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A.R. Siddiq, A.R. Kennedy

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A novel method for the manufacture of porous structures with multi-component, coated pores

A. R. Siddiq and A. R. Kennedy[#]

Faculty of Engineering, University of Nottingham, Nottingham, UK

[#] Corresponding author: Tel +44 115 9513744

Email: andrew.kennedy@nottingham.ac.uk;

Abstract

A novel process is demonstrated which is able to produce porous structures with internal coatings. This is achieved using sacrificial porogens which are coated with a powder and which are then infiltrated by compression moulding using a molten polymer. The coating powder is transferred to the pore and multi-material or compositionally-gradient coatings are produced. The interconnectivity of the porous structure is reduced when the pores are coated, but can be increased by reducing the degree of powder coverage of the porogen.

Keywords

Porous material; surface modification; polymer processing; coating

1.0 Introduction

Open cell porous materials are widely used as energy and sound absorbing structures, heat exchangers, catalytic supports, filters and in biomedical devices. In each application the porosity and pore size are tailored to best serve the function required. In several of the above

cases, there is a desire to “functionalise” the surface of the porous structure to provide or enhance catalytic activity, adsorption behaviour, anti-microbial or osseoconductive action. As the substrate materials can be metals, ceramics or polymers, the manufacturing processes vary considerably and are often, especially in the case of porous metals, highly involved [1]. This complexity also extends to the coating processes for which the capability for coating large 3-dimensional, open pore structures is hampered by limited penetration for PVD and electrochemical processes, with additional problems of non-uniform coating thickness and pore clogging for processes such as CVD, dip and sol gel coating. This paper demonstrates a novel, unique, yet simple process for co-creating and coating porous structures, based on a patented process co-developed by the authors [2].

2.0 Experimental Methods

Porous structures were made by loading 150 g of salt beads (2.0-2.5 mm “Finish” dishwasher salt) into a 180 mm diameter steel tool. The bed of beads was roughly levelled and then 50 g of PEEK powder (150PF PEEK, Victrex) was distributed evenly on top. The tool, with the upper punch inserted, was placed in a press and heated to 400°C, to facilitate melting of the PEEK, under an applied load of 10 tonnes (approximately 4 MPa). After 30 min at the target temperature, cooling was applied, the mould opened and the part ejected. To create porosity, the salt was removed from the samples by dissolution in warm water.

To produce structures with coated pores, the space holder was coated with the material which would later form the coating. This was facilitated by spraying 50 g of salt beads, contained within a glass beaker, with 2 g of water, using a fine mist spray, adding the “coating” powder (typically <100 µm in diameter) and agitating the mixture by manual swirling of the vessel. To ensure complete coverage, excess powder was used. After coating, the mixture was dried in an oven at 80°C for 3 h and excess “coating” was removed by swirling the beads in a sieve with 0.5 mm apertures. Polished samples were viewed in the optical and scanning electron

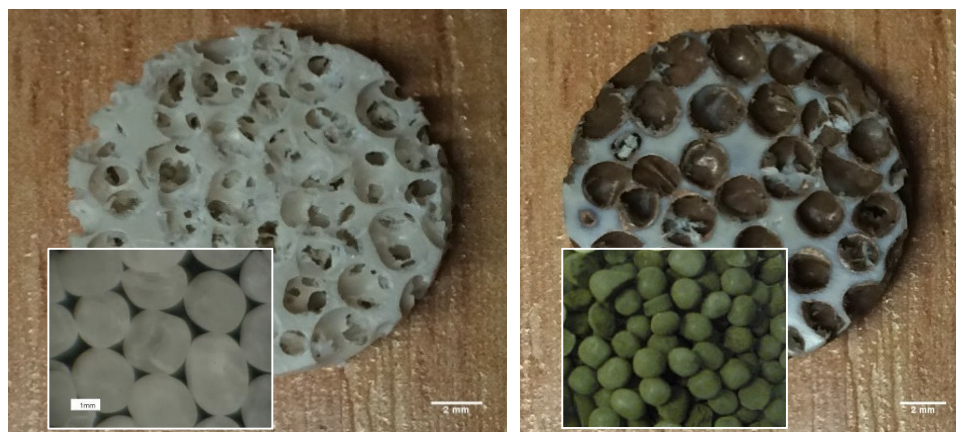
microscopes (after Pt coating). Pore surfaces were also viewed in cross section after infiltrating the porous structures with epoxy resin.

3.0 Results and Discussion

Observations from the coating process revealed that successful coverage with fine powder relies on uniform “dampening” of the salt beads. This generally required at least 2g of water per 50g of salt, but will be dependent upon the surface area of the beads. It was found that the use of powders larger than those presented here ($>150\ \mu\text{m}$) resulted in lower coverage rates as the inertia of the powder was sufficient for them to become detached when sieved.

Figure 1a shows the typical morphology for a porous PEEK structure. It is clear that molten PEEK was readily infiltrated, under pressure, into the large gaps between these beads (shown in the inset) which, because of their deviation from sphericity, enables them to pack more densely than spheres, enhancing the inter-bead contact. The porosity in the part is slightly higher than that for the tapped packing fraction for the beads (0.69) since some consolidation of the beads occurs in the tool when the load is applied, before the PEEK melts.

The process is similar to the production of porous metals [1,3,4] by pressure-assisted casting methods. The low surface tension for molten PEEK (approximately 1/30 of that for molten Al) means that much lower pressures could be used, as the capillary radius for infiltration is very small, but the considerably higher viscosity for the polymer (approximately 40000 times that for molten Al) dictates the use of higher pressures in order to achieve filling in a convenient time period. As is the case for molten Al [3], the PEEK is unable to penetrate into very small gaps at the contact points between beads and this creates windows between the pores that give the structure interconnectivity. The high degree of connectivity for the porous PEEK structure is evident in Figure 1a, where multiple, large windows between the pores are clearly visible.



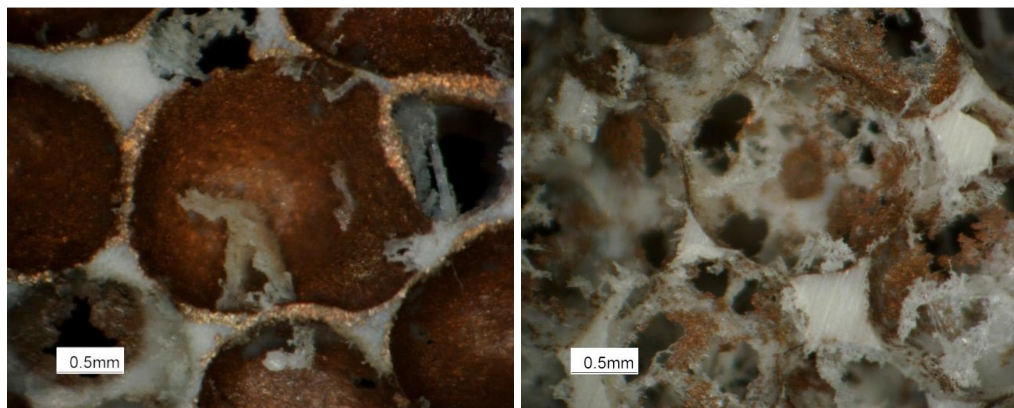
a

b

Figure 1 a) Porous PEEK and loosely-packed salt beads (inset) and b) porous PEEK coated with Cu and (inset) Cu-coated beads.

Figure 1b shows an image of a porous structure made using beads coated with $< 45\mu\text{m}$ copper powder (but which is typical of all the 10+ coating types investigated to date) and presents an image (inset) of loose Cu-coated beads. It can be seen from this image, and that in Figure 2a, that during the moulding process the Cu coating on the beads is transferred to the PEEK cell walls. Holes or “windows” that connect neighbouring pores are evident in Figure 2a, but it is clear that the number of connecting windows per pore in coated samples is greatly reduced compared with the high level of interconnectivity observed in Figure 1a. This difference is believed to be a result of enveloping the salt in a “rough” powder coating which reduces the contact area between adjacent particles. It is also probable that large interconnections are only formed where the coating has been removed at contact points, as a result of abrasion during consolidation of the particle bed during compaction. Despite this, an interconnected structure is observed and although significantly increased immersion times are required compared to uncoated PEEK structures, residual salt levels are low. Figure 2b shows that pore interconnectivity can be increased by reducing the level of coverage of the Cu powder, in this example to 60% of that which was measured (by mass gain) for complete coverage. Partial coverage increases the likelihood of direct salt-salt contact and the formation of large windows

between pores. Reduced coverage of the beads is evidenced by areas of PEEK on the cell wall surfaces and thinner coating layers (compared with Figure 2a).



a b
 Figure 2 Cu-coated porous structures showing increased interconnectivity as the coverage of powder decreases from a) 100% to b) 60% of the mass of Cu powder required for complete coverage

It is worth pointing out that in Figure 2, filigree PEEK structures can be observed, emanating from the pore walls and protruding into the centre of some pores. These are created by PEEK infiltrating small cracks in the particles created during compression moulding. These features could be reduced by a reduction in “infiltration” or moulding pressure, but in this study the 10 tonne force was already the minimum available. Infiltration of the small cracks is demonstrative of the very small (sub-micron) capillary radius and indicates the potential for producing porous structures using very much smaller salt beads or particles (which are also less likely to crack under loading).

Secondary electron SEM images in Figure 3 show the morphology of the coatings more clearly. Owing to the nature of the “coating” process, coverage of the pores will not be in the form of a continuous film; rather, the coating is discontinuous and textured, a replication of the coating of the salt beads by the metal powders. The images show that a large proportion of those particles

attached to the salt become firmly embedded in the PEEK, protruding from the cell walls. The exposure of the Cu particles is, of course, essential for their efficacy in functionalising the surface of the porous structure. A simple droplet spreading test showed good wetting for molten PEEK on salt ($\theta < 90^\circ$) but much poorer wetting of metals such as Cu, Ti and Ni (where $\theta \gg 90^\circ$). Thus it might be expected that the PEEK only partially envelops the powder layer on the surface of the beads, generating sufficient mechanical interlocking that the coating layer is not removed with the salt when immersed in water, but leading to protrusion of metal particles from the PEEK surfaces

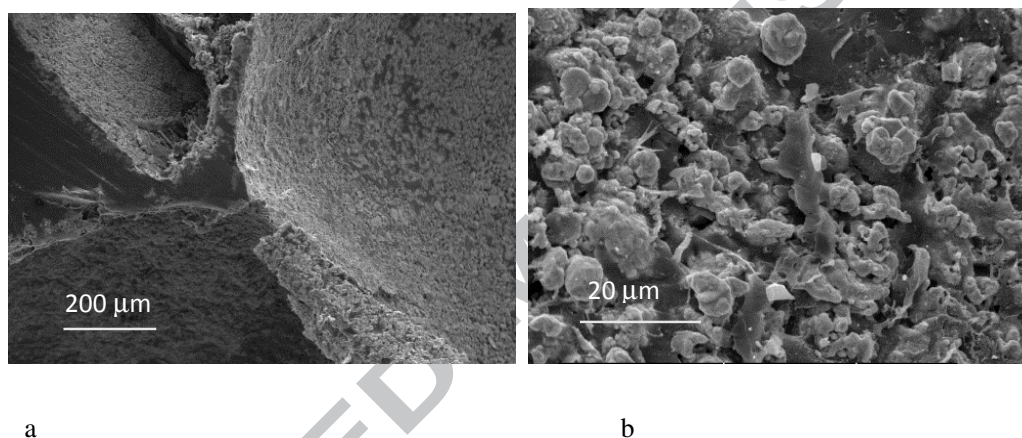


Figure 3 SEM images of Cu-coated porous PEEK structures showing protrusion of the Cu particles from the pore surfaces

A unique benefit of the novel process is demonstrated in Figure 4, where individual pores coated with a number of different materials (in this case $<45\mu\text{m}$ Cu, $<18\mu\text{m}$ Ni and $<38\mu\text{m}$ SiC particles) are shown. Figure 4a shows that the layer thickness is limited to a few particles and that the coverage level is high. The backscattered electron image in Figure 4b enables the different material types to be clearly differentiated. Although not shown, the process also enables adjacent pores to be coated with different materials in either a random or more structured fashion, enabling the creation of samples with compositionally-graded coatings.

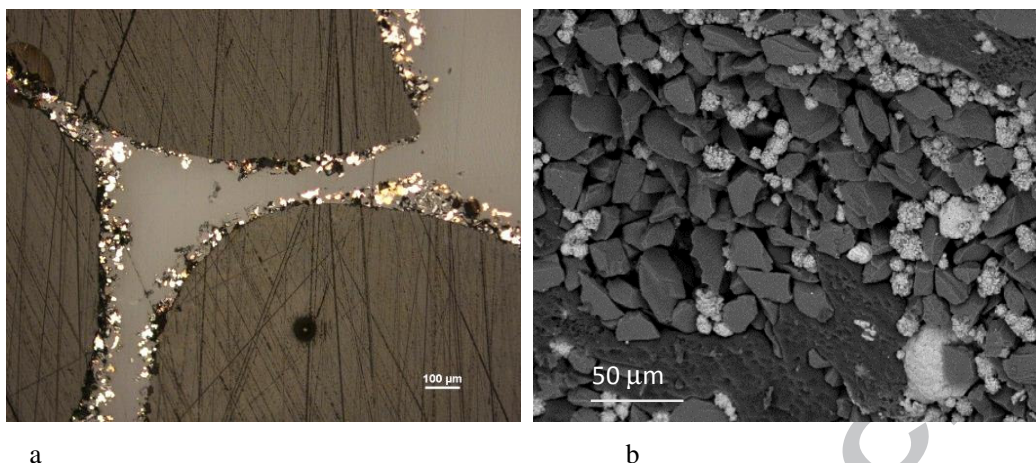


Figure 4 Images of a) PEEK struts in cross section and b) cell walls, both coated with a mixture of Ni, Cu and SiC powders

4.0 Conclusions

A unique and versatile process has been demonstrated which is able to produce porous structures with internal coatings not limited to a single coating material. The coating material can be any metal, ceramic or polymer powder, as long as it is stable at the processing temperature and that it is not as readily soluble in water as salt. The coating process is devoid of problems such as lack of penetration or clogging and could be extended to smaller pore sizes (using smaller space-holders and finer powders). The interconnectivity of the pore structure can be tailored by the degree of coverage of the beads and low coverage levels could be employed to use expensive materials sparingly and efficiently. Although not shown here, preliminary studies have shown that the process is capable of being translated to porous Al systems using similarly-coated beads and vacuum-assisted casting.

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Figure Captions

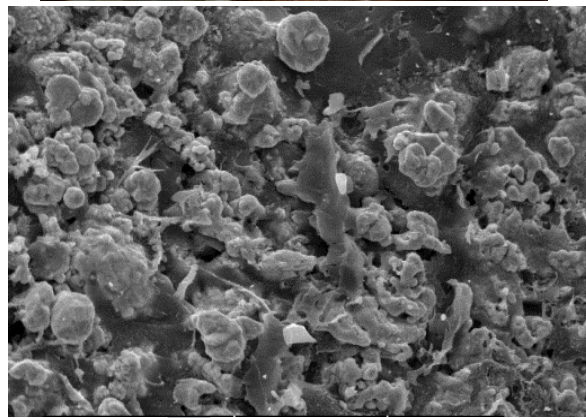
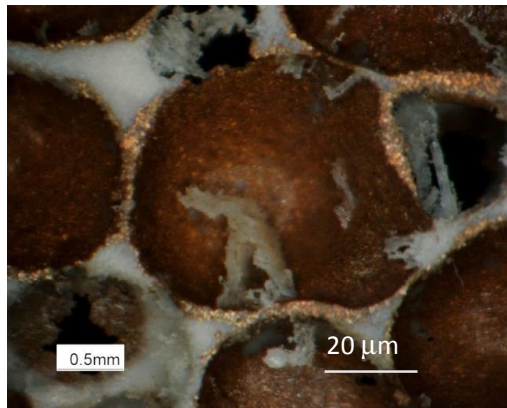
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Figure 3 SEM images of Cu-coated porous PEEK structures showing protrusion of the Cu particles from the pore surfaces

Figure 4 Images of a) PEEK struts in cross section and b) cell walls, both coated with a mixture of Ni, Cu and SiC powders

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Cu-coated porous PEEK structures showing uniform coverage and protrusion of the Cu particles from the pore surfaces

A novel method for the manufacture of porous structures with multi-component, coated pores

A. R. Siddiq and A. R. Kennedy[#]

Faculty of Engineering, University of Nottingham, Nottingham, UK

[#] Corresponding author: Tel +44 115 9513744

Email: andrew.kennedy@nottingham.ac.uk;

Research highlights:

- A novel process produces porous structures with internal coatings
- The process not only creates the porous framework but “coats from the inside out”
- Multiple materials to be coated onto individual pores
- It offers unique capabilities for functionalising the surfaces of porous structures