

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 11/2/99		3. REPORT TYPE AND DATES COVERED FINAL REPORT 1/95-6/99	
4. TITLE AND SUBTITLE Smart Materials by Extrusion Solid Freeform Fabrication				5. FUNDING NUMBERS DAAH04-95-1-0416	
6. AUTHOR(S) Paul Calvert					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Materials Science and Engineering, University of Arizona Tucson AZ 85721				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSORING / MONITORING AGENCY REPORT NUMBER <i>ARO 34377.6-MS</i>	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Extrusion freeform fabrication allows materials to be built layer by layer to form a solid. By combining different materials it is possible to attain new combinations of properties and to design the response of a material for the local stresses on a part. Most biological structures are built layer by layer and show excellent adaption of structure to function. This method has been used to form hydrogels and then mineralize them to very volume fractions of inorganic material. The resulting composites are tough, stiff and strong. The approach has also been used to make electrically stimulated muscle-like actuators of two types of hydrogel, crosslinked polyacrylic acid and crosslinked polyacrylamide. One layer of gel contracts in the applied field, the other layer acts as a passive, soft reservoir which takes up the extruded water without limiting contraction of the active layer. This system has been adapted to make an electrically-driven reversible gel "jack". When a field is applied the sample changes thickness by 10% in about 60 seconds and then returns to the original state when the field is reversed. This is close to what would be needed for a synthetic electrical muscle in that it provides a large, reversible linear expansion at constant volume.					
14. SUBJECT TERMS Intelligent Materials, Freeforming, Hydrogels, Artificial Muscle, Bone-like composites				15. NUMBER OF PAGES 5	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL		

NSN 7540-01-280-5500

89)

Std. 239-18

Standard Form 298 (Rev.2-
Prescribed by ANSI
Z39-102

19991215 042

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Manuscripts Submitted & Published

- P. Calvert "Biomimetic Inorganic-Organic Composites" in Biomimetic Materials Chemistry, ed. S. Mann, VCH Pubs. Weinheim, 1996 pp.315-336
- R.S. Crockett, J. O'Kelly, P.D. Calvert, B.D. Fabes, K. Stuffle, P. Creegan and R. Hoffman, "Predicting and controlling resolution and surface finish of ceramic objects produced by stereodeposition processes" in Solid Freeform Fabrication Proceedings 1995 eds. H.L. Marcus, J.J. Beaman, D.L. Bourell, J.W. Barlow and R.H. Crawford, U. Texas, Austin. pp. 17-24
- J. Lombardi, G. George, L. Rintoul and P. Calvert, "Freeform fabrication of polymers and composites" Polymer Preprints 37(1) 221-222 (1996)
- J.W. Burdon and P.D. Calvert, "Development of nanophase particles in a crystalline polymer" Proc. SAMPE Intl. Tech. Conf. 27 578-589 (1995)
- P. Calvert, G. George and L. Rintoul, "Monitoring of cure and water uptake in a freeformed epoxy resin by an embedded optical fiber" Chem. Mater., 8 (1996) 1298-1301.
- P. Calvert and P. Rieke, "Biomimetic mineralization in and on polymers" Chem. Mater. 8 1715-1727 (1996)
- J. Burdon, M. Oner, P. Calvert, "Growth of oxalate crystals on films of acrylate polymers" Mat. Sci. & Eng.C 4 133-137 (1996)
- H. Denham, G. George, L. Rintoul, P. Calvert "Fabrication of polymers and composites containing embedded sensors" Proceedings of the 3rd Intl. Conf. Intelligent Materials Lyon, 1996 Eds. P.F. Gobin, J. Tatibouet, pp.742-7
- H. Grijalva, M. Inoue, S. Boggavarapu, P. Calvert, "Films of amorphous and crystalline copper sulfides, CuS" J. Mater. Chem. 6 (1996) 1157-1160.
- P. Calvert "Potential applications of nanotubes" in Carbon Nanotubes, preparation and properties ed. T.W. Ebbesen, CRC Press, Boca Raton FL, 1997 pp. 277-292
- R.S. Crockett & P. D. Calvert "The liquid-to-solid transition in stereodeposition techniques" in Solid Freeform Fabrication Proceedings 1996 eds. H.L. Marcus, J.J. Beaman, D.L. Bourell, J.W. Barlow and R.H. Crawford, U. Texas, Austin pp. 257-264
- H. Denham, G. George, L. Rintoul, P. Calvert, "Fabrication of polymers and composites containing embedded sensors." Proceedings of the SPIE _ The International Society for Optical Engineering 2779 (1996) p742_7.
- P. Calvert, R. Crockett, "Chemical solid free-form fabrication: making shapes without molds" Chem. Mater. 9 650-663 (1997)
- J. O'Kelly, R. Crockett, H. Martin & Paul Calvert, "Biomimetic processing of gel glasses and organic-inorganic hybrids" J. Sol-gel Sci. & technology (1997) 8 641-644
- Paul Calvert "Protein Composite Materials" in Protein Based Materials, eds. K. McGrath & D. Kaplan, Birkhauser, Boston, 1997 pp.179-216
- H.B. Denham, T.A. Anderson, E. Madenci & Paul Calvert, "Embedded PVF2 sensors for smart composites" SPIE Proceedings 3040 (1997) 138-147
- Paul Calvert and Z. Liu, "Extrusion freeform fabrication of bone-like mineralized hydrogels and muscle-like actuators" in Solid Freeform Fabrication Proceedings 1997 eds. D.L. Bourell, J.J. Beaman, R.H. Crawford, H.L. Marcus and J.W. Barlow, U. Texas, Austin pp. 11-15

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

J. Cesarano, T. A. Baer and P. Calvert "Recent developments in freeform fabrication of dense ceramics from slurry deposition" in Solid Freeform Fabrication Proceedings 1997 eds. D.L. Bourell, J.J. Beaman, R.H. Crawford, H.L. Marcus and J.W. Barlow, U. Texas, Austin pp. 25-32

J.L. Lombardi and P.D. Calvert, "Extrusion freeforming of Nylon 6 materials" in Solid Freeform Fabrication Proceedings 1997 eds. D.L. Bourell, J.J. Beaman, R.H. Crawford, H.L. Marcus and J.W. Barlow, U. Texas, Austin pp. 473-479

R.S. Crockett, P.D. Calvert "Rheology and Freeform Fabrication: Modeling Material Flow in Deposition Techniques" in Solid Freeform Fabrication Proceedings 1997 eds. D.L. Bourell, J.J. Beaman, R.H. Crawford, H.L. Marcus and J.W. Barlow, U. Texas, Austin pp. 717-724

P. Calvert, T.L. Lin, H. Martin "Extrusion freeform fabrication of chopped-fibre reinforced composites" High Perf. Polym. (1997) 9 449-456

Calvert P, Liu Z "Freeform Fabrication of Hydrogels" Acta Materialia (46) 2565-2571 (1998)

J.L. Lombardi and P. Calvert, "Extrusion freeforming of Nylon 6 materials" Polymer (40) 1775-1779 (1999)

P. Calvert, J. Frechette, C. Souvignier, "Mineralization of multilayer hydrogels as a model for mineralization of bone" Mater. Res. Soc. Symp. Proc. 489 "Materials Science of the Cell" eds. B. Mulder, C.F. Schmidt, V. Vogel, 1998, pp.153-160

P. Calvert, "Freeforming of polymers" Curr. Opinion in Sol. St. & Mater. Sci. 3, 585-588 (1998)

P. Calvert, J. O'Kelly, C. Souvignier, "Solid Freeform Fabrication Of Organic-Inorganic Hybrid Materials" Mater. Sci. Eng. C 6, 167-174 (1998)

J. Peng, T.L. Lin, P. Calvert, "Orientation effects in short-fiber composites" Composites A 30 133-138 (1999)

J. Cesarano III, R. Segalman, P. Calvert "Robocasting" Ceramic Industry April 1998 94-102.

H.B. Denham, J. Cesarano III, B.H. King, P. Calvert "Mechanical behavior of Robocast alumina" in Solid Freeform Fabrication Proceedings 1998 eds. H.L. Marcus, J.J. Beaman, D.L. Bourell, J.W. Barlow and R.H. Crawford, U. Texas, Austin pp.589-593

Paul Calvert, Zengshe Liu, "Electrically stimulated bilayer hydrogels as muscles" SPIE Proceedings 3669 236-241, (1999)

P. Calvert, J. Peng, C. Souvignier, "Solid freeform fabrication of composites by direct deposition and by in situ mineralization" Mater. Res. Soc. Symp. Proc. 542 "Solid freeform and additive fabrication" eds. D. Dimos, S.C. Danforth, M.J. Cima, 1999, pp.3-12

U.S. Patent 5,906,863 (25 May 1999)

U.S. Patent 5,932,290 (3 August 1999).

REPORT DOCUMENTATION PAGE (SF298)

(Continuation Sheet)

Honors/awards:

Invited speaker:

Workshops: BASF, Ludwigshafen; Army Research Office (2), Nashville & Research Triangle; ONR/DARPA, Oxford.
Gordon Conference on Biomineralization; MRS Fall invited speaker.
Dept. Colloquia: Univ. Kentucky, ORNL, Univ. S. Mississippi, Univ. Cincinnati
Visiting Prof.: Sandia Natl Lab. 1995-9

Personnel

P. Calvert (P.I.)

Z. Gardlund, Research Prof.

Zhengshe Liu, Postdoctoral Fellow

S. Boggavarapu, Grad. Student

Chad Souvignier, Grad. Student

L. Raymond, Grad. Student

Jiong Peng, Grad. Student MS 1999

J. Frechette, Christian Harjanto, Haripin Chandra, S. Larkin, J. Amdahl, F. Ma; Undergrads.

Inventions

Patents awarded: U.S. 5,906,863 (25 May 1999), U.S. Patent 5,932,290 (3 August 1999).

(concerns related work on freeforming composites with ACR Co.). Patent on robocasting applied for with Sandia Natl. Labs.

Progress and Accomplishments

The last interim report covered the final experimental work, which effectively ceased during the extension period in January 1999. The experimental details of the work are published as listed above. This final report will therefore address the overall accomplishments and what we now see to be the opportunities for further development and application.

Over the last few years, freeform fabrication methods have become a standard part of the design process. The main methods are stereolithography, a laser polymerization of liquid monomer, selective laser sintering of polymer powders and fused deposition modeling using a thermoplastic filament. Each method has drawbacks in terms of speed, precision and mechanical strength of the final product but there is every reason to expect continued improvements. Our own work on freeforming of composite materials has shown how excellent mechanical properties can be obtained from a variant of fused deposition modeling. Under development are methods for ceramics and metals which could have significant impacts respectively on the applicability of ceramics in engine parts and on mold making.

Separate from these issues of freeforming current materials is the question of whether materials can be freeformed that cannot be made in other ways. Functional gradient materials are one obvious example. Another example is materials with embedded sensors and electrical connections. Sandia National Lab. has a strong interest in metal-ceramic parts, for instance. We are currently exploring methods to build fine-scale electrical components in to freeformed parts.

Bone-like composites

The current work included a study of the freeforming of hydrogels followed by their mineralization with apatite or carbonate in analogy with bone and shell formation. The goal was to shed light on the biomineralization process and thereby to develop a route to highly reinforced synthetic composite materials. The chief insight was that very high levels of inorganic material could be produced if a gel were formed containing 95% water, the mineral phase grown in by a diffusion process and then the whole part allowed to dry out. In this way, mineral contents were produced up to 80 vol% and could be taken higher. The resulting materials were tough, strong (up to 90 MPa) and stiff (up to 6 GPa). This is in contrast to conventional short glass-fiber/polymer composite or clay/polymer composite where volume fractions above 40 vol% lead to a crumbly product. Quite why the mineralization approach works so well, is less clear. Blending fibers into gel and then drying it, does not work and we have had no success with formation of silica-polymer hybrids in a swollen state, followed by deswelling. We believe that diffusion-controlled particle growth in polymer is essential to produce a regular spacing of particles that will then allow shrinkage of the intervening gel to make a hard part. These studies of mineralization do shed light on mineralization of synthetic materials in vivo, which is a serious problem, and on newer biomimetic approaches to implant coatings.

REPORT DOCUMENTATION PAGE (SF298)

(Continuation Sheet)

What would the material be good for? A biocompatible implant material is an obvious target. The gelling polymer would need to be biocompatible. The agarose that we have used so far would probably not be suitable. Collagen gels could be used but would be very expensive in the bulk needed for this process. A suitable gelling protein could almost certainly be designed. The aim would be for an implant that was as strong as the woven bone which first forms at a fracture site. If this could be inserted with strong bonding and a good match of properties, the material would be subject to remodeling by osteoclasts and osteoblasts in the normal way that occurs in natural woven bone. The limitation on this application is that many possible bone implants are under development, at this point a novel approach would have to be really compelling to justify the massive investment in animal tests and certification.

Hard composites, with properties intermediate between polymer and glass could be made in this way. So far, we have demonstrated high strength and a high mineral content but the modulus is not as high as we would expect. The material would need to be formed in an inorganic oxide and a synthetic polymer, we now know enough to realize that this will require careful design since simple combinations of acrylates and silica or titania do not work. To build precision parts, a cycle of build, mineralize and deswell would lead to unacceptable distortion during shrinkage. An approach based on building plates which are then machined would be viable. Hard coats for polymers are of great interest. Transparent coats are needed to permit the development of plastic windshields and other plastic optics would currently benefit from better hardcoats. Our materials are not transparent and would need to be nanoscaled to become so. On the other hand, hard coats for plastic gears and other wear parts are also desirable. Some form of dipping process would be necessary.

Muscles

A second aspect of this project was the development of a multilayer gel system which acts like an artificial muscle. Anionic gels will expand in base and shrink in acid. When a field is applied, by electrodes attached to the gel, it bends. The source of the effect is complex but probably results from acid release at the positive electrode and base at the negative electrode. Artificial muscles can be made in this way but a bending action is hard to use with a robotic arm. A simple, electrically driven, contraction of expansion would be more desirable. We showed that this can be achieved by combining two gels. The swollen anionic gel at the positive electrode contracts and the soft neutral gel at the negative electrode responds by taking up the water expelled from the positive side. The combination of stiff anionic gel and soft neutral gel results in an overall expansion in the thickness direction and contraction in the lateral directions. Hence the system will rise and fall under electrical stimulation. This shows that an artificial electrical muscle will be based on a combination of polymers designed to give the desired response, it is a system not a material. The current system is slow because the layers are thick, about 1 cm total when swollen. It is also soft and will not develop much force in this current format. The big advantage over other actuators is that the expansion is large, 10% or more. Compared to other gel approaches, it has the advantage of depending on internal water displacement.

How could this material be applied? For speed of response, the scale should be finer and this requires a different chemical system for our deposition approach. The acrylate polymerizations are very air-sensitive and so cannot be done well in thin layers except under nitrogen. We envisage a plate with, for instance alternating stripes of neutral and acid-sensitive gel. The stripes would have individual electrodes. By applying field, the acid stripes would shrink and the neutral stripes swell, generating a series of ridges that would raise the upper surface. Many other geometries are possible. The force will be increased by increasing the density of the gel. Swelling and deswelling may be driven by exchanges of divalent ions rather than by pH. The system in fact has many of the aspects of a battery so that any detailed analysis of the response to applied field must take into account the electrochemical reactions, the ion diffusion processes, binding to the polymer and the establishment of concentration gradients through the system.

The key facts about artificial muscles at the moment are that they are badly needed for robotics and that no suitable system exists. A fine scale combination of at least two polymers and electrodes will be needed to achieve something truly muscle-like.

Technology Transfer

Our extrusion freeforming method is being actively pursued by Advanced Ceramics Research Corp. of Tucson (ACR). We have two joint patents. They have sold a number of extrusion heads as an upgrade to customer's existing Fused Deposition Modelers. They are also offering a service for making ceramic, thermoplastic and composite parts from 3D CAD designs. The method originated from a series of joint projects between the University and ACR and this collaboration continues. The collaboration with Sandia National Labs. continues. Their "Robocasting" variant on our method is being used to make metal-ceramic graded structures.