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Properties of ceramic injection moulding formulations

Part 3 *Polymer removal*

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The oxidative and thermal degradation of nine suspensions, with polypropylene as the main organic component and a fixed silicon powder loading, were studied by thermogravimetry. Samples were in the form of finely divided shavings and moulded bodies. The acceleration of weight loss in oxidizing atmospheres was dependent on sample size, indicating oxygen diffusion control. Minor additions in the formulations exerted considerable influence on the form of the thermograms. Samples heated in nitrogen presented an exfoliated skin defect which did not appear in oxidizing atmospheres. An important observation was that the form of the thermogram could not be directly related to the incidence of defects in the powder assembly and was therefore an incomplete guide in the screening of potential blends. Nevertheless, a low temperature dependence of weight loss was shown to be desirable for process control.

1. Introduction

The entry of ceramic materials into the commercial arena as viable components in heat engine technology demands that attention be given to the fabrication of complex shapes from fine powder assemblies. Injection moulding is one of the means to this end [1, 2]. After dispersing the ceramic powder in a suitable organic vehicle and injection moulding, the organic component must be removed prior to sintering the ceramic. The present work introduces the problems associated with polymer removal. The long-term aim is to define material properties which are necessary for success at each stage of the operation and finally to make an intelligent materials selection on the basis of accumulated criteria. The present work follows from previous studies [3–5] of ceramic injection moulding using compositions based on polypropylene and a fixed ceramic content.

Injection moulding compositions with a fixed silicon powder loading and a range of readily available thermoplastics were examined by capillary rheometry [3] and, on this basis, a further range of compositions with polypropylene as the main binder component was selected [4]. This work presented three rheological properties which guide the selection of polymer blends. Subsequently [5], moulding trials revealed further material properties which influenced the incidence of defects during solidification in the mould.

The present work extends these investigations by examining the factors which allow removal of the polymer without the incidence of cracking, voiding or skin effects. Methods for polymer removal have been reviewed [2] and although each method has disadvantages, thermal decomposition either in oxidizing or non-oxidizing atmospheres has been favoured. In particular, the work of Mutsuddy [6] suggests that oxidative degradation of thermoplastics in air is a preferred procedure for binder removal. Priority was given to locating a simple test which could be used to screen potential ceramic moulding compositions. Such a test would assist in completing the list of property requirements previously specified.

The work of Johnsson and co-workers [7] described a process control system for thermal degradation of ceramic binders in which weight loss was recorded and used to control the furnace temperature such that a linear rate of weight loss was obtained. Implicit in much of the published work is the assumption that the rate of weight loss is the main factor in determining the incidence of defects in moulded particle assemblies. This suggests that thermogravimetry of polymer blends should offer guidance in material selection; a steady rate of weight loss over a wide temperature range being preferable to a sudden decomposition.

Gross defects in moulded bodies can occur during the injection moulding operation [5] and if present at that stage, may interfere with the interpretation of defects observed after polymer removal. For this reason, a range of samples were prepared by compression moulding which allows solidification under an applied pressure. Each cylinder was radiographed to ensure freedom from internal moulding defects.

2. Experimental details

2.1. Materials

The materials and their densities used in the present

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TABLE I Compositions of ceramic moulding blends

No.	Composition in wt %								
	Si	IPP	APP	MCW	PEW	LDPE	PPW	SO	SA
F1	82.46	15.59	–	–	–	–	–	–	1.95
F3	82.44	11.71	–	3.90	–	–	–	–	1.95
F5	82.40	11.73	–	–	3.91	–	–	–	1.96
F6	82.38	11.75	–	–	–	3.91	–	–	1.96
F7	82.22	11.85	–	–	–	–	–	3.95	1.98
F10	82.96	–	15.15	–	–	–	–	–	1.89
F11	82.71	7.68	7.68	–	–	–	–	–	1.93
F12	82.63	5.79	5.79	3.86	–	–	–	–	1.93
F38	82.25	5.26	–	5.26	–	–	5.26	–	1.97

experiments were as follows:
Silicon (2300 kg m^{-3}): vibratory milled by Pilamec Ltd [3]. Polypropylene (IPP) (905 kg m^{-3}): GY545M from ICI Ltd, Welwyn Garden City, UK. Atactic polypropylene (APP) (870 kg m^{-3}): MF5 from APP Chemicals, Shropshire, UK. Microcrystalline wax (MCW) (910 kg m^{-3}): 1865Q from Astor Chemicals, West Drayton, UK. Polyethylene wax (PEW) (920 kg m^{-3}): AC6 from Allied Chemical Corp., Birmingham, UK. Low density polyethylene (LDPE) (926 kg m^{-3}): LD657 from Esso, Southampton, UK. Polypropylene wax (880 kg m^{-3}): PP2300 from Hoechst UK Ltd, Middlesex, UK. Silicone oil (SO) (975 kg m^{-3}): 200 from Dow Corning, Glamorgan, UK. Stearic acid (SA) (941 kg m^{-3}): from BDH Chemicals, Essex, UK.

The compositions with the addition of formulation F38 [3–5] are given in Table I. The silicon content after mixing was obtained by ashing to 600° C in air and these values are also given in Table I. The organic components are assumed to make up the remainder weight in the same ratios as mixed. In each case the volume loading of silicon was 65 vol %.

2.2. Mixing

The procedure for blending by twin screw extrusion has been described previously [3, 4] together with processing temperatures. In addition, composition F38 was processed at the following temperatures: 140–160–160–160–175° C (feed–die).

2.3. Moulding operations

Step wedge bars 20 mm in width with steps of 2.5, 5, 7.5, 10, 15 and 20 mm were fabricated on a Bone-Cravens-Daniels 350-120 injection moulding machine. An example is shown in Fig. 1. The shape allows defects in various sections to be examined. Fig. 2 shows a straight bladed rotor moulded on the same machine with composition F3. Cylindrical discs 31 mm diameter, 31 mm in length were compression moulded in a metallurgical mounting press with a pressure of 12 MPa held until the sample cooled to 100° C. Composition F10 and F38 were compression moulded at 170° C and the remainder at 220° C. All discs were contact radiographed to ensure that they were free from moulding defects. An example of the quality of compression moulding is shown in the radiograph print in Fig. 3.

2.4. Thermogravimetry

Samples in the form of shavings and small mouldings were examined in a Stanton thermobalance with a heating rate of 0.033° C sec^{-1} in static air and in flowing white spot nitrogen. The flow rate of nitrogen was set to 40 l/h after finding that a rate of 29 l/h was sufficient to inhibit the oxidation of a fine copper powder at a heating rate of 2° C/min to 600° C. Large moulded components were examined in a thermogravimetric furnace at the laboratories of Turner and Newall Ltd. This consisted of a Lenton 1400° C muffle furnace in which the sample was suspended in a wire tray from a Precisia 2500D balance with a sensitivity of 0.1 g. An RS232 interface was used to input data from the balance to a Sharp MZ80K computer. An external input to the temperature controller set a ramp of 6.67×10^{-3} ° C sec^{-1}. The weight was read every 2.5 or 5 min and if the weight fell by >0.2 g the furnace temperature was reduced by 10° C. The samples were not embedded in powder because this was considered to interfere with weight loss control because of condensation of degradation products [7].

3. Results and discussion

3.1. Effect of atmosphere

Fig. 4 shows the dynamic thermogram for composition F1 under four different conditions each with a heating rate of 2° C/min. With flowing nitrogen where oxidative degradation was prevented, the effect

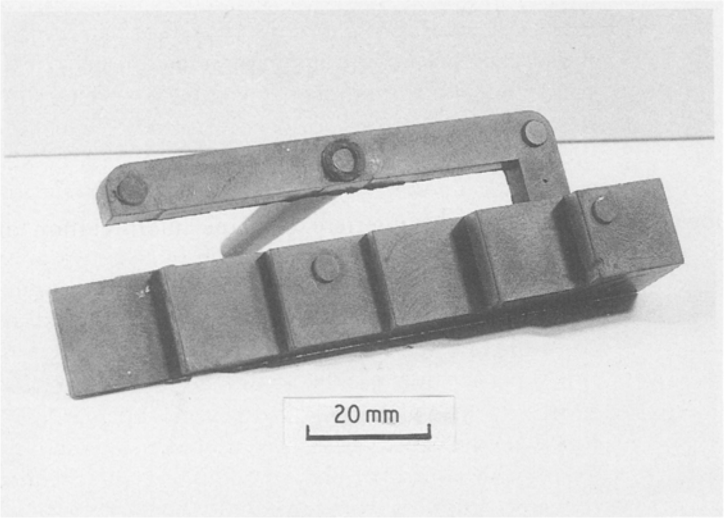


Figure 1 The step wedge moulded component.

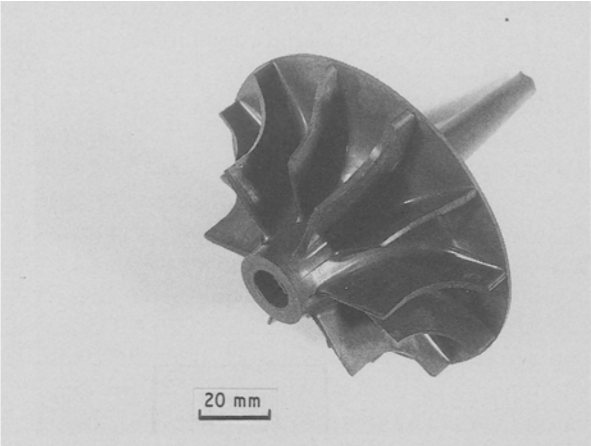


Figure 2 The ceramic rotor.

of the sample size was negligible. Thus, the weight loss curve for the sample in the form of a cube coincided with that for the finely divided material and the shape of the curve was defined by the kinetics of thermal degradation and evaporation of the polypropylene and stearic acid components of the blend. It can be concluded that the outward diffusion of degradation products through the suspension did not control the rate of weight loss for the cubic sample. It was not possible to detect a significant unpyrolysed residue from the weighing of samples heated in nitrogen. For a random chain scission process the maximum volatilization rate $-dh/dt$ at a given temperature is related to the critical chain length for evaporation L by:

$$-\frac{dh}{dt} = \frac{kL}{e} \qquad (1)$$

where k is a rate constant and e is the base of the natural logarithm [8]. Chains containing L or more carbon atoms continue to decompose while those with fewer carbon atoms evaporate. The fact that the finely divided sample and the bulk sample produced the same thermogram suggests that evaporation was not a rate limiting step since the samples had grossly different specific surface areas. It appears that if the loss of low molecular weight fragments is impeded by diffusion in the bulk, internal pressure causes the sample either to crack or to burst.

A comparison of the thermograms for finely divided samples heated in air and in flowing nitrogen (Fig. 4) shows that oxidative degradation accelerated the binder removal process in agreement with established studies [9]. It is noteworthy that the polypropylene, having been processed at 225° C, may have already undergone some oxidation. The steadier rate of weight loss over a temperature range from 100 to 350° C at first suggests that oxidative degradation may be preferable. However, comparison with the thermogram for the bulk sample heated in air shows that the sample size had a dramatic effect on kinetics. This is in agreement with previous work [9] which shows that for sample thickness $> 250\,\mu$m the oxidation of polyolefins is controlled by the rate of diffusion of oxygen. Thus, in air, thermograms for bulk mouldings would be expected to fall between the thermogram for fines and the thermogram for thermal degradation; the curves for larger samples being displaced to the right. This indicates that a different thermogram and thus a different controlled heating programme would be needed for components of different dimensions heated in air, in agreement with the work of Mutsuddy [6].

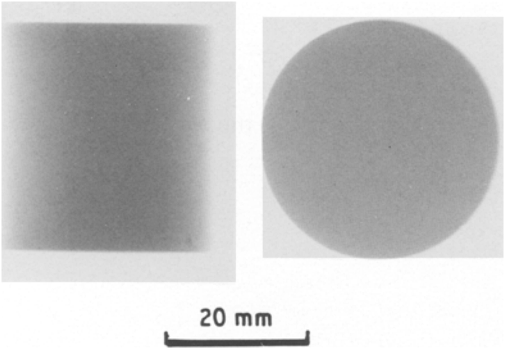


Figure 3 Radiograph print of a cylindrical compression moulded sample.

Clearly, it is now possible to describe the process more usefully with the superposition of two models. In the case of thermal degradation of the binder, where oxidative reactions are prevented, the basic model [10] is of molecular weight degradation occurring uniformly throughout the bulk of the ceramic body under the influence of kinetic parameters definable by conventional t.g.a. studies on small samples. The production of low molecular weight species is accompanied by evaporation of fragments with chain length less than a critical length from the surface of the body. These two processes establish a concentration profile which provides a driving force for outward diffusion of molecular fragments through the suspension. The objective of the control process is therefore to manipulate time, temperature and external pressure to prevent boiling of low molecular weight species in the centre of the sample [10]. This process is amenable to analysis for simple systems but for the polypropylene used in this work where there are at least 12 products of pyrolysis ranging from methane to C_{13} [11] the analysis is very complex.

Where the binder is removed in oxidising environments, an additional surface reaction is superimposed on thermal degradation. This process is already well described by the shrinking unreacted core model of Szekely *et al.* [12]. The reaction interface recedes into the porous body with either the reaction being rate controlling or the diffusion of either oxygen in, or reaction products out, of the porous body controlling the rate of weight loss. In the latter two cases, the gaseous diffusion in porous bodies defines the relevant model [13]. These results (Fig. 4) suggest that the oxidative reaction in the case of polypropylene is superficial and that for large components the production of defects at the centre of the moulding would be controlled by the first model. However, the effect of the superposition of the shrinking unreacted core process by the use of an oxidizing atmosphere is likely to reduce the effective component dimensions slightly during the course of the reaction and thus reduce diffusion distances from the core through the residual

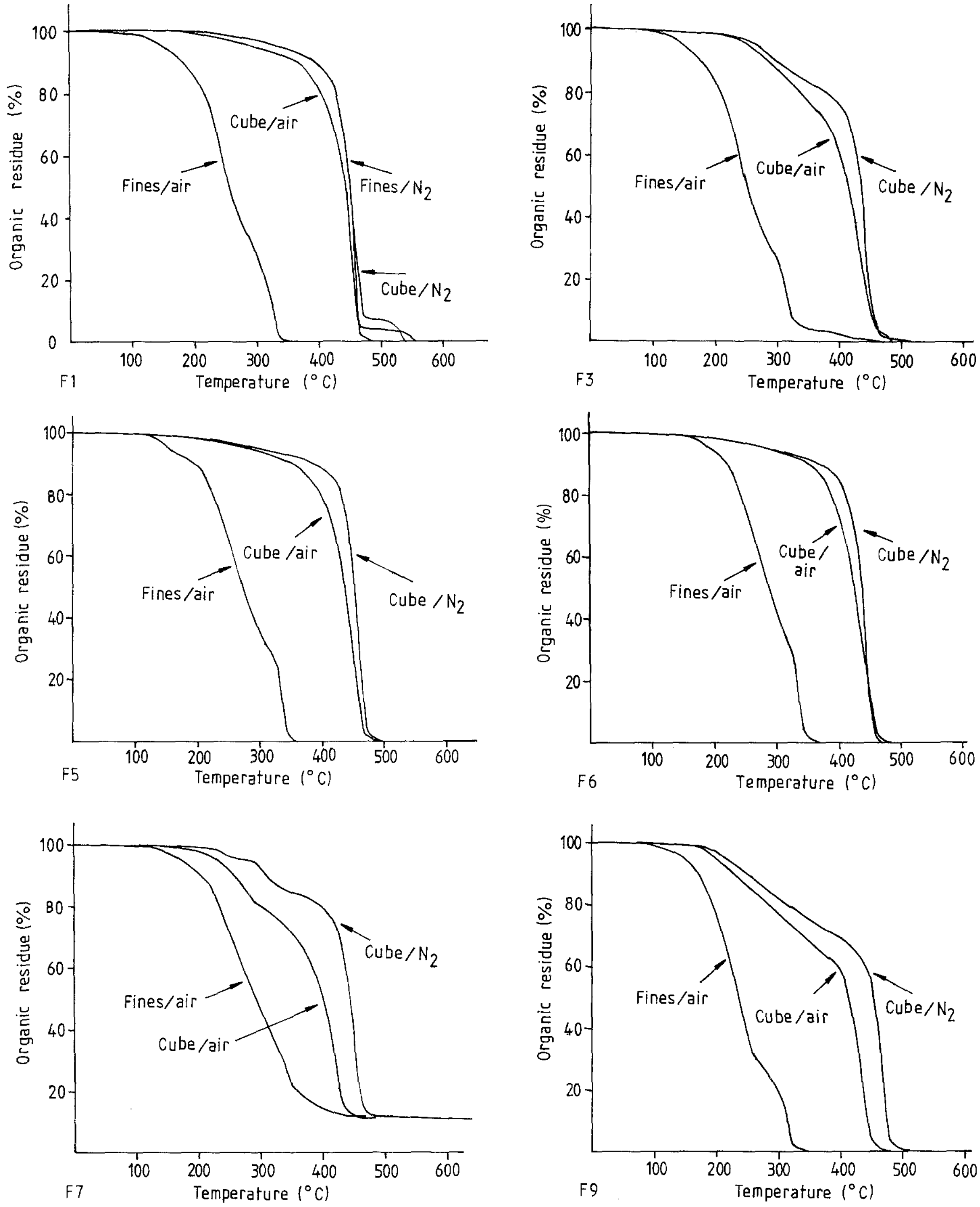


Figure 4 Thermograms for formulations F1, F3, F5, F6, F7 and F9 heated at 2° C/min in air and nitrogen.

polymer. Clearly, for the experiments at a heating rate of 2° C/min, the benefit of surface oxidation is slight. At lower heating rates, however, the competition between surface oxidation and thermal degradation may have different outcomes and this is discussed below.

3.2. Activation energies

The Freeman and Carroll method [14] was used in an attempt to obtain the order of reaction n, and activation energy from the thermograms in Fig. 4 for composition F1. Unfortunately the plots of:

$$\frac{\Delta(1/T)}{\Delta \log h} \text{ against } \frac{\Delta \log(-dh/dt)}{\Delta \log h} \qquad (2)$$

produced curves, suggesting that parallel weight loss processes were operating. Thus the loss of the stearic acid, which makes up 11 wt % of the organic material, by evaporation, may be superimposed on the thermal or oxidative degradation. It was considered inadvisable to deduce kinetic data from these curves and indeed the method has been criticised on grounds of sensitivity [15]. Assuming the weight loss follows the form [16]:

$$-dh/dt = k(a - x)^n \qquad (3)$$

where k is a rate constant, a is the initial sample mass, and x is the amount evaporated, the activation energy is accessible. Plots of natural logarithm of first-order specific rate constant against reciprocal temperature [16] produced acceptable lines and for the sample of F1 in nitrogen gave an activation energy of 150 kJ mol

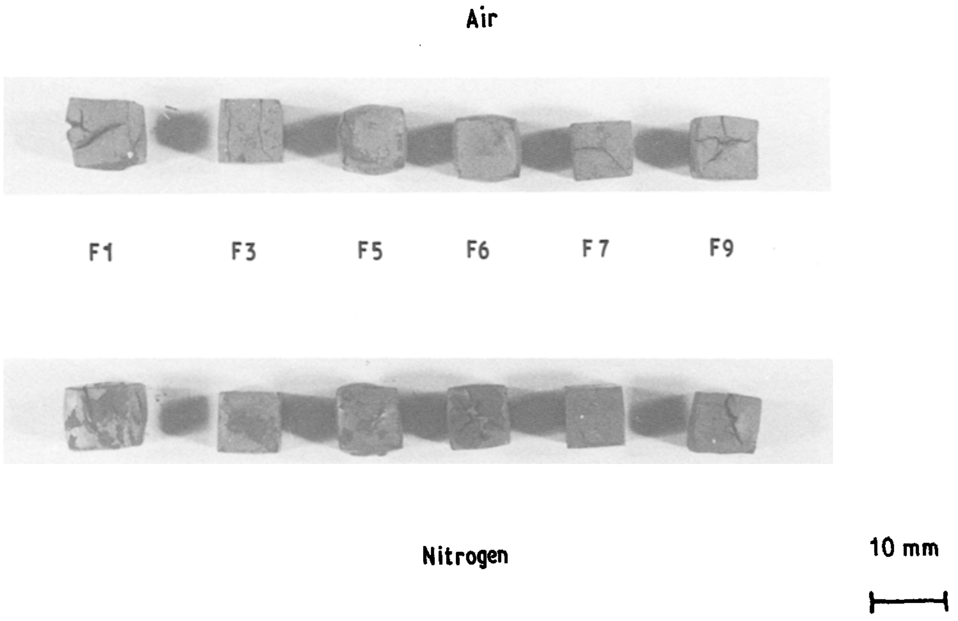


Figure 5 The appearance of 7 mm cubes of samples from Fig. 4.

in the region 390 to 420° C and $68\,\mathrm{kJ\,mol^{-1}}$ in the region 340 to 390° C. These values are less than the known values for the thermal decomposition of pure polypropylene. Kiang and co-workers [11] obtained $213\,\mathrm{kJ\,mol^{-1}}$ for isotactic polyproylene by thermogravimetry in the region 250 to 450° C. They also found that the degradation followed first order kinetics. The overall activation energy E results from initiation (Ei), propagation (Ep) and termination (Et) steps such that:

$$E = Ep + \tfrac{1}{2}E\mathrm{i} + \tfrac{1}{2}E\mathrm{t} \qquad (4)$$

The activation energy for hydrogen transfer (75 to $79\,\mathrm{kJ\,mol^{-1}}$) represents the propagation step. The value of Ei was taken as 322 to $351\,\mathrm{kJ\,mol^{-1}}$ which is the energy for C–C scission. The termination reaction which relies on the collision of free radicals is assumed to show the activation energy for diffusion in the bulk ($41\,\mathrm{kJ\,mol^{-1}}$). This gives estimated values for E from 213 to $234\,\mathrm{kJ\,mol^{-1}}$ in agreement with experiments. In the present work, the polypropylene was already oxidized prior to thermal decomposition as a result of processing at elevated temperatures. Thus chain scission resulting from oxidised species would be expected to reduce the value of Ei [17]. Furthermore, the organic fraction of formulation F1 contains 11 wt % stearic acid, the evaporation of which would be a parallel process superimposed on the thermogram and lead to a lower apparent activation energy, particularly at lower temperatures, as was observed.

For the sample of fines of composition F1 heated in static air an activation energy of $68\,\mathrm{kJ\,mol^{-1}}$ was obtained in the region 190 to 250° C and $27\,\mathrm{kJ\,mol^{-1}}$ in the region 120 to 190° C. The overall activation energy is given by [18]:

$$E = E_{\mathrm{h}} + \tfrac{1}{2}E_{\mathrm{a}} - \tfrac{1}{2}E_{\mathrm{t}} \qquad (5)$$

where E_{h}, E_{a} and E_{t} are, respectively, the activation energies for hydroperoxide formation, alkoxy radical formation and inactive product formation. This gives theoretical activation energies for polypropylene oxidation of 63 to $71\,\mathrm{kJ\,mol^{-1}}$ which is close to experimentally-measured values [18] and close to the value observed in the present work at higher temperatures. The superposition of the curve for stearic acid degradation is likely to be the cause of the lower activation energy at lower temperatures.

The values obtained for the cubic sample of F1 heated in air were $146\,\mathrm{kJ\,mol^{-1}}$ in the region 360 to 390° C and $71\,\mathrm{kJ\,mol^{-1}}$ in the region 310 to 360° C. These clearly have little meaning since they are a consequence of at least three parallel processes. However, the apparent activation energies do give a quantitative indication of the temperature dependence of weight loss.

3.3. Thermogravimetry of small mouldings

In studying the thermograms for finely divided material of compositions F1 to F9 heated in air (Fig. 4), it is noteworthy that the curves are almost coincident. Thus the reaction kinetics in air for these compositions are insensitive to the minor component of the blend. Samples containing polyethylene (F5 and F6) show slightly greater stability in air as expected. In contrast, the thermograms for bulk cubic samples differ considerably. Clearly, if a screening test for the selection of ceramic binders is sought, the thermogravimetry of powdered material in air or of small polymer samples is insensitive to differences caused by minor additives. Such testing is also ruled out by the observation that the oxidative degradation of finely divided material bears little resemblance to the thermogravimetry of bulk samples.

As a screening test, however, the thermogravimetry of the 7 mm cubes revealed significant differences between compositions particularly in the early stages of the process and in addition showed clear differences in the appearance of samples (Fig. 5). This added information may be just as useful as the weight loss trace. Primarily, the differences between compositions are attributable to the superposition of thermal degradation or evaporation curves for the

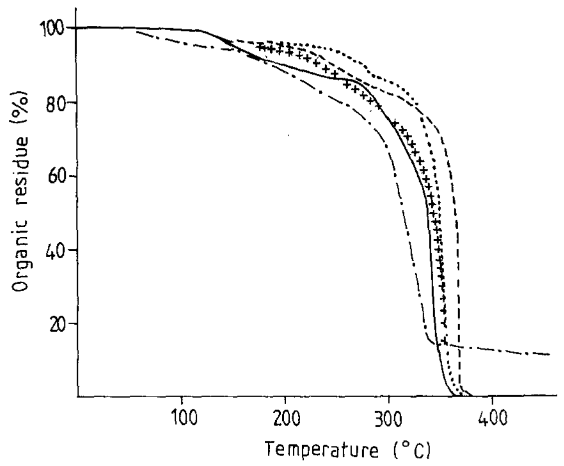


Figure 6 Thermograms for (——) F1, (– – –) F3, (· · · ·) F5, (+ + + +) F6 and (–·–·–·–) F7 for 31 × 31 mm discs heated at 2° C/h in air (smoothed curves).

components of the blend. In contrast, the oxidative decomposition for powdered samples masks such differences and may involve interactions between components during degradation [19]. If the behaviour seen in the case of F1 is general, then the thermograms for bulk samples in air may be interpreted as the thermal degradation curve with an added surface reaction involving oxidative degradation and, indeed, for each formulation the positions of the curves support this interpretation.

One further difference which influences the decomposition in air is that samples which cracked early in the process are effectively reduced in size and this would tend to displace the thermogram to the left. Unfortunately, the facility to observe the samples in the furnace was not available and while such cracking may have influenced sample F7 heated in air, it is not clear that it has influenced F3 or F9 in this way.

The samples heated in nitrogen all show exfoliated skin defects with the exception of compositions F7 and F9 (Fig. 5). In contrast, for all the samples heated in air this defect was absent. Others [20, 21] have noted this surface defect and it has sometimes been attributed to a surface inhomogeneity introduced by the injection moulding process. For example, it could be caused by a different powder arrangement at the mould wall caused by flow into the mould [21]. The fact that it is here observed on samples of injection moulding ceramic compound which have been compression moulded and then abraded suggests that this is not the case in this instance.

All the samples show macroscopic defects and this can be partly attributed to the fast heating rate. The defects fall into the following categories; exfoliated skin, bloating and cracking. The binder removal process can be divided into three stages; initial reheating to the softening point, the stage when the suspension is fluid but before it has been embrittled by degradation and loss of binder and finally a brittle stage where the binder content is substantially diminished [22].

An interesting feature of these experiments is that, with the exception of sample F1, the cubes which show severe bloating do not have cracks and the samples which are cracked do not show severe bloating. Bloating occurs at the intermediate stage while the suspension is soft and deformable; the boiling of low molecular weight degradation products in solution near the centre of the component occurring at an appropriate concentration and temperature [11].

In samples which have cracked, however, the sample size is effectively reduced and thus diffusion distances are smaller as the crack provides a new surface. Sample F1 consisting of polypropylene with no minor binder, in addition to showing unfavourable rheology [4], and excessive shrinkage [5] also appears to offer unfavourable thermal decomposition kinetics. It may be used as a reference with which to compare the effect of the minor components of the organic blend on decomposition. Composition F3 with microcrystalline wax and F7 with silicone oil show the least severe defects, especially the samples heated in nitrogen. Their quality is surprising, in view of the fast heating rate of 2° C/min. It is convenient that these compositions also showed acceptable rheology [4] and low shrinkage [5]. Formulation F7 is limited to applications where ca. 2% silica residue based on the ceramic is acceptable.

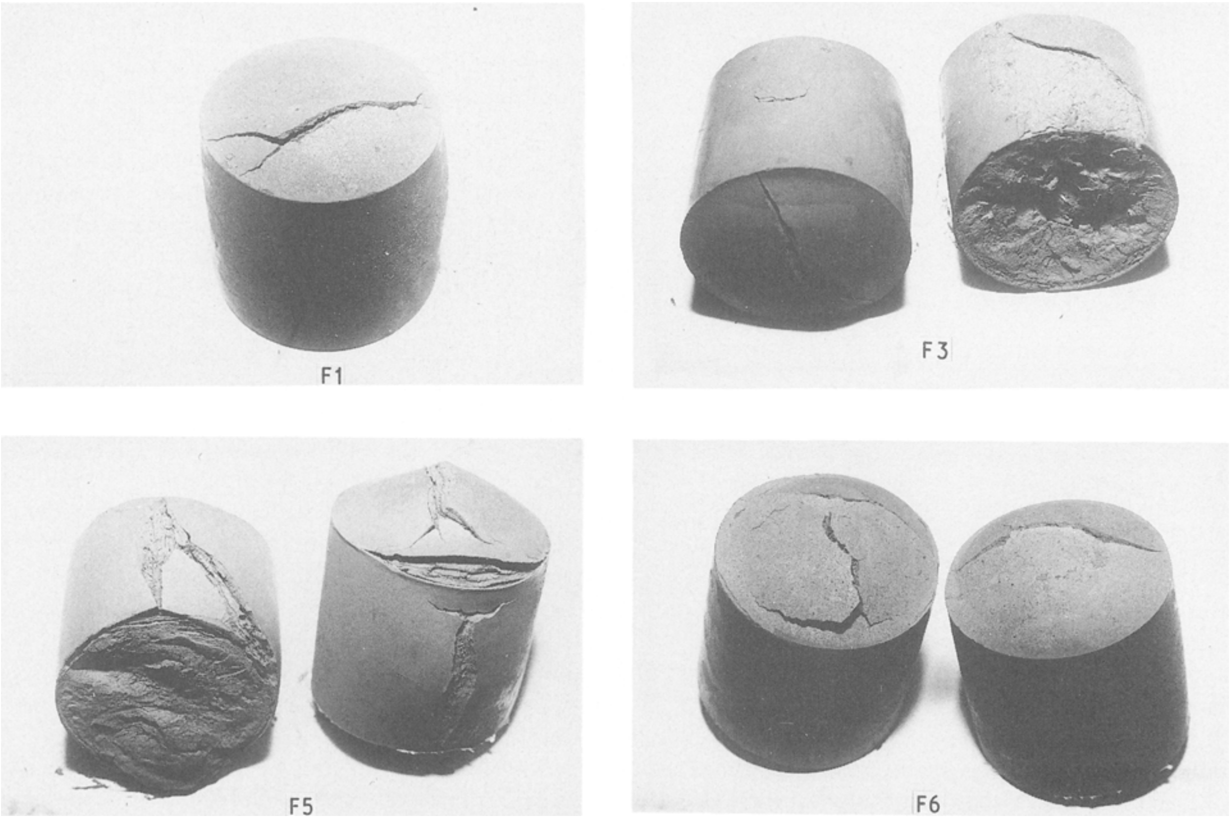
Formulations F5 and F6 containing, respectively, polyethylene wax and a high melt flow index low density polyethylene, show boating in both air and nitrogen. In addition, in nitrogen both reveal an exfoliated skin. These compositions also showed unfavourable rheology [4] and shrinkage [5]. Formulation F9 with dioctylphthalate as the minor component shows severe cracking. This is surprising, since it is often recommended that low molecular weight oils or plasticizers should emerge by evaporation and facilitate the further removal of binder [23].

A striking feature of the thermograms is that there is no clear relationship between the form of the weight loss curve and the nature of defects in the cubic samples. The steady weight loss of formulation F9 in both air and nitrogen over a wide temperature range from 190 to 480° C is accompanied by bursting of the sample. The sharp weight loss for formulation F7 in nitrogen between 300 and 480° C produced an almost sound product despite the fast heating rate and the same observation applies to formulation F3 heated in nitrogen. Formulation F6 which presented a similar thermogram to F1 showed mild bloating rather than bursting. Similar behaviour was seen in F5 heated in air where the thermogram was similar to that for formulation F6. Clearly, the form of the thermogram is an incomplete guide in assessing the suitability of polymer blends.

3.4. Thermogravimetry of large mouldings

Samples of the formulations previously studied were compression moulded to produce discs 31 mm long and 31 mm in diameter. The thermogravimetric loss was studied by heating in static air at 2° C/h. The curves and resulting discs are shown in Figs 6 and 7, respectively, for formulations F1 to F7.

It is immediately obvious that the region of steep weight loss is displaced from 450 to 350° C, corresponding to the reduced heating rate. It is also clear



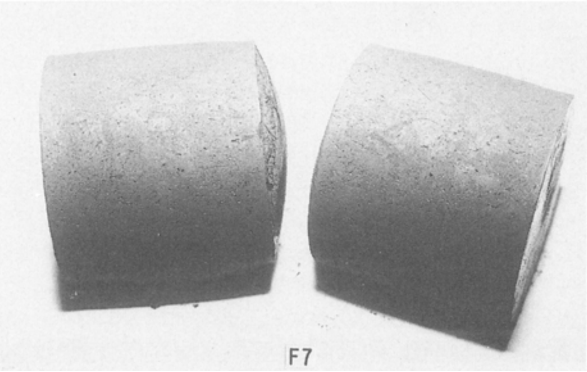


Figure 7 The appearance of 31 mm cylinders from Fig. 6.

that as the rate of heating was decreased, the differences between the shape of the thermograms diminished, thus reducing the usefulness of the dynamic thermogram as an indicator for the screening of compositions. The reason for this can be discerned from the activation energy measurements. For the competition between thermal and oxidative degradation the lower activation energy process would be expected to dominate at lower temperatures and, therefore, have greater influence on the dynamic thermogram at low heating rates. Thus oxidative degradation is expected to be more pronounced at a heating rate of 2° C/h than for the samples heated at 2° C/min. Fig. 4 shows that the oxidative degradation of fines produced almost identical weight loss curves. Thus not only is the weight loss in air strongly influenced by sample size, but the form of the thermograms is also more strongly influenced by heating rate than would be the case for a single degradation process.

In the case of F1, a combination of bloating and cracking can again be seen suggesting that bloating occurred at a stage where the central region was fluid and the outer region was embrittled by loss of binder. In the large samples, F3 behaved in a similar way to F1 but with a clearly defined surface layer ~ 1 mm in thickness. A surface defect was also observed in F5 suggestive of an embrittled layer depleted in binder and subject to deformation from internal swelling. The F6 discs show similar defects to those in F1 and F3 discs. The discs fabricated from F7 show some promise in that they reveal bloating at a stage when the entire body was fluid and a cracked surface region did not occur.

Further deficiencies in the thermogravimetric approach are revealed by these experiments. It is not known at what point the defects originated since the sample could not be observed. The fact that a fixed linear temperature ramp was used concealed the benefits that reduced heating rates or holds at critical stages might have had, informing only that at some unknown stage 2° C/h was an excessive heating rate. In this way, the work of Johnsson and co-workers [7] has considerable advantages. However, it is also clear that the volume of gas needed to create the cracking and bloating observed has extremely small mass. Thus thermogravimetry may not be the best method of monitoring the reaction. It is interesting to consider the application of alternative experimental methods used in the study of polymer degradation kinetics such as thermal volatilization analysis [24].

3.5. Polymer blends based on atactic polypropylene

Formulations F10, F11 and F12 drawn from previous work [3] and including atactic polypropylene with a lower molecular weight were examined by the same

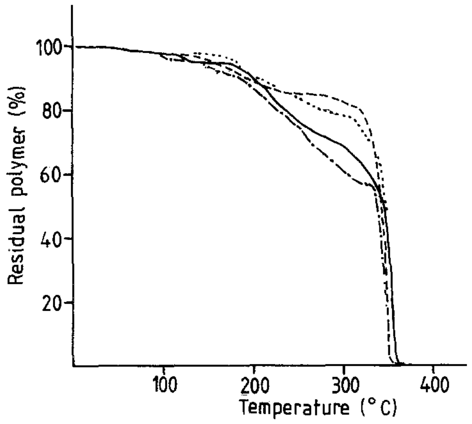


Figure 8 Thermograms for (– – –) F10, (——) F11, (· · · ·) F12 and (–·–·–·–) F38 for 31 × 31 mm discs heated at 2° C/h in air (smoothed curves).

procedure using large discs. The addition of atactic polypropylene permitted acceptable flow behaviour [3] and also reduced moulding shrinkage [25] in accordance with previous work [5] because of its lower crystallinity. In addition formulation F38, which incorporates an isotactic polypropylene wax, was used in order to widen the molecular weight distribution of the isotactic polypropylene fraction of the blend. The thermograms for formulations F10, F11, F12 and F38 are shown in Fig. 8 and the corresponding discs in Fig. 9. It is immediately obvious that the form of the thermograms for formulations containing atactic polypropylene differ from the curves for isotactic polypropylene blends. In each case, a slow weight loss commenced in the region 150 to 170° C and continued until a substantial fraction of the polymer was removed, before the onset of rapid weight loss at 350 to 360° C.

The discs prepared from formulation F10 which contain only atactic polypropylene as the main binder show some cracking but only slight signs of bloating. This composition revealed a large dependence of viscosity on temperature [3] and was found to be unacceptable for the moulding of slender components because of deformation on mould ejection [25]. In contrast, formulations F11 and F12 each based on a major binder which is a 1 : 1 actactic–isotactic blend reveal only slight defects in the 2° C/h ramp in air. These compositions also have acceptable rheology [3] and sufficient strength to resist deformation on mould release [25].

The correlation between the appearance of discs of F11 and F12 and the steady weight loss revealed on the thermogram would retrieve some credibility for the thesis that the shape of the thermogram can be used to screen compositions, were it not for formulation F38. In this formulation, isotactic polypropylene, isotactic polypropylene wax and atactic polypropylene appear in equal parts. The thermogram reveals steady weight loss between 120 and 330° C, being similar to the thermogram for F11, yet the discs show extensive cracking on the sides as well as the ends.

The incorporation of atactic polypropylene with a number average molecular weight 2900 into the isotactic polypropylene with molecular weight 32 000 widens the molecular weight distribution and is expected to modify the rate of production of volatilizable species. The incorporation of isotactic polypropylene of molecular weight 3000 (formulation F38) apparently modified the molecular weight

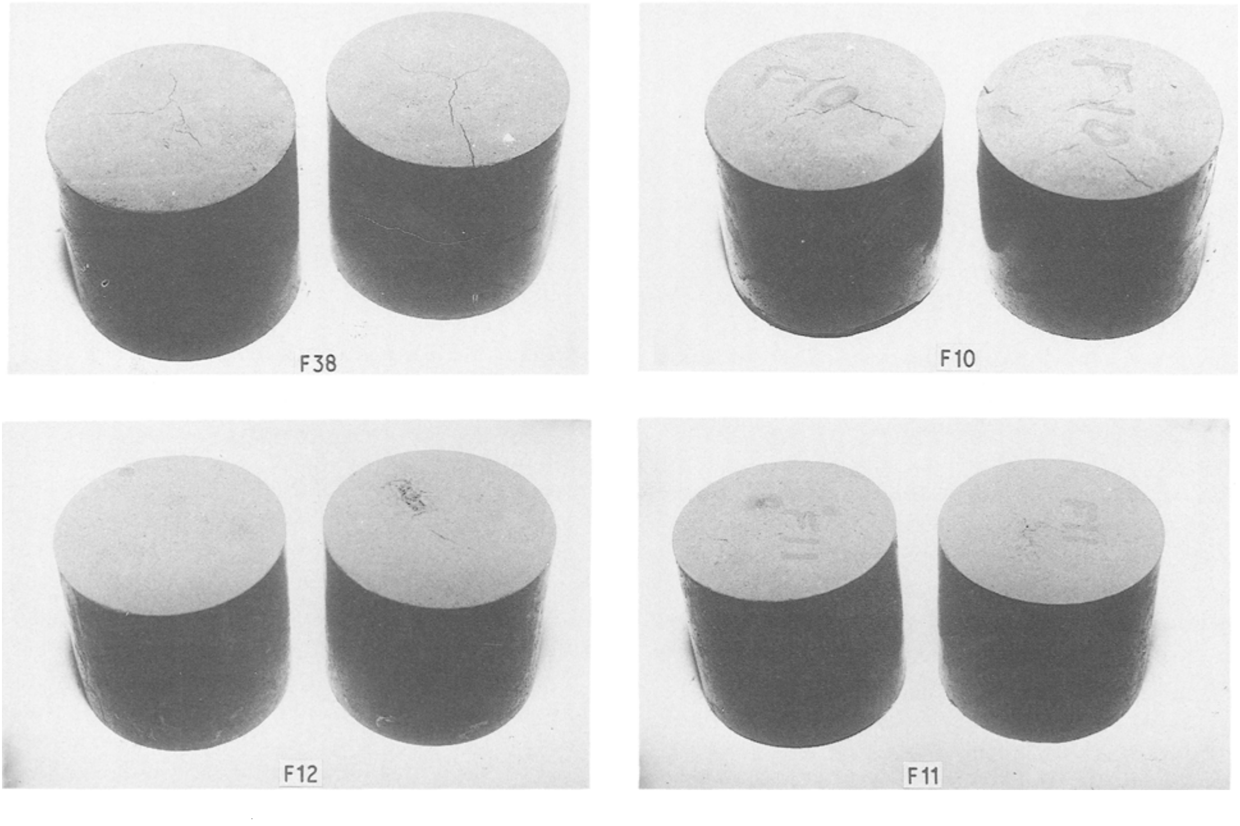


Figure 9 The appearance of 31 mm cylinders from Fig. 8.

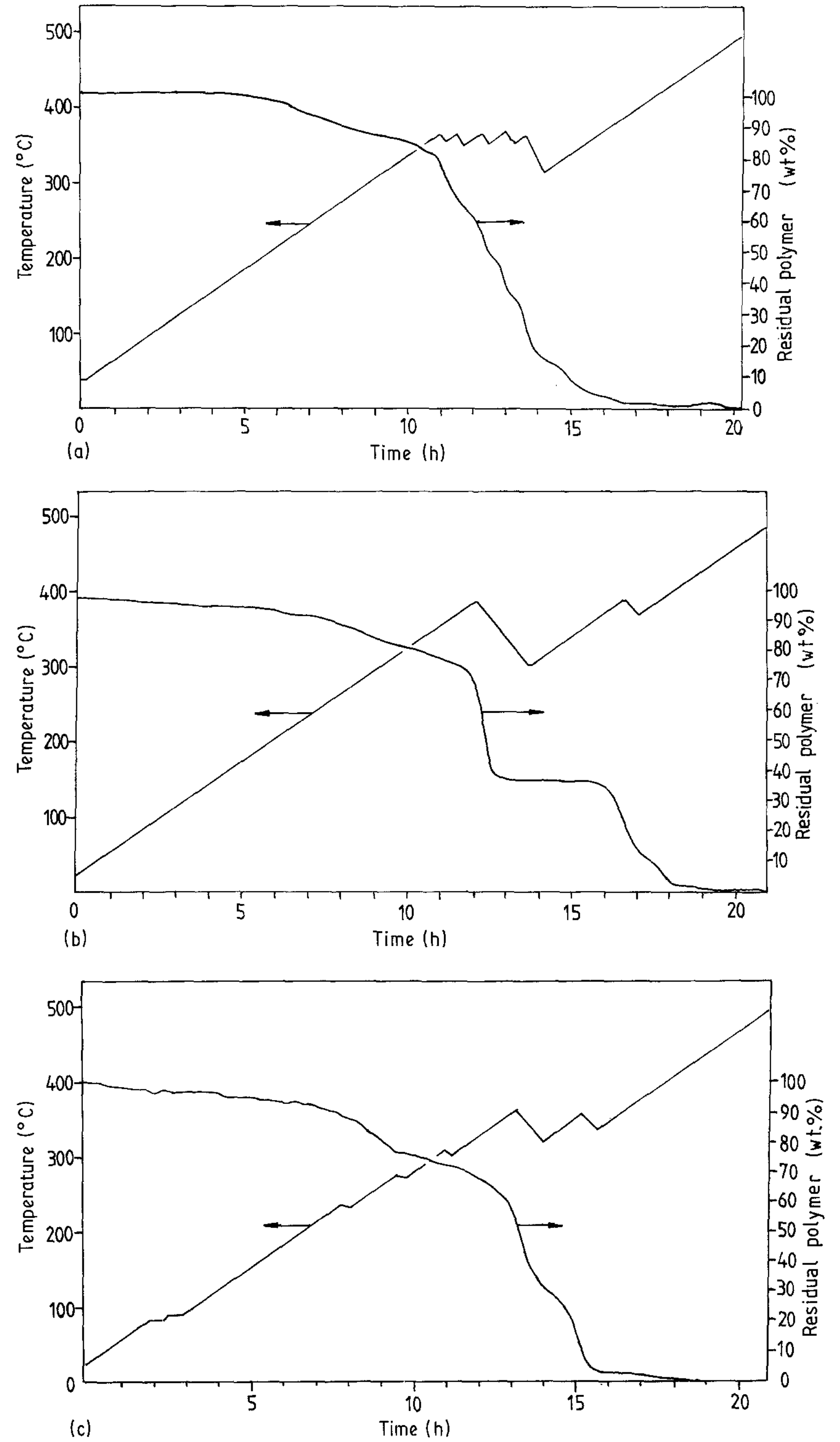


Figure 10 Weight loss-temperature-time curves for (a) the rotor of composition F3, (b) two step wedge components of composition F3, (c) two step wedge components of composition F7.

distribution further and the cracking observed may have occurred early in the process. The importance attached to the molecular weight distribution for polypropylene as a ceramic binder is illustrated by the work of Saito *et al.* [26]. These workers relied on the superposition of thermograms for different molecular weight fractions to produce a composite thermogram with approximately linear weight loss.

3.6. Controlled weight loss

Using an arrangement similar to Johnsson *et al.* [7] but operating in a static air atmosphere samples of composition F3 were heated with a weight loss-temperature control loop. Fig. 1 shows a step wedge moulding and Fig. 2 shows a rotor moulding used in this trial. The method, in principle, overcomes some of the objections to a linear temperature ramp. In particular, it allows adjustment of the ramp or the introduction of holds at critical stages of the binder removal process.

Fig. 10 shows the weight loss-temperature-time characteristic for a rotor of composition F3, two step wedges of composition F3 and two step wedges of composition F7. In each case, the initial heating rate in air was 24° C/h. The furnace was programmed to reduce the temperature by 10° C when the difference between successive readings was >0.2 g. In both cases, a slight weight loss commenced at ca. 220° C and continued steadily until the region 360 to 380° C. In the case of the rotor, the process control programme activated at 363° C and the system produced a steady weight loss until polymer degradation was complete. In the case of the step wedge, the control programme commenced at 380° C but was unable to control the rapid weight loss that ensued. The initial weight of the two step wedges was 79.2 kg compared with the initial weight of the rotor which was 116.5 g and this would tend to reduce the sensitivity of the control process for the step wedges. However, a much greater control problem was the high thermal inertia of the furnace. From the time when control commenced, a period of up to 20 minutes elapsed before the furnace temperature began to fall.

The different behaviour of the step wedges and the rotor may be attributable in part to the shape. For the step wedge, a greater proportion of the volume exists as thick sections and this would tend to reduce the weight loss by oxidative degradation. A further factor is that if the rotor cracked early in the schedule, its surface area/volume ratio would be increased and binder removal would be facilitated. Once again it was not possible to observe the ceramic body in the furnace.

These results present the following preliminary guidance. In both cases, the resulting ceramic bodies were severely cracked, indicating that the overall heating rate was too great. In order to function in the control loop, the furnace should have a low thermal mass. The slope of the descending part of the temperature plot in Fig. 10a is in fact the natural cooling curve for the furnace and not the programmed temperature decrease. The shape of the moulded component has a pronounced influence on the weight loss behaviour in air. This agrees with Mutsuddy's claim that separate temperature schedules are needed for each sample shape and size [6]. In air, the degradation of polyolefins is exothermic and the generation of heat in the component during binder removal would tend to confound the negative feedback control of the process. Fig. 10b should be compared with Fig. 10c which shows the controlled weight loss curve for two step wedge bars of composition F7 containing silicone oil. On this occasion, the weight loss control loop activated successfully because the composition of the binder presented a thermogram with steady weight loss (Fig. 4).

It can be concluded that in order to take part in a controlled process the organic binder should have a low temperature dependence of weight loss, avoiding the sudden decomposition shown in Fig. 10b. Thus, the main value of thermogravimetric studies appears to be to select a material amenable to process control rather than to predict the likelihood of defects from the form of the thermograms.

4. Conclusions

This systematic study of ceramic injection moulding blends based on polypropylene presents the following conclusions which will guide future work.

1. The kinetics of thermal degradation were not influenced by sample size and in flowing nitrogen neither diffusion of products through the suspension nor evaporation from the surface were rate-controlling steps for samples in the form of 7 mm cubes.
2. For oxidative degradation, the rate of weight loss was dependent on sample dimensions, suggesting that oxygen diffusion into the suspension was rate-controlling and that the oxidative reaction would be most pronounced on the surface. Thus weight loss kinetics in oxidising environments depend on component dimensions.
3. For neither type of degradation was it possible to relate unequivocally the type or extent of defects to the form of the thermogram. Gross correlations were apparent in that the introduction of lower molecular weight atactic polypropylene produced a steadier initial weight loss and improved the quality of components. However, examples were presented of sharp weight loss traces accompanied by high quality samples and the converse.
4. Thermogravimetry, as a test for screening moulding compositions, suffered from the following additional disadvantages: the sample could not be viewed during heating and thus the point at which defects occurred could not be identified. The linear rate of heating concealed the beneficial effect that temperature holds might have had at critical temperatures.
5. For weight loss-controlled thermogravimetry, a low thermal mass furnace is preferred. The main value of a steady sample weight loss over a wide temperature is the advantage it offers for process control.
6. The success achieved by blending of atactic and isotactic polypropylene is thought to be attributable to the molecular weight distribution thereby achieved. This influences the rate of production of volatilizable products during the degradation process.

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References

1. M. J. EDIRISINGHE and J. R. G. EVANS, *Int. J. High Tech. Ceram.* **2** (1986) 1.
2. *Idem. ibid.* **2** (1986) 249.
3. *Idem. Br. Ceram. Trans. J.* **86** (1987) 18.
4. *Idem. J. Mater. Sci.* **22** (1987) 269.
5. *Idem. ibid.* **22** (1987) 2267.
6. B. C. MUTSUDDY, in Proceedings of the International Conference on Non-Oxide Technological and Engineering Ceramics (N.I.H.E. Limerick, July 1985).
7. A. JOHNSSON, E. CARLSTROM, E. HERMANSSON and R. CARLSSON, *Proc. Brit. Ceram. Soc.* **33** (1983) 139.
8. C. D. DOYLE, in "Techniques and Methods of Polymer Evaluation I. Thermal Analysis", edited by P. E. Slack and L. T. Jenkins (Marcel Dekker, New York, 1966) p. 152.
9. R. H. HANSEN, in "Thermal Stability of Polymers", edited by R. T. Conley, Vol. 1 (Marcel Dekker, New York, 1970) p. 153–187.
10. J. K. WRIGHT, M. J. EDIRISINGHE and J. R. G. EVANS, to be published.
11. J. K. Y. KIANG, P. C. UDEN and J. C. W. CHIEN, *Polymer Degradation & Stability* **2** (1980) 113.
12. J. SZEKELY, J. W. EVANS and H. Y. SOHN, "Gas–Solid Reactions", (Academic Press, London, 1976) Ch. 4.
13. R. M. GERMAN, *Int. J. Powder Met.* **23** (1987) 237.

14. E. S. FREEMAN and B. CARROLL, *J. Phys. Chem.* **62** (1958) 394.
15. L. REICH and D. W. LEVI, *Macromolecular Reviews* **1** (1967) 173.
16. W. W. WENDLANDT, Thermal Methods of Analysis, Interscience (1964) p. 32.
17. L. A. WALL, in "Analytical Chemistry of Polymers II Molecular Structure and Chemical Groups", edited by G. M. Kline (Wiley, New York, 1962) p. 194.
18. S. STIVALA, J. KIMIRA and L. REICH, in "Degradation and Stabilization of Polymers I", edited by H. H. G. Jellinek (Elsevier, New York, 1983) p. 35.
19. J. K. WRIGHT, M. J. EDIRISINGHE and J. R. G. EVANS, to be published.
20. "Injection Moulding Machine for New Ceramics", Japan Steel Works (Hiroshima plant), Trade Literature, 1984.
21. R. GILISSEN and A. SMOLDERS, "High Tech Ceramics", Mater. Sci. Monograph 38A, edited by P. Vincengini (Elsevier, 1987) p. 591.
22. J. G. ZHANG, M. J. EDIRISINGHE and J. R. G. EVANS, to be published.
23. C. L. QUACKENBUSH, K. FRENCH and J. T. NEIL, *Ceram. Eng. Sci. Proc.* **3** (1982) 20.
24. I. C. McNEILL, *European Polym. J.* **6** (1970) 373.
25. J. G. ZHANG, M. J. EDIRISINGHE and J. R. G. EVANS, *Industrial Ceramics*, in press.
26. K. SAITO, T. TANAKA and T. HIBINO, UK Patent 1426317, March 1973.

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