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Characterization of polymers in particulate systems

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SUMMARY: Small amounts of polymers (ca. 1 wt.-%) are often used in the processing of ceramics to bond the particles. The purpose is to enhance mechanical properties, notably the strength, of intermediate or green products obtained after consolidation of the powder. In this paper, the influence of polymers on mechanical properties of green (Mn,Zn)-ferrite products is investigated. Frequently used polymers are methyl methacrylate - ethyl acrylate copolymer and poly(vinyl alcohol) (PVA). Because PVA generally produces low-strength compacts and is sensitive to moisture, a blend of the copolymer and PVA was used. The glass transition temperatures (T_g) of the polymers and green products were determined. The good correspondence between the T_g's indicates that the polymers dominate the mechanical behaviour when tensile stresses are applied. In practice, compacts usually have an axisymmetric shape and are subject to diametral compression during handling. Therefore, ring-shaped compacts were crushed at different velocities. The crushing velocity has a strong influence on the compact strength when the copolymer is used and only a small effect when the compact contains the PVA blend. This indicates that the copolymer can absorb a rapid buildup of stress through plastic deformation. By contrast, the rate of plastic deformation in the PVA blend is relatively slow. Further insight is obtained by subjecting rectangular compacts to three-point bending. By interpreting the experimental data with a mechanical model, the deformation of compacts containing acrylic is found to be elasto-plastic. With compacts containing the PVA blend, a yield point is observed. This indicates that elasto-plastic deformation is preceded by elastic deformation.

1. Introduction

The processing of (Mn,Zn)-ferrite products usually involves three stages[1]:

(i) preparation of a powder from the raw materials; (ii) consolidation of the powder to form a compact; (iii) sintering of the compact to obtain a dense and strong product.

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(Mn,Zn)-ferrite products are widely used in the electronics industry due to their excellent electromagnetic properties[2]. Their mechanical properties are relevant for the application of (Mn,Zn)-ferrite products: high strength is required to withstand stresses arising from temperature gradients or thermal shock. Strength is also important in the processing of ceramics since a compact has to withstand handling after ejection from the die. Because the cohesion between ferrite particles is not strong, polymers are added during the processing. The increased strength can be attributed to adhesion of the polymers to the particle surface and to the toughness of the polymers. In order to distribute the polymers over the particles, a water-based slurry is prepared and subsequently spray-dried. During spray-drying, granules are formed which have superior flow properties when compared with ferrite particles. In short, the strength of compacts is influenced by:

- polymer strength, which decreases sharply at temperatures above the glass transition temperature T_g;
- adhesion of the polymer to the particles, which depends on chemical compatibility of the polymer and (Mn,Zn)-ferrite;
- cohesion of the particles, which is influenced by the compact density, size and shape of the particles and chemical composition. Of these, only the compact density is varied in this study;
- compact shape and size;
- stresses applied on the compact.

In this study, three water-soluble polymers are compared: ethyl acrylate (EA) - methyl methacrylate (MMA) copolymer, poly(vinyl alcohol) (PVA), and a blend of PVA and the copolymer. Three batches of granulated ferrite particles containing the copolymer, PVA or a PVA - copolymer blend were produced by spray-drying water-based suspensions. By spray-drying a slurry of particles, water and polymers, spherical granules are produced which possess a superior flowability when compared with original ferrite particles. Characteristics of spray-dried granulates are given in Table 1. The difference in the bulk or filling density of the granulate is due to variation in the solid content of the slurry (55 versus 70 wt.-%). Then the glass transition temperatures of the neat polymers and of compacts containing polymers were determined.

Table 1: Characteristics of ferrite granulate processed with polymer additive

Polymer	Polymer content wt.-%	Average size m	Bulk density g/cm^3
EA-MMA copolymer	0.86	180	1.52
PVA-copolymer blend	0.72	205	1.52
PVA	1.00	182	1.40

In practice, ferrite compacts usually have an axisymmetric shape which implies that radial compression occurs during handling after compaction. Consequently, measurement of the maximum crushing force which a cylindrical or ring-shaped compact can absorb during diametral compression provides an indication of the strength of ferrite compacts. Besides the influence of the polymers, the effects of the compact density, compact size and crushing velocity on the compact strength were investigated. During crushing, the compact is subjected to compression, shear and tension simultaneously. An alternative is to subject narrow, rectangular compacts to bending. Although the compact is simultaneously stretched and compressed during bending, its mechanical properties are likely to be determined by the tensile stresses. The properties of the polymer are likely to become apparent when the deformation prior to failure is small. The deformation behaviour of the polymers is then characterized by modelling the force-displacement relation. A mechanical model representing the deformation behaviour of the polymer, polymer strength and adhesion of the polymer to the particles was developed. Data obtained from the bending of compacts containing the copolymer and compacts containing PVA - copolymer blend are used to determine the model parameters.

Finally, the choice of polymer is based not only on the strength of the compact but also on the volatility of the polymer and the burnout characteristics. The latter is relevant because the polymer has to be removed before the sintering process in a controlled way without leaving residues. A high volatility is advantageous as this promotes evaporation of the polymer prior to self-combustion. An indication of the volatility of the polymers is obtained from combined thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC). Tablet-shaped compacts pressed from each granulate are analysed with TGA in order to establish the temperature range in which the polymers are evaporated or burned out of the compact. Evaporation is associated with absorption of heat, whereas self-combustion of polymers produces heat. The net effect is measured with DSC.

2. Glass transition temperature

In selection of these polymers, the glass transition temperature (T_g) is taken into account. In order to obtain strong compacts, the T_g should be higher than the ambient temperature. However, the T_g should be lower than the temperature at which compaction takes place. This promotes deformation of the polymer which, in turn, lowers interparticle friction. Less interparticle friction is advantageous as it reduces the required compaction pressure. On the other hand, a relatively low T_g promotes sticking of particles to the die surface.

In practice, friction between the particles during compaction produces heat.

Although the rise in temperature is reduced by the Joule-Thompson effect, the compaction temperature is expected to be higher than the ambient temperature. Because the temperature of the polymer adjusts itself to the ambient temperature after ejection from the die, the T_g should have a value between the temperature during compaction and the ambient temperature.

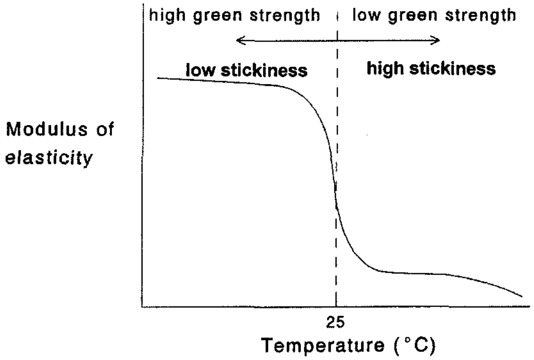

Figure 1:
Optimum glass transition temperature

As illustrated in Figure 1, a T_g between 20 and 30 °C is suitable. The T_g was determined by dynamic mechanical thermal analysis (DMTA) for neat polymers (Table 2). Thin, rectangular products were vibrated at a frequency of 0.1, 1, 10 and 100 Hz in the temperature range from -25 to 100 °C. The heating rate was set at 0.2 °C/min. Surprisingly, there is little difference between the T_g of polymers in compacts or in the neat form. This leads to the conclusion that for given loading conditions, the polymer determines mechanical properties of the compact.

Table 2: Glass transition temperatures T_g

Polymer	T_g (°C)	Polymer	T_g (°C)
Poly(ethyl acrylate)	-24	EA-MMA copolymer	29
Poly(methyl methacrylate)	105	PVA - copolymer blend	25
PVA	23		

3. Diametral compression of compacts

3.1. Experimental

Granulates containing the copolymer, PVA or PVA - copolymer blend were pressed into ring-shaped compacts with densities 2.70 and 3.00 g/cm^3. Two compact sizes were used: (i) outer diameter 16 mm, inner diameter 11 mm, and height 10 mm and (ii) outer diameter 30 mm, inner diameter 18 mm, and height 14 mm.

The compact was crushed at constant velocity by parallel plates attached to the cross-head. Tests were conducted at selected velocities between 0.05 and 400 mm/min. For each compact density and size, type of granulate, and crushing velocity, five compacts were tested. The variation in the maximum applied force was less than 3 % for all experiments.

3.2. Interpretation

In diametral compression, the compacts are subjected to compressive, shearing and tensile stresses simultaneously. In order to transpose the applied force to a stress, a massive cylindrical compact is considered. In diametral compression, the largest tensile stress is found along the outer surface. Assuming purely elastic behaviour, the magnitude of this tensile stress (σ_t) is given by[3]:

$$\sigma_{t,max} = 2F/(\pi dh) \qquad (1)$$

where F is the applied force, d the diameter and h the height of the compact. If this stress produces failure, the compact splits in two halves. The tensile strength can be determined with cylindrical compacts and diametral compression only if suitable padding[4,5,6] is used.

The compressive stress σ_c varies with the height: directly below the compression plate and at the supporting surface, the compressive stress is, in principle, infinitely large. A minimum of the compressive stress is observed in the centre of the compact[7]:

$$\sigma_{c,min} = 6F/(\pi\, dh) \qquad (2)$$

Because compressive stresses reduce the effect of tensile stresses, failure in ring-shaped compacts is initiated where the compressive stresses are at a minimum, i.e. on the inner surface. The corresponding stress is obtained by modification of Eq. (2)[8]:

$$\sigma_{c,min} = 6F(d_o + d_i)/[\pi\, (d_o - d_i)^2 h] \qquad (3)$$

where d_o is the outer diameter and d_i the inner diameter of the compact.

It was found that the strength of compacts increases with the density. This is due to a decrease in the pore size, increase in the number of contacts between the particles and increased adhesion between particles at the expense of smearing of the polymer. The size of the compact also influenced the strength. The strength of the 16-mm rings was 10-15 % higher than the strength of the 30-mm rings. This is caused by the differences in inhomogeneity of the compact and in the flatness (contact surface) of different rings. The effect of the polymer is not independent of the crushing velocity and will be considered separately.

3.3. Influence of the crushing velocity

The maximum stress, as applied on 16-mm rings, is given in Figure 2. The influence of the crushing velocity and the type of polymer is related to processes which occur on microscopic level. When a small stress is exerted on a compact, it is balanced by interparticle friction and deformation of polymer bonds. At this stage, the deformation of the compact is small and possibly elastic or reversible. As soon as the applied stress becomes larger, it is possible that the deformation becomes plastic or irreversible. This is a result of particle rearrangement, breaking of polymer bonds or detachment of the polymers from particles. If the applied stress is compressive, the deformation leads to reduction in the pore size and possibly to smearing of the polymer between particles. As a result, the strength is likely to increase. With diametral compression, however, a tensile stress is also applied. Particle rearrangement now leads to the pore growth, lowering the compact strength by increasing the probability of the bond breakage. In this case, the polymer bonds have a pronounced effect on the strength. When the buildup of tensile stress is slow, time-dependent viscous deformation of polymer bonds may occur. On the other hand, a fast buildup of tensile stresses implies that the viscous deformation can no longer alleviate the applied stress. This mechanism could be used to explain the observed dependence of the strength on the crushing velocity.

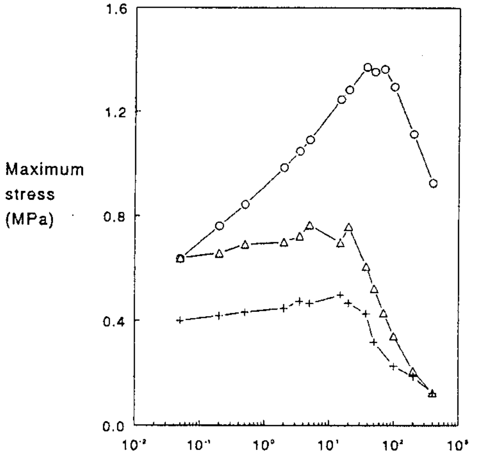

Figure 2:
Maximum crushing stress supported by 16-mm rings (○ EA-MMA copolymer, + PVA, △ PVA - copolymer blend)

With low crushing velocities, the buildup of tensile stresses is sufficiently slow to allow viscous deformation of the polymer to occur. Hence, the ultimate strength of the polymer bonds is more or less independent of the crushing velocity. For acrylic and PVA, the net strengths turn out to be roughly equal. Differences in the strength could also be related to differences in the polymer content (see Table 1). As the crushing velocity increases, the buildup of stresses in compacts cannot be alleviated through viscous deformation alone and the effect of time-independent elastic deformation becomes important. The more elastic the polymer is, the faster is the buildup of stress in the polymer and the sooner the polymer bonds rupture. The increase in strength of the copolymer with higher crushing velocities is clearly an indication that the elastic component of the deformation is small. With PVA and PVA - copolymer blend, on the other hand, the elastic component is large, leading to a large reaction force which induces rupture of polymer bonds. Essentially, the roughly constant strength of compacts containing PVA or PVA - copolymer blend indicates that the viscous deformation of these polymers is not significant. More insight into the deformation behaviour of compacts containing the copolymer and PVA - copolymer blend was obtained by bending compacts. Bending tests have the advantage that they are more readily modelled.

4. Bending tests

4.1. Experimental

Granulates containing the copolymer and PVA - copolymer blend are used to press rectangular compacts with the densities 2.60, 2.80 and 3.00 g/cm^3. Furthermore, compacts with a density of 2.40 g/cm^3 are pressed from the powder containing the copolymer only. Compacts with this density containing PVA - copolymer blend have insufficient strength to be handled. The compacts have the dimensions: length 48 mm, height 6 mm and width 5 mm. In the three-point bending test, the cross-head moves downwards with a constant velocity of 12 mm/min (Figure 3).

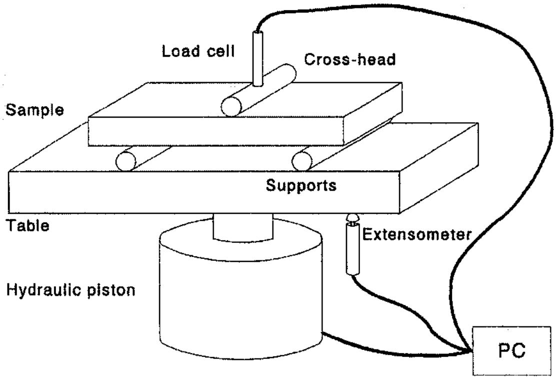

Figure 3:
Experimental setup for three-point bending tests

The compact is supported by two free-rolling cylinders. The force-deflection relation is measured for five compacts of each density and each polymer system by collecting roughly 500 data points. A characteristic curve is shown in Figure 4. The variation in the force required to produce failure is less than 3 % when performing each experiment five times.

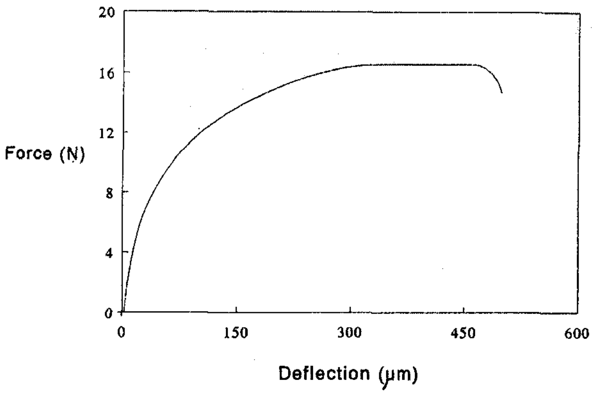

Figure 4:
Typical measured curve in a three-point bending test

4.2. Non-linear elastic beam theory

According to the non-linear elastic theory of beams, the applied force F is related to the stress σ as follows[8]:

$$\sigma = Mz^n/I_n \quad (4)$$

where M is the bending moment, z the vertical displacement, n an empirical parameter and I_n the moment of inertia. The bending moment M is given by Fx/2, where x is the axial coordinate. The moment of inertia I_n equals:

$$I_n = bh^{n+2}/[(n+2)2^{n+1}] \quad (5)$$

Evaluating the expressions for M and I_n at midspan (x= L/2) and at the bottom surface of the compact (z = h/2) results in:

$$\sigma = F(n+2)/(2bh^2) \quad (6)$$

Because the stress σ depends on the parameter n, an appropriate value for n has to be selected in advance.

The strain ε is the ratio of the deflection δ and the radius R of curvature of the neutral axis. The latter maintains a constant length throughout the bending process and is located at z = 0. The radius of curvature R is expressed as

$$R = (L^2/4 + \delta^2)/2\,\delta \quad (7)$$

Because the deflection δ is small compared with the span L, Eq. (4) can be simplified. The strain ε then equals

$$\varepsilon = 8(\delta/L)^2 \quad (8)$$

The relation between the stress σ and the strain ε is given by

$$\sigma = C\varepsilon^n \quad (9)$$

where C is the elasticity modulus E if n = 1 or the elasto-plastic modulus H if $0 < n < 1$. With Eqs. (6), (8) and (9), the values for C and n can be determined from force-deflection data. The values for C and n are given in Table 3.

Table 3: Characteristics of deformation behaviour

Polymer	Density (g/cm^3)			
	2.40	2.60	2.80	3.00
Modulus C (MPa)				
EA-MMA copolymer	1.389	2.928	5.435	7.995
PVA - copolymer blend	-	2.029	3.485	5.420
Hardening parameter n				
EA-MMA copolymer	0.608	0.334	0.284	0.253
PVA - copolymer blend	-	0.877	1.843	1.783

For compacts containing PVA - copolymer blends, the hardening parameter n adopts unrealistic values, larger than unity. This confirms that the deformation behaviour of these compacts is likely to be characterized by two stages. This could be elastic deformation followed by elasto-plastic deformation. For compacts containing the copolymer, the range of the hardening parameter n indicates that elasto-plastic deformation occurs. The decrease in the hardening parameter n with increasing density suggests that plastic deformation becomes increasingly significant.

The combination of elastic and elasto-plastic deformation can be represented as follows:

$$\sigma = E\,\varepsilon \quad \text{for } \sigma < \sigma_y \tag{10}$$

and

$$\sigma = \sigma_y + H\,\varepsilon^n \quad \text{for } \sigma_y \leq \sigma < \sigma_f \tag{11}$$

where σ_y is the so-called yield stress. Equations (10) and (11) contain four unknown parameters. The number of parameters can be reduced by developing a mechanical model.

4.3. Mechanical model

The significance of the basic mechanical elements, illustrated in Figure 5, is given in Table 4.

Table 4: Types of mechanical elements

Type of element	Function	Relation	Parameter
Spring	elastic behaviour	$\sigma = E\,\varepsilon$	elasticity modulus E
Dashpot	plastic behaviour	$\sigma = \eta\,(d\varepsilon/dt)$	viscosity η
Friction element	yielding	$\sigma = \sigma_y$	yield stress σ_y
Friction element	failure	$\sigma = \sigma_f$	failure stress σ_f

Elasto-plastic behaviour can be represented by a spring and a dashpot in series. The transition between elastic and elasto-plastic deformation is introduced by placing a friction element in parallel with the dashpot. Figure 6 shows that failure is represented by a friction element, which is placed in series. Because the stress required to produce failure σ_f is measured, this model contains only three unknown parameters.

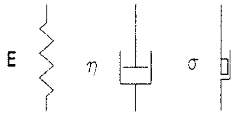

Figure 5: Basic mechanical elements

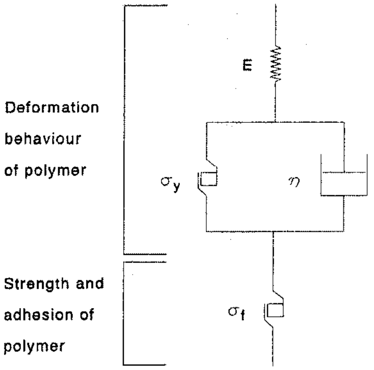

Figure 6: Proposed mechanical model

Keeping the velocity of the cross-head constant and equal to e, the following relation applies:

$$e = (d\varepsilon/dt)_{spring} + (d\varepsilon/dt)_{dashpot} = (d\sigma/dt)/E + \sigma/\eta \qquad (12)$$

where t is time. Integrating with respect to the stress σ yields

$$\sigma = \eta e(1 - \exp(-E\,t/\eta)) \qquad (13)$$

For stresses smaller than σ_y, the stress-strain relation is given by $\sigma = E\varepsilon$. The time t required to reach the yield stress σ_y then equals $\sigma_y/(E\,e)$. Consequently, the time t in Eq. (13) can be substituted by:

$$t = (\varepsilon - \sigma_y/E)/e \qquad (14)$$

The model equations can now be established

$$\sigma = E\varepsilon \quad \text{for } \sigma < \sigma_y \qquad (15)$$

$$\sigma = \sigma_y + \eta e(1 - \exp(-E(\varepsilon - \sigma_y/E)/\eta e)) \quad \text{for } \sigma_y \le \sigma < \sigma_f \qquad (16)$$

$$\sigma = \sigma_y + \eta e \quad \text{for } \sigma = \sigma_f \qquad (17)$$

Because the stress at failure, σ_f, is known, the viscosity η can be expressed in terms of the yield stress σ_y:

$$\eta = (\sigma_f - \sigma_y)/e \qquad (18)$$

Substituting for the viscosity η into Eq. (17) reduces the number of unknown parameters to two. Note that the stress at fracture equals the maximum tensile stress sustained by the compact.

Determination of parameters of the mechanical elements requires that the force-deflection data are converted to stress-strain data using Eqs. (6) and (8). This implies that the value of the hardening parameter n has to be selected. We have used the values given in Table 3. The stress at failure σ_f corresponds to the maximum tensile stress sustained by the compact. Table 5 confirms that compacts containing the copolymer are stronger than compacts containing PVA - copolymer blend. Values of the parameters are given in Table 6. The viscosity η is found from Tables 5 and 6 using Eq. (18).

Table 5: Failure stress during bending test

Polymer	Density g/cm^3	Failure stress σ_f (MPa)	Polymer	Density g/cm^3	Failure stress σ_f (MPa)
EA-MMA copolymer	2.4	0.199	PVA - copolymer blend	2.6	0.123
	2.6	0.473		2.8	0.533
	2.8	0.957		3.0	0.934
	3.0	1.348			

Table 6: Model parameters from bending test

Polymer	Density g/cm^3	E modulus MPa	Yield stress σ_Y MPa	Polymer	Density g/cm^3	E modulus MPa	Yield stress σ_Y MPa
EA-MMA copolymer	2.4	18.31	0.066	PVA - copolymer blend	2.6	20.29	0.106
	2.6	50.18	0		2.8	34.85	0.296
	2.8	75.62	0		3.0	54.20	0.412
	3.0	79.95	0				

Clearly, the deformation behaviour of compacts containing the copolymer is elasto-plastic only when, with compacts containing PVA - copolymer blend, elastic deformation precedes elasto-plastic deformation. For compacts containing PVA - copolymer blend, the ratio of the maximum elastic stress (σ_Y) and the maximum allowable stress (σ_f) decreases with increasing density. This points to an increased significance of plastic deformation at higher densities.

5. Removal of polymers from compacts

The change in the compact weight as a function of temperature was measured by thermogravimetric analysis (TGA). During the measurements, air is passed through the sample chamber while temperature is increased at a rate of 2.5 °C/min. The development of heat in compacts is recorded by differential scanning calorimetry

(DSC). Figures 7 and 8 show TGA and DSC curves measured with tablet-shaped compacts (density 3.2 g/cm^3) containing the copolymer, PVA or PVA - copolymer blend.

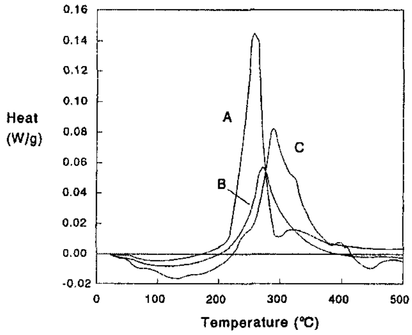

Figure 7: TGA curves measured on compacts (*A* EA-MMA copolymer, *B* PVA-copolymer blend, *C* PVA)

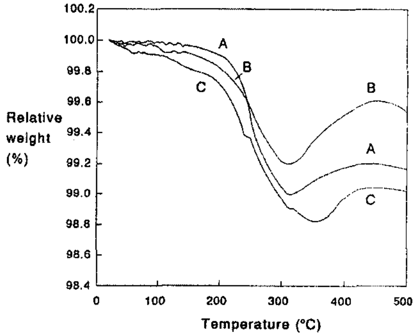

Figure 8: DSC curves measured on compacts (*A* EA-MMA copolymer, *B* PVA-copolymer blend, *C* PVA)

Quantitative characteristics of TGA and DSC curves are given in Table 7.

Table 7: Analysis of TGA and DSC curves

Polymer	T_b[a] °C	T_m[b] °C	T_r[c] °C	Max. rate wt.-%/ °C	Max. heat W/g
EA-MMA copolymer	183	257	308	0.057	0.14
PVA - copolymer blend	198	275	325	0.017	0.06
PVA	220	293	380	0.016	0.08

[a] temperature at which the net heat evolution is zero; [b] temperature of highest heat evolution rate; [c] temperature at which the polymer is removed.

Evaporation of shortest polymer chains starts below 100 °C. The net heat is zero if the heat required for evaporation equals the heat produced by self-combustion. The temperature when the net heat is zero increases in the following order: copolymer < PVA - copolymer blend < PVA. The same order is observed for the temperature at which the maximum heat evolution occurs. Clearly, the burnout of the copolymer produces more heat than the burnout of PVA; in addition, the temperature range in which the copolymer burns out, is narrower. Strong heat evolution during the initial stages of sintering is detrimental as it can induce crack formation. This suggests that, compared with the copolymer, the superior volatility of PVA is attractive. Therefore, a trade-off between the compact strength and burnout characteristics determines whether PVA or the coplymer is a more suitable binder.

6. Final remarks

The strength of compacts containing different polymers could be explained on the basis of the deformation behaviour of the polymers. This correlation is strong because the strength is generally measured by subjecting the compact to tensile stress. When applying tensile stress, the interparticle friction is less significant than the bonding of the particles by polymers. Differences in polymer properties can therefore have a strong effect on mechanical properties of the compacts. When selecting a polymer, the strength of the polymer and the adhesion of the polymer to the particles are important. A high compact strength is required in order to prevent production loss arising from damage during handling and transport. However, during hardening of the compact, a high volatility of the polymer is also important. Consequently, the type of polymer is subject to optimization. The ethyl acrylate - methyl methacrylate copolymer has a high strength but poor volatility. This implies that it would be suitable for relatively small products. PVA, on the other hand, has a lower strength but a better volatility. This makes PVA more suitable as a binder in larger products or in relatively simple product shapes.

References

1. H.J. Glass, G. de With, M.J.M. de Graaf, R.J.A. van der Drift, J. Mater. Sci. **30** (1995) 3162
2. F.X.N.M. Kools, D. Stoppels, 'Kirk-Othmer Encyclopaedia of Chemical Technology', 4th ed., **10** (1994) 381
3. S. Singh, 'Theory of Plasticity', Khanna Publishers, Delhi 1981
4. A. Rudnick, A.R. Hunter, F.C. Holden, Mater. Res. Standards (1963) 283.
5. S.P. Timoshenko, J.N. Goodier, 'Theory of Elasticity', 3rd ed., McGraw-Hill, Singapore 1982
6. J.T. Fell, J.M. Newton, J. Pharm. Sci. **59** (1970) 688
7. R.H. Marion, J.K. Johnstone, Am. Ceram. Soc. Bull. **56** (1977) 998
8. G. de With, J. Mater. Sci. Lett. **3** (1984) 1000