices which impose high shear stress to the blends.

The dispersion of powders in liquids is influenced in part by the wetting characteristics of the liquid on the solid surface. The dispersion of ceramic titanate powders in a range of organic liquids has been related to the hydrogen-bonding capability of the liquid[87] which can be expressed as its cohesive energy density.[88] In systems where it is not possible to change the entire liquid phase the interfacial interactions can be modified by so-called coupling agents added as pre-treatments to the powder or directly to the melt. One of the simplest such surface-active agents is stearic acid which has found frequent use[32] as a minor vehicle component.

The effect of such coupling agents on viscosity is a matter of controversy. Intuitively, if agglomerates are dispersed, the particle size distribution would be evened out and, according to the arguments presented above, the viscosity should increase. This has been observed by Bigg[89] using low density polyethylene and 5–44 μm steel spheres at 60% volume loading. Addition of a silane and a titanate coupling agent increased the viscosity of the blend considerably. However, this effect cannot be attributed entirely to the breakdown of agglomerates since the starting powder was not well agglomerated. Results of such experiments are surprisingly contradictory. Han *et al.*[90] report that both organic and silane coupling agents reduced the viscosity of calcium carbonate-filled polypropylene but that organic titanate coupling agents increased the viscosity of polypropylene–glass systems. Bretas and Powell[91] found that both titanate and silane coupling agents increased the viscosity of polyethylene–40 vol% glass. Other workers[92–94] observed decreases in viscosity due to coupling agents. Much of the confusion may be due to the *ad hoc* way in which the quantity of coupling agent is added; typically 0·2–2 wt% based on the filler.[95] The adsorbed coupling agent may hold a layer of polymer tightly to the particle, thus increasing its effective diameter and the effective volume fraction of filler. The excess coupling agent, being a bulky low molecular weight species, may act as a plasticiser for the polymer.

The confusion that surrounds the role of agglomerates is not helped by the suggestion of Mutsuddy[47] that agglomerates raised the viscosity of injection moulding blends contrary to the above arguments. Precise density determinations are needed to assess the increase in effective volume fraction of powder due to undisplaced gases.

3. OPTIMUM ORGANIC VEHICLE CONTENT

There is at present no simple way of calculating the optimum organic vehicle content for different types of powder from powder characteristics. In a patent Bailey[96] stated that the binder concentration should be at least 2 vol% in excess of the void volume and that it can vary from 102 to 115% of the void volume where the ceramic particles should be just ‘floating’ in minimum binder. Mutsuddy[97] has applied a technique used extensively in the printing ink industry and in the characterisation of carbon black fillers for elastomers. A torque rheometer was used to provide a quantitative assessment of the critical powder volume concentration in the plastic forming of ceramic mixes. In this technique, the ceramic powder was mixed with an oil, the oil being added at a constant rate. The volume of oil at which the maximum torque occurred was used to obtain the critical powder volume concentration (CPVC). The CPVC value differs slightly in practice from the optimum powder loading for different powder types but the method considerably shortens an extensive experimental optimisation process.

4. SELECTION OF ORGANIC VEHICLE

For the extrusion of ceramics it is sufficient that an organic vehicle should confer fluidity to the powder. For injection moulding it must also be possible to bring about a change in material properties of the mixture, during residence in the cavity, such that the moulded article has sufficient resistance to shear stresses to withstand knock-out and handling. This change in properties should obviously take place within a reasonable time. Clearly, although dimensional tolerances can be rectified by minor post-sintering machining operations, the distortion of moulded components during ejection or handling results in scrap.

These requirements can be met by the cooling, in the cavity, of thermoplastic, both crystalline and amorphous, or the freezing of water-based polymer solutions. The crosslinking of thermosets by injection into a heated cavity fulfils the same requirements, as indeed does the thermogelling of water-soluble polymers.

Organic vehicle systems used to injection mould ceramics are almost exclusively composed of two or more components. The components used can be classified into one of four categories:[98]

1. *Major binder component:* This material determines the general range of final binder properties.
2. *Minor binder component:* Often used is a thermoplastic or oil which is removed early in the binder removal cycle. It is often claimed that this generates pore channels to the interior part allowing easier removal of the other components;[98] however, this is undoubtedly an over-simplification.
3. *Plasticisers:* The function of these minor additives is to increase the fluidity of the ceramic–binder mixture.

4. *Processing aids:* These minor additives are used mainly as surfactants to the ceramic powder. They improve the wetting characteristics between binder and ceramic during mixing.

Selection of the organic vehicle system to suit the ceramic powder is necessary for successful moulding but as yet selection has been more a matter of experience than a scientific development.

4.1. Selection criteria

Qualitatively, the major binder should present the following properties (there is at present insufficient published work to define quantitatively the upper and lower bounds of such properties):

—Confer fluidity upon the powder sufficient for defect-free filling of the cavity.
—Wet the solid powders in order to aid dispersion and remove entrapped gas.
—Show stability under mixing and moulding conditions.
—Confer adequate strength to the body during the initial stage of polymer removal.
—Leave a low residue after burn-out.
—Have an adequate shelf life.
—Be readily available at acceptable cost.

A plasticiser has been referred to as a high boiling solvent possessing an affinity for various kinds of polymers.[99] In the ceramic injection moulding context it should present the following properties:

—Compatibility with the binders: It should not react but form an intimate mixture with the binders increasing the free volume of the polymer and thereby lowering viscosity.
—Low volatility: This ensures the retention of the plasticiser compound during processing which is necessary for consistency of ceramic powder volume loading.

The processing aid may consist of more than one component. Ideally, a low cost processing aid is required and it should perform the following functions:

—Modify adhesive forces between polymer and filler, thus dispersing the organic vehicle components throughout the mix and enhancing deagglomeration of filler particles.
—Reduce melt viscosity.
—Allow easy mould release.

The criteria for the selection of an organic vehicle system is that it will, first, give correct rheological properties to the ceramic–binder mix during injection moulding and, secondly, become amenable to successful removal.

Rheology of these systems has been studied extensively by researchers using the capillary rheometer.[100] Spiral-flow measurements too have been cited by several workers.[46,48,100] The use of spiral flow moulds to assess the mould-filling ability of a material is well established and has greater similarity to the moulding situation than the more exact flow curves obtained by rheometry.[101] Mutsuddy[47] has also used a dynamic oscillatory-type viscometer to minimise particle migration effects that may be present in capillary rheometer measurements wherein the material at the capillary wall may be depleted in powder. However, this method has less similarity to injection moulding conditions.

The major difficulty at present is the task of arriving at a model to relate experimental observations to the flow behaviour during actual injection moulding. Attempts to use models, like the Weir model,[102,103] suitable for straight polymers have been found to be unsuccessful.[100] Computer modelling of fluid flow during injection moulding[104] is being investigated in order to develop models suitable for ceramic–binder systems.

Therefore, qualitative and semi-quantitative guidelines for the ceramic–binder system rheology have been advocated. Firstly, the formulation should have either Bingham or pseudoplastic flow characteristics. It has been found that if the mix has a very high yield stress it extrudes into the mould cavity like a thread of ribbon that coils upon itself, tending to trap air and induce mechanical stresses.[38] On the other hand, a very low yield stress has caused the moulded part to deform in the binder removal stage.[38] Moore[105] described a method by which the yield stress can be estimated from capillary rheometer data but this construction cannot be applied to some high polymer systems.[106] It has been claimed that good flow during injection moulding requires a viscosity of less than 1000 Pa s (10^4 Poise) in the shear range usually encountered in the gates and mould, which ranges between 100–1000 s^{-1}, although it could occasionally reach 10 000 s^{-1}.[47] Thus, it can be inferred that a suitable ceramic–binder system mix should have viscosities below 1000 Pa s in the 100–1000 s^{-1} shear range. Recent work has attempted to define parameters from capillary rheometer results and relate these to the mouldability of formulations.[106] The parameters selected were the gradient of the viscosity shear rate graph, the fluidity, and the rate of change of viscosity with temperature. The analysis was performed at the shear rate and temperature at the nozzle (entry to the mould). Extraction of organic vehicles from injection moulded ceramics is a potentially time-consuming operation. Thermal degradation of the organic vehicles has been widely used and the relevant parameter is the decomposition rate[107] in the bulk which frequently differs considerably from the decomposition of thin films. The decomposition rate can be controlled by the selection of a proper binder system, containing a mixture of polymers with different decomposition characteristics, in order to broaden the burn-out region.[108,109] Solvent extraction,[110] evaporation[111] and capillary action to remove the organic vehicles[112] have also been used and these impose different criteria. Capillary action requires low viscosity systems such as waxes or oils. Evaporation under reduced pressure was viable with paraffin waxes[111] and solvent extraction has been found to function with partially oxidised waxes blended with coumarone-indene resin.[110]

5. POLYMER SYSTEMS IN USE

Polymer systems may be broadly classified as thermoplastic or thermosetting.

A subsidiary classification could be made according to the demands of the blending and moulding equipment.[8] Some moulding equipment uses low pressures and therefore low viscosity mixtures[112] and is close generically to resin casting, employing mainly oils and waxes. Mixtures of intermediate viscosity, low molecular weight thermoplastics and thermosetting resins can be prepared by using blade-type mixers. The full benefit of high shear mixing and high pressure moulding can only be obtained with high molecular weight thermoplastics.

Much of the published work on organic vehicle formulations is deficient in precise experimental technique and this has often made it difficult to interpret the significance of results.

5.1. Thermoplastic systems

Many thermoplastics which are themselves routinely injection moulded satisfy most of the conditions stipulated in order to be effective binders and have been used extensively, especially for silicon-based ceramics. Japanese patent publications[113] mention a mixture that includes a styrene–butadiene copolymer. In this instance diethyl phthalate was used as a plasticiser and stearic acid as a lubricant. In another instance a mixture of styrene–butadiene copolymer and thermosetting resins has been used.[114] Polyolefins such as polyethylene, polypropylene or polybutene are first recorded in use in the United States.[115] In this case, however, the binder was added in large amounts which gave rise to problems in removal and dimensional control.

Partial substitution with substances like wax, phthalic acid, stearic acid or low boiling point oils has been recommended.[116] A mixture of polystyrene plasticised with light oil and beeswax[116] has also been attempted but when incorporated in large proportions the light oil tended to coagulate during injection moulding. Since a large volume fraction of oil and resin was used in the ceramic mixture a low green density resulted. Diethyl phthalate has been employed as a substitute for light oil.[116]

More recently, atactic polypropylene was used as a successful injection moulding mix.[117,118] It is reported that atactic polypropylene rendered the mix sufficiently fluid for injection moulding and also allowed the thermal decomposition rate to be freely adjusted. The latter effect was made possible by mixing different fractions, having molecular weights of 5000–12 000. This patent goes on to state that an even more effective injection moulding formulation was achieved by adding other thermoplastic resins such as ethylene vinyl acetate, polystyrene and polymethylmethacrylate. Plasticisers and lubricants were also used. The plasticisers included diethyl phthalate, dibutyl phthalate, dioctyl phthalate and diallyl phthalate. The lubricants included stearic acid, paraffin wax and ester wax. Atactic polypropylene, the amorphous waste product from isotactic polypropylene production, has the advantage of being one of the lowest cost polymers on the market. Recent work at Toyota Motor Corporation[36] used polypropylene-based thermoplastic binders, with phthalates as minor additives. After successful injection moulding and vehicle removal, ceramic swirl chambers yielded a Weibull modulus of 20·3. Since the removal stage is just as liable to introduce critical defects as the moulding stage this high Weibull modulus appears to indicate the suitability of polypropylene binder systems.

Litman *et al.*[108] working with silicon powder loadings of up to, or in excess of, 70 vol% experimented with several thermoplastic binders. These included low and high density polyethylene, polystyrene, polypropylene, nylon, acrylonitrile–butadiene–styrene, styrene–acrylonitrile and polyurethane. Only polypropylene was found suitable. Others were rejected on the basis that their melt viscosity was relatively high at standard processing conditions and increased further as the filler was added. They also found that loading of the polypropylene was further improved by adding hydrogenated peanut oil, which acted as a diluent and lubricant, reducing the viscosity significantly. Litman *et al.*[108] have also reported success with a series of low molecular weight polyethylenes and microcrystalline waxes.

Patent literature[119] describes the use of thermoplastic, rubber-related ABAB block copolymers. A is a linear branched polymer that is glassy or crystalline at room temperature and has its softening point in the range of about 80–250°C. B behaves as an elastomer at processing temperatures. Although the patent[119] claimed almost any thermoplastic was suitable for A blocks, the examples cited used polystyrene. Polybutadiene, polyisoprene and poly(ethylene butylene) were used as B blocks. Plasticisers such as naphthanic or paraffinic oils or waxes were optionally added. In addition, supplementary resins and fillers such as carbon black that increase the stiffness, elastomers that increase the tear strength and anti-oxidants that retard oxidation were used. Processing aids used include methyl acetylricinoleate, stearic acid, polyethylene, polyethylene wax, mixtures of natural waxes and wax derivatives, different types of vegetable fat and partially oxidised polyethylene.

An interesting development has been reported by Burroughs and Thornton[120] and also by Matkin *et al.*[121] whereby the binder used was a silicone resin which was not fully removed prior to sintering but was converted to silica and incorporated in the final microstructure of the body. Such formulations are limited to ceramics where an additional 2 wt% of silica can be tolerated. This is the case for some silicon nitrides prepared by either reaction bonding or sintering but would be unsuitable in high purity refractory oxides.

Swedish research workers[107] have used polyethylene and stearic acid with 57 vol% filler loading of silicon nitride powder. The use of polyethylene has also been described in the patent literature.[96] In this instance it was mixed with polyethylene glycol. Tritolyl phosphate and glycerol monostearate were added to the mixture as release agents. This binder system was particularly successful in the injection moulding of electrical insulating bodies, semi-conductors and cores for metal casting. Mutsuddy[47] chose a low molecular weight ethylene–vinyl acetate copolymer with a melt flow index of 200 and a density of 0·920 $\mathrm{Mg\,m^{-3}}$ as the major binder. Several plasticisers have been mentioned for ethylene–vinyl acetate copolymers;[122] phthalates and butyl stearate are among them. Moteki[123] has evaluated some phthalates which are compatible with polystyrene and has recommended diethyl phthalate as a compatible plasticiser for alumina–polystyrene formulations. Farrow and Conciatori[124] have successfully injection moulded alumina using polyacetal binders. Low density polyethylene, atactic polypropylene and an ethylene–vinyl acetate copolymer were also added to the mixture. The binder system provided easy and defect-free burn-out.

There are several instances[125–129] where typical thermoplastic systems were used in formulations containing silicon carbide powder. These included polyethylene, acrylic resins, acrylonitrile–butadiene–styrene, nylon, ethylene–acrylic acid copolymers, polystyrene, polybutylene, polysulphone and polyethylene glycol. Polystyrene was found to be particularly acceptable. Sugano[130] has described the injection moulding of silicon carbide powder using plasticised polystyrene as a vehicle. The author emphasised the importance of plasticisers to control fluidity and draws attention to the effect of high injection temperatures in creating residual stresses in the moulded article which are themselves relieved by plasticiser addition. Sugano also pointed out what is no doubt a universal but unstated observation that ceramic injection moulding formulations do not display die swell typical of high polymers. Nevertheless, recent work in the UK indicated that polystyrene binder systems in silicon powder give rise to poor rheological properties.[131]

A method of producing β-silicon carbide injection moulded components using α-silicon carbide with a particle size not more than 400 mesh has been described.[129] The binder system consisted of poly(*n*-butyl methacrylate), di(*n*-butyl phthalate), epoxy resin and dicyandiamide. Colloidal graphite was included for subsequent siliciding.

In general, thermoplastic systems contain a variety of other minor additions, such as wax, various types of oil and different fatty acids and their derivates. These are claimed to function as minor binders, plasticisers and processing aids. Frequently the quantities added are arbitrary or unstated. In the CATE turbine blade programme[98] the major binder content was 80 vol% of the total organic vehicle content while the minor binder, plasticiser and processing aid contents were 8, 8 and 4, respectively, of the total organic vehicle content.

5.2. Thermosetting systems

One of the first ceramic injection moulding formulations used has been described by Strivens[39] and is given below:

Component	*% Volume*	*Function*
Ceramic powder*	63·0	filler
Epoxy resin	7·3	binder
Coumarone-indene resin	3·2	diluent
Phenylformaldehyde resin	2·2	hardener
Wax	24·3	plasticiser and mould release

This composition was selected after a study of wax–resin systems, during which more than 100 commercially available waxes were investigated. Wax–resin systems could be one of three basic types—compatible, dispersible or incompatible. Compatible systems have been very difficult to injection mould. Also the moulding efficiency generally increased with fineness and

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* Steatite body.

stability of the wax–resin mixture. Waxes based on certain glycol esters of montanic acid or on similar oxidised and esterified hydrocarbon long-chain molecules appear superior. Strivens also used many other formulations in his research and these are described in the early patent literature.[74,109]

For silicon carbide powders a thermosetting plastic has often been used as the major binder.[45,46,132] Although it generally involves a longer cycle time in the mould, it possesses the distinct advantage of producing strong bodies in the as-moulded condition. Also it provides the large carbon content needed for reaction sintering.

The typical composition used at the USA Ford Motor Company's Research and Engineering Centre contains:[132]

Component	*% Volume*
Silicon carbide	47
Phenolfurfural–phenolformaldehyde copolymer	47
Graphite	5
Zinc stearate	1

The patent literature[133] gives examples where thermosets such as epoxy resins or phenolic resins were used. The major advantage was that these reduced thermal deformation of the moulded mass during polymer removal. Nevertheless, this required a large proportion of resin.

5.3. Other systems

Sarkar and Greminger[134] draw attention to the advantages of water-soluble polymers, principally methyl, hydroxyethyl and hydroxypropylmethyl cellulose. These materials allow room temperature processing, ease of dispersing the ceramic powder, the benefit of a two-stage vehicle removal with humidity-controlled drying and the low cost of transient polymer, but may be offset by the disadvantage of hydrolysis of some nitride powders intended for high temperature use.

The use of water-soluble polymers such as the cellulose ethers has been developed into a successful injection moulding process for metal powders.[135,136] Advantage was taken of the thermo-gelling properties of such solutions, whereby the composition solidifies upon injection into a die heated to 90°C. Glycerin and boric acid were added to aid mould release.

The cellulose ethers and polyacrylamides have been used by Birchall *et al.*[137] to process cement powders to produce macro-defect-free cement. Such shapes as bottle caps have been compression moulded using this method.[138]

The advantage from the ceramics viewpoint is the ability to remove the bulk of the binder (water) by controlled humidity drying, leaving a 'porous' body for polymer removal by pyrolysis. The removal stage can thus be reduced from the order of days, for the carefully controlled heating of thermoplastic binder, to hours.[136]

A composite organic vehicle composition, comprising an incompatible mixture of a water-soluble polymer and a sparingly water-soluble organic substance dispersed in emulsion form, has been used in powder moulding processes including injection moulding.[139] It is claimed that such formulations gave rise to high quality articles. The ceramic powder used in these instances has been alumina or magnesia; the water-soluble polymer was polyvinyl alcohol, methyl cellulose or gelatin, and the organic substance was wax, stearic acid or liquid paraffin. It is noteworthy that water-soluble polymer-based blends may suffer loss of strength in high humidities.[140]

Some Soviet investigations[12] have used clay–wax systems as an alternative to clay–water mixtures. The mixture quoted contained porcelain body, paraffin and beeswax. It was kept liquid in the machine and shaping occurred as a result of the liquid wax stiffening in a cooled mould. In this way cups were made complete with handles.

Waxes have been used extensively in moulding formulations.[107,111,124,141] The wetting characteristics of partially oxidised waxes are the most beneficial factor. It has been suggested that in this respect they are very much better than low density polyethylene. At the Ford Motor Company's Research and Engineering Centre an unstated two-component organic system created problems of density variations during moulding due to vaporisation of components.[30] For these reasons the system was abandoned for a more conventional wax binder system[30] which allowed 73·5 vol% loading of silicon powder.[48]

Mouldable ceramic formulations that comprise a mixture of clay, such as kaolin, with inclusion of hard mineral substances, such as quartz, feldspar, dolomite or wollastonite, have been developed by a German company.[142] Metal stearates such as calcium, magnesium, zinc and aluminium stearate were used as agents for improving flow. Electrolytes such as alkali metal carbonates and/or ammonium carbonate were added to assist removal from the mould. The adhesion of the damp ceramic composition to the mould surface was further reduced by the addition of alkyl sulphonates.

Another US patent[143] describes the use of an organic vehicle having a high solid state vapour pressure. The patent defines this type of organic binder as being solid at normal room temperature but having a melting point of about 200°C and a vapour pressure of at least 1 mm within the temperature range from 20°C to the melting point. Examples of suitable organic materials are naphthalene, paradichlorobenzene and camphor.

These binders reduced the time required for removal and also substantially reduced the associated linear shrinkage to 1% over conventional formulations.[143] The sublimation technique was used with ceramic powders such as silica glass, alumina, beryllia, magnesia and mullite, the principal application being precision cores for metal castings. A colloidal ceramic having a particle size of substantially less than 0·1 μm, such as finely divided alumina or silica, was added to inhibit dilatancy. The addition of a thermosetting material such as gum, shellac or silicone resin further improved the reduction of the binder removal time. This composition provided an excellent combination of good plastic flow properties for injection moulding, rapid bake-out of organic binder within 12 h or less without distortion, shrinkage or excessive porosity, and easy burn-out of the thermosetting resin without forming a shell-like layer on the ceramic.

Recent trade information[144] reveals that two types of ceramic binder systems CB-3 and CB-7 are commercially available but no further details of the constituents have been stated.

6. CONCLUSION

The potential for large-scale production of ceramic components for, *inter alia,* heat engines is critically dependent on the development of shaping techniques. Injection moulding is receiving attention as one of the most promising routes. The success of the moulding process is itself dependent on the correct formulation of the organic vehicle component and the achievement of the optimum filler loading. The general rules for the preparation of injection moulding blends in so far as these have been established are set out above. The development of moulding techniques and removal of organic vehicle will be reviewed in a future article.

There is no doubt that developments over the last half century have been haphazard and there are discernible reasons for this. The difficulty of defending hard-won proprietry knowledge for an organic binder system which is ultimately sacrificed has meant that disclosure in the open literature has been limited. Earlier blending and moulding equipment favoured low temperature, low viscosity waxes and oils while modern moulding techniques, borrowed from polymer composite technology, favour high melting point polymers. The requirements for moulding nitride and oxide ceramics are that carbon residue should not be present, whereas the moulding of silicon carbide, in particular reaction-sintered silicon carbide which accounts for a substantial proportion of published work, requires that residual carbon remain prior to sintering. Furthermore, only the moulding of oxide ceramics permits water-based systems. These diverse requirements lead to the quite different choices of polymer blends described above.

Future developments are likely to be driven by the need to lower the proportion of defective mouldings, to mould artefacts which include thick sections and to incorporate ceramic fibres, potentially with preferred orientation, into mouldings. This will lead to a refinement of polymeric binders for subsequent pyrolysis in air, the use of decomposition in controlled atmospheres and the use of materials for removal by other techniques, notably sublimation or evaporation. Looking further ahead, there are several possibilities for organic vehicle components which decompose to the relevant ceramic and perhaps, ultimately, for the fabrication of a ceramic body by injection moulding a polymer precursor.

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Received 2 January 1986; accepted 10 January 1986