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PMMA Encapsulation of Alumina Particles through Aqueous Suspension Polymerisation Processes

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SUMMARY: Two routes based on aqueous suspension polymerisation of methylmethacrylate (MMA) were investigated for the preparation of poly(methylmethacrylate) (PMMA) beads containing alumina particles. The compatibility of alumina surface with MMA was achieved through the condensation of 3-(trimethoxysilyl)propylmethacrylate (γ-MPS). The "dynamic" process consisted in the dispersion of the modified alumina/MMA mixture as liquid droplets in an aqueous polyvinylalcohol solution by vigorous stirring, which is maintained during polymerisation. The "static" process utilised a water-agarose gel as a suspending phase. The present paper deals with the experimental parameters optimisation, the hybrid alumina/PMMA beads characterisation and the discussion about advantages and drawbacks of both methods.

Introduction

Since the work by Charnley in the early 1960s, self-curing polymethylmethacrylate (PMMA) cements have been leading to the development of a successful technique for the fixation of joint prostheses to bone 1). Acrylic bone cements are prepared by mixing a liquid MMA monomer part and a solid one consisting of pre-polymerised PMMA beads, a mineral powder acting as X-ray opacifier and a free-radical initiator (typically benzoyl peroxide BPO). The viscosity increase is simultaneously controlled by the partial dissolution of PMMA beads by the liquid monomer and by the monomer polymerisation initiated by BPO decomposition.

Nevertheless, the lack of adhesion between the acrylic matrix and the inorganic particles is sometimes responsible for a premature rupture. So, one alternative route could be the use of radiopacifying inorganic particles covalently bonded to the matrix and previously embedded in PMMA beads (hybrid organic-inorganic beads). This can be achieved through the preliminary treatment of the fillers surface with a silane bonding agent (Scheme 1), such as 3-(trimethoxysilyl)propylmethacrylate (γ-MPS), leading to an organophilic coating and capable of later copolymerising with the acrylic monomers 2).

Few papers in the literature deal with the encapsulation of inorganic particles through a suspension polymerisation technique: Bakhshaee *et al.* reported a study with carbon blacks 3) and Vincent and coll. described the encapsulation of silica particles in PMMA beads 4).

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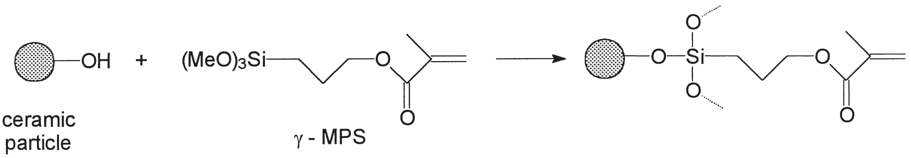

Scheme 1

This paper deals with the elaboration techniques of the organic-inorganic hybrid PMMA beads through aqueous suspension polymerisation processes: the conventional technique, consisting in dispersing the monomers as liquid droplets in an aqueous polyvinylalcohol solution (suspension stabiliser) by vigorous stirring, which is maintained during polymerisation ("dynamic" process) and a more recent process, utilising a water-agarose gel as a suspending phase ("static" process) $^{5)}$.

Experimental

Materials: alumina particles used in this study were commercial powders: α-alumina (CR30 from Baikowski Chimie) with d_{50} = 0.5 μm and a specific surface area of 26.6 $m^2.g^{-1}$. Toluene, 3-(trimethoxysilyl)propylmethacrylate (γ-MPS), benzoyl peroxide (BPO), methyl methacrylate and agarose from Sigma-Aldrich were used without further purification. Polyvinylalcohol was purchased from Prolabo (Rhodoviol 4/125).

Grafting of silane molecules onto alumina surface: γ-MPS grafting reactions were carried out in toluene as previously described $^{2)}$.

Alumina encapsulation through the conventional aqueous suspension polymerisation of MMA (dynamic process): a 1-litre glass reactor (with a hemispherical bottom) was equipped with an anchor-like stirrer, a thermostatic water jacket and a reflux condenser. Polyvinylalcohol (PVA) was dissolved in 500 ml of warm deionised water. 5 g of γ-MPS-treated alumina powder were ultrasonically dispersed in 50 ml of MMA, in which BPO was previously dissolved at room temperature. The resulting mixture was dispersed in 250 ml of PVA solution at 1000 rpm for 5 min (Turbotest 33/300 AA from VMI-Rayneri equipped with a defloculating propeller turbine). The mixture was then poured in the polymerisation reactor, where 250 ml of PVA solution were previously degassed under an argon stream. The polymerisation was performed with a stirring speed of 750 rpm for 7 hours.

Alumina encapsulation through the gelled suspension polymerisation of MMA (static process): the water-agarose dispersing solution was prepared by adding agarose (2 g) to deionised and degassed water (200 g). The solution was then poured in the polymerisation reactor, whose jacket was fed at 41°C. The BPO/MMA/γ-MPS-treated alumina mixture was dispersed in the reactor with a stirring speed of 750 rpm. The stirrer was switched off when the temperature reaches the gelling point of the agarose solution (42°C). The polymerisation was performed at 70°C and when it was completed, the gelled phase was reverted to an aqueous solution by simply stirring and warming up to 90°C.

Characterisation techniques: before any characterization, the hybrid PMMA beads were thoroughly washed with warm water and dried in an oven at 40°C. They were sieved by using a two-sieve cascade with apertures of 250 and 100 μm. After gelation of the hybrid PMMA beads in epoxy resin and polishing of the specimens, aluminium X-ray map Electron Probe MicroAnalysis (EPMA) were performed by using a CAMECA SX 630 microprobe (10 kV). Molecular weights were calculated from Size Exclusion Chromatography (SEC) analysis in THF using polystyrene standard calibration (three-column pack: 250, 1500 and 10^4 Å).

Results and Discussion

The study of the condensation of an excess of 3-(trimethoxysilyl)propylmethacrylate (γ-MPS) onto the alumina particles in toluene has already been described in a first paper 2). The surface density of grafted γ-MPS is *ca.* 7 μmol.m^{-2} and suggests that powder surfaces consist of silane multilayers whose number is controlled by the steric hindrance of γ-methacryloylpropyl groups. The surface of γ-MPS-treated alumina is hydrophobic and these particles may be readily dispersed in liquid MMA.

The encapsulation polymerisation was first performed through the conventional suspension polymerisation in which MMA is suspended as the discontinuous phase of droplets in an aqueous continuous phase and polymerised. In order to establish the initial monomer droplets size distribution and to avoid droplets coalescence, polyvinylalcohol was used as suspension stabiliser. As generally observed in typical MMA suspension polymerisation, the higher the PVA amount, the finer the hybrid PMMA beads (Table 1). More surprisingly, $m_{alumina}/m_{MMA}$ ratio is also critical to achieving the desired particle-size distribution in the final product: the larger the γ-MPS-treated alumina amount, the bigger the hybrid PMMA beads (Table 2). This may be due to the alumina particles modifying the adsorptive properties of the monomer mixture and increasing the apparent density of the polymerising droplets. Therefore, the probability of droplets breakage and coalescence would be higher. The BPO amount acts strongly upon the molecular weight distribution (Table 3), as for free-radical bulk polymerisation whose polymerisation kinetics are very similar to those of the suspension process. So PMMA molecular weight may be controlled by m_{BPO}/m_{MMA} ratio.

Table 1. Effect of m_{PVA}/m_{MMA} ratio on hybrid PMMA/alumina beads characteristics
[m_{MMA} = 50 g ; m_{BPO} = 2.5 g ; $m_{alumina}$ = 5 g ; T = 80°C ; duration = 7 hours]

m_{PVA}/m_{MMA} / %	Yield / %	PMMA beads size distribution / %			$\overline{M_n}$	$\overline{M_w}$
		250 μm	100 μm			
1	79	97	ε	ε	36 000	94 000
2	83	92	8	ε	32 000	90 000
3	56	73	24	3	47 000	110 000
4	84	65	29	6	30 000	88 000
8	42	29	36	35	43 000	102 000

Table 2. Effect of $m_{alumina}/m_{MMA}$ ratio on hybrid PMMA/alumina beads characteristics
[m_{MMA} = 50 g ; m_{BPO} = 0.5 g ; m_{PVA} = 2 g ; T = 90°C ; duration = 7 hours]

$m_{alumina}/m_{MMA}$ / %	Yield / %	PMMA beads size distribution / %			$\overline{M_n}$	$\overline{M_w}$
		250 μm	100 μm			
10	42	9	28	63	121 000	248 000
20	53	33	48	19	115 000	220 000
30	42	87	11	2	143 000	310 000

Table 3. Effect of m_{BPO}/m_{MMA} ratio on hybrid PMMA/alumina beads characteristics
[m_{MMA} = 50 g ; m_{PVA} = 0.5 g ; $m_{alumina}$ = 5 g ; T = 80°C]

m_{BPO}/m_{MMA} / %	Duration / h	Yield / %	$\overline{M_n}$	$\overline{M_w}$
0.1	24	20	95 000	274 000
1	7	48	52 000	241 000
5	7	79	36 000	94 000
10	7	83	20 000	53 000

The scanning electron micrograph displays the spherical shape of hybrid PMMA beads (part lower than 100 μm). The aluminium X-ray EPMA map shows that alumina particles are quite well arranged in PMMA beads (Fig. 1).

A new suspension polymerisation process, utilising a water-agarose gel as a suspending phase was recently reported by Giusti *et al* 6). By this "static" technique, PMMA powders adequate for bone cement production were obtained 5). We studied the feasibility for encapsulating alumina in PMMA beads through this technique. Several experiments were performed varying the polymerisation temperature and m_{BPO}/m_{MMA} ratio.

As underlined by Polacco *et al*, the thermal control of the process is worse than in the usual "dynamic" technique : the gel structure embeds the individual droplets, but also limits dissipation of the heat produced by the exothermic propagation step of the polymerisation 7).

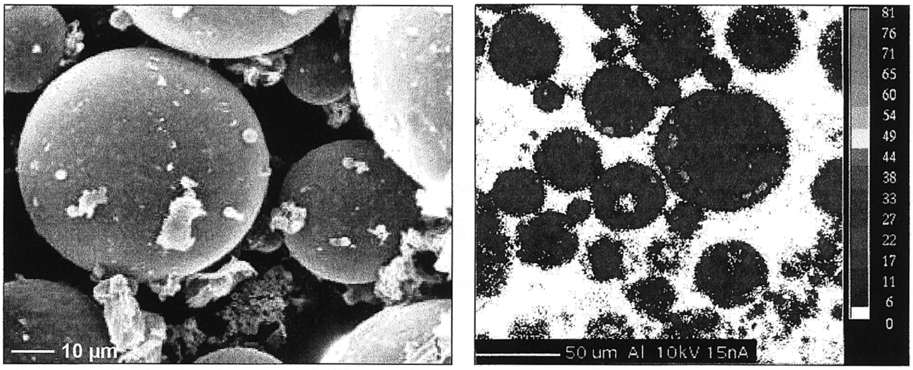

Fig. 1: Scanning electron micrograph and aluminium X-ray EPMA map of alumina / PMMA beads obtained by the conventional "dynamic" suspension polymerisation process.

This problem could arise in scaling-up the reactor. When the temperature limit for the stability of the gel (90°C) is reached, the polymerising droplets coalesce and no PMMA beads are obtained, as in our experiment performed at 85°C (Table 4). Table 5 shows that PMMA molecular weight can be controlled by m_{BPO}/m_{MMA} ratio. For similar m_{BPO}/m_{MMA} ratios, PMMA chains are longer when the beads are obtained by the "static" process than by the "dynamic" process. Because of the lower polymerisation temperature and the water-agarose gel presence, amounts of evaporated monomer out of the imperfectly airtight reactor are lower and polymer yields are better.

Table 4. Effect of the temperature on hybrid PMMA/alumina beads characteristics [m_{MMA} = 50 g ; m_{BPO} = 0.5 g ; $m_{alumina}$ = 5 g ; duration = 24 hours]

Temperature / °C	Yield / %	PMMA beads size distribution / %			$\overline{M_n}$	$\overline{M_w}$
		250 µm	100 µm			
70	70	ε	21	79	158 000	555 000
85	/	ε	ε	ε	150 000	300 000

Table 5. Effect of m_{BPO}/m_{MMA} ratio on hybrid PMMA/alumina beads characteristics [m_{MMA} = 50 g ; $m_{alumina}$ = 5 g ; T = 70°C ; duration = 24 hours]

m_{BPO}/m_{MMA} / %	Yield / %	PMMA beads size distribution / %			$\overline{M_n}$	$\overline{M_w}$
		250 µm	100 µm			
1	70	ε	21	79	158 000	555 000
2	61	ε	38	62	182 000	546 000
5	91	7	26	67	117 000	456 000
10	82	4	29	67	78 000	296 000

The scanning electron micrograph and the aluminium X-ray EPMA map allow to verify the spherical shape of hybrid PMMA beads and show that the lack of agitation and the higher density of alumina favour the inorganic particles concentration in the bottom hemisphere of the beads (Fig. 2).

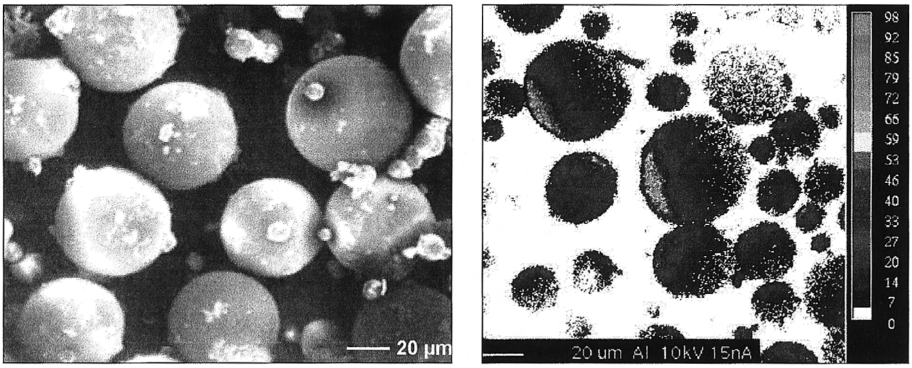

Fig. 2: Scanning electron micrograph and aluminium X-ray EPMA map of alumina / PMMA beads obtained by the "static" suspension polymerisation process in the water-agarose gelled system.

Conclusion

Both suspension polymerisation techniques allow to encapsulate γ-MPS-treated alumina particles. The conventional "dynamic" process allows to obtain quite homogeneous materials. The "static" technique in a water-agarose gel is promising, but the arrangement of alumina particles in PMMA beads is disturbed by sedimentation and an industrial production would need an effective temperature control system. Attempts are currently underway to formulate acrylic bone cements from these hybrid alumina/PMMA beads and to study their mechanical properties.

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References

1. J. Charnley, *J. Bone J. Surg.*, **42B**, 28 (1960).
2. M. Abboud, M.R. Turner, E. Duguet and M. Fontanille, *J. Mater. Chem.,* **7**, 1527 (1997).
3. M. Bakhshaee, R.A. Pethrick, H. Rashid and D.C. Sherrington, *Polym. Commun.*, **26**, 185 (1985).
4. E.C. Cooper and B. Vincent, *J. Colloid Interface Sci.*, **132**, 592 (1989).
5. P. Giusti, L. Lazzeri, G. Pizzirani, G. Polacco, C. Rizzo and M. Palla, *J. Mater. Sci.: Mater. Med.*, **5**, 858 (1994).
6. P. Giusti, M. Mantilli, M. Palla and G. Pizzirani, *Italian Patent 67967 A 90* (1990).
7. G. Polacco, D. Semino and C. Rizzo, *J. Mater. Sci.: Mater. Med.*, **5**, 587 (1994).