

FORMGRIP Process Produces Metallic Foam Structures That Can Be Integrated with Conventionally Produced Components

A melt-processing technique for the production of closed-cell metal foams has been recently developed at the University of Cambridge. It is potentially well suited for the generation of complex assemblies in which a foamed metal is integrated with conventionally produced components. The technique, termed FORMGRIP (foaming of reinforced metals by gas release in precursors), consists of a two-stage operation: (1) precursor preparation via a melt route and (2) baking (foaming) of the precursor material in a mold to produce shaped components. The process is also adaptable for continuous production of foamed rods and bars.

The multifunctional nature of closed-cell metal foam makes it of potential value for applications such as sandwich structures, double-hull fillers/stiffeners, firewalls, components for energy-absorption and blast-protection structures, permanent cores for castings to replace sand cores, and buoyancy devices. One of the key issues for wider industrial use of this type of engineering material is the development of cost-effective processing methods that facilitate near net-shape production of foams with controlled porosity and cell size. Manufacturing large volumes based on melt processing has potentially more attractive process economics and tolerance to impurities than powder routes, which, on the other hand, normally allow closer control over the foam macrostructure. The FORMGRIP process combines some of the attributes of both approaches.

In the first stage of the process, a gas-generating powder or foaming agent

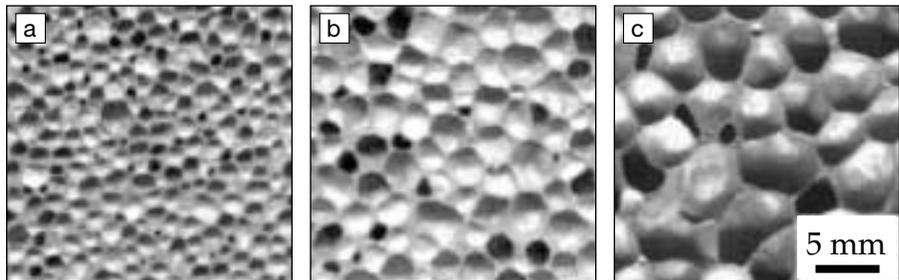


Figure 1. Optical micrographs of sections through Al-9wt%Si/SiC_p composite foams, showing the versatility of the FORMGRIP process for control of the foam porosity level, P: (a) P = 69%, (b) P = 79%, and (c) P = 88%.

(e.g., titanium hydride, TiH₂) is dispersed in a semiliquid metal-matrix composite (Al-9wt%Si alloy, reinforced with SiC particles) melt. A low-porosity (~14–25%) foamable precursor is produced by allowing this melt to solidify after casting. A key requirement for the effective preparation of the precursor material is that only a limited amount of hydrogen is evolved during this stage of the process. Two factors facilitate this objective. The first is a foaming-agent thermal-oxidation pretreatment sequence in air that results in changes in the hydrogen concentration in the hydride and formation of a diffusion-barrier oxide layer on the powder surface. Both of these phenomena are important for controlling the onset and kinetics of hydrogen evolution. The second factor is an increase in the melt viscosity by using semiliquid processing and/or a fine dispersion of ceramic material. The stock material is thus effectively a metal-matrix composite in which the size, shape, and level of the ceramic content can vary over a wide range. The foam invasion into the mold is induced by thermally activated gas release as remelting occurs. The

process provides for flexibility in the design of foam structures through control over both the kinetics of hydrogen evolution and the drainage processes that occur during foam evolution. This is facilitated by manipulating parameters such as thermal histories during the precursor baking and composite melt viscosities (ceramic particle content and size). Examples of typical foam macrostructures are shown in Figure 1.

Opportunities

The FORMGRIP method for processing metallic foams is still under development. The researchers at Cambridge are currently interested in undertaking further work in collaboration with commercial concerns. Information relating to the research can be found on their web site at www.msm.cam.ac.uk/mmc/mmc.html.

Source: Prof. T.W. Clyne, Director of DERA-Cambridge Gordon Laboratory, Department of Materials Science & Metallurgy, Pembroke Street, University of Cambridge, Cambridge CB2 3QZ, UK; tel. 44-1223-334-332, fax 44-1223-334-567, and e-mail twc10@cam.ac.uk.

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A Two-Step Deformation Technique Strengthens Pure Titanium to Greater Than 1000 MPa

A two-step deformation process has been developed by researchers at Ufa State Aviation Technical University in Russia and Los Alamos National Laboratory (LANL) that more than doubles the strength of commercially pure titanium from about 400 MPa to greater than 1000 MPa. The process combines warm equal-channel angular (ECA) pressing to refine the grain size with cold deformation (rolling and/or extrusion) to further increase the density of

defects, such as dislocations, that produce hardening.

Bulk ultrafine-grained pure titanium with high strength has potential industrial value, particularly in biomedical applications. Pure titanium is chemically and biologically more compatible than titanium alloys in regard to biological fluids and tissue, but because its strength is half that, for example, of the titanium alloy Ti-6Al-4V, it has been inadequate for load-bearing implants such as hip and knee prostheses. However, the vanadium and aluminum in the titanium alloy are potentially toxic, and normal wear can lead to deterioration of the implant and the release of these alloying elements into

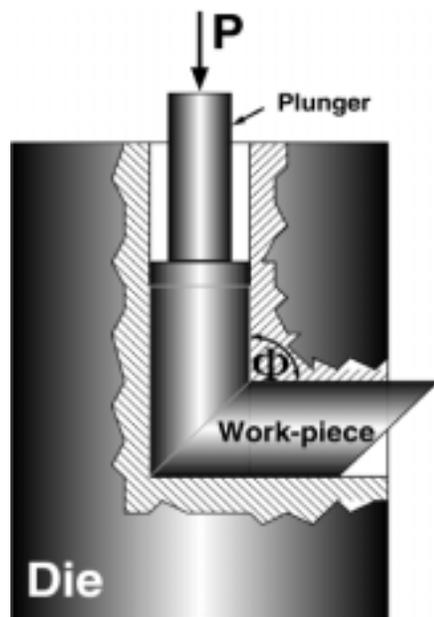


Figure 1. Equal-channel angular (ECA) pressing process.

the body. Therefore, pure titanium is more desirable.

ECA pressing produces bulk quantities of porosity-free materials with nanometer-to-submicron grain sizes that have superior mechanical properties, including high strength. During pressing, a billet of titanium is passed through a die containing two intersecting channels of equal cross section

(see Figure 1). The net dimensions of the work piece are maintained so that the process can be repeated as often as needed to obtain the desired grain size.

For example, in the first step, the researchers pressed titanium billets 26 mm in diameter and 120 mm long through an ECA die eight times, at a moderate temperature with 90° clockwise rotations of the billets between two consecutive passes. The billets retained their original dimensions, while the metal's grain size was reduced from 10 μm to about 260 nm. This reduction in grain size increases the strength of the pure titanium by 70%. In the second stage of the process, the billets are further deformed at room temperature by rolling, extrusion, or a combination of both, thereby reducing the cross-section area by 35–75%. This creates large quantities of crystalline defects, such as dislocations, that significantly increase the strength of the pure titanium. The yield strength of the ultrafine-grained pure titanium increases from 380 MPa to 940–1100 MPa after the two-step process, depending on the processing parameters. Its strength is thermally stable up to 300°C, and annealing of the as-processed titanium at temperatures below 300°C improves the metal's ductility without markedly decreasing its strength. With respect to stress-corrosion of the nanostructured titanium compared with the alloy or coarse-grained titanium, the researchers expect it to be similar because while there are only a few reports on the corrosion of nano-

structured metals, in general very little difference has been observed between nanostructured materials and their coarse-grained counterparts.

Because of its biocompatibility, nanostructured pure titanium has the potential to replace the Ti-6Al-4V alloy presently used in most medical implants and devices, including hip prostheses, hearing aids, dental implants, heart valves, and pacemakers. However, to date it has not been tested *in vivo*.

Opportunities

Los Alamos National Laboratory (LANL) is seeking to license this technology to industry. End users can also purchase the ultrafine-grained pure titanium from LANL's industrial partner, Synmatix Corporation. LANL also seeks collaboration with industry to further develop this technology for other metals and alloys.

Source: For the technology, contact Yuntian Theodore Zhu and Terry C. Lowe, MS G755, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA; tel. 505-667-4029; e-mail yzhu@lanl.gov or tlowe@lanl.gov. For licensing, contact David J. Salazar, MS C334, Los Alamos National Laboratory, Los Alamos, NM 87545, USA; tel. 505-665-6697 or e-mail davidj@lanl.gov. For purchasing commercial quantities of ultrafine-grained titanium, contact Emil Strumban, Synmatix Corporation, 26677 West Twelve Mile Road, Southfield, MI 48034, USA; tel. 810-358-9616, fax 810-358-968, or e-mail EMILST@aol.com.

Reactive Extrusion Process Produces Biodegradable Films and Injection-Molded Products Based on Soy Protein-Polyester

Biodegradable plastic films and injection-molded products based on reactive blends of soy protein and aliphatic polyesters have been produced by a new technology under development at Michigan State University (MSU). Soy protein is reactively blended with selected aliphatic polyesters using a twin-screw extruder to produce a fully biodegradable thermoplastic. The aerobic biodegradability of the protein-polyester resin under controlled composting conditions shows complete conversion of the carbon in the resin to carbon dioxide in 45 days, indicative of complete biodegradability. This protein-polyester resin can be used for making lawn and leaf bags, carry-out bags, trash bags, and agricultural mulch film, as well as injection-molded products.

Soy protein is among several proteins that are reported to be film-forming. Modified (physically or chemically) proteins show thermoplastic behavior and can be solution-cast or even extruded into films. However, such films are brittle (percent elongation to break, ~3–25%) and possess low tear strength, poor water resistance, unreliable heat sealability, and poor tensile strength (3.1–5.2 MPa; 450–754 psi). From a polymer perspective, proteins can be represented as an amino acid polymer. About 60 mol% of the amino acids are hydrophilic and contain reactive functional groups—carboxyl, amino, and hydroxyl (carried by the side chain R group). Nine of these amino acid polymer chains (polypeptides) associate to form a large protein molecule with a molecular weight of 180,000–210,000—the 7S protein (conglycinin). Another major protein fraction is the 11S unit (glycinin), with molecular weights of 320,000–350,000. These represent the principal components

of soy protein. Typically, three grades of protein products are commercially available from a soybean-processing plant. Soy protein concentrate (65–72% protein content) has been selected by the developers for manufacturing the biodegradable soy protein-polyester plastic blends, based on its cost performance.

Recently, three forms of aliphatic copolyesters have been introduced as feasible candidates for biodegradable plastic films. Each copolyester's development differs from the others only in the nature and amount of the aliphatic diol, diacid, and terephthalic acid used. However, cost, biodegradation rate, and lack of some requisite properties have impeded their marketability.

The MSU researchers have developed a reactive extrusion process to blend biodegradable thermoplastic polyesters and copolyesters with a thermoplastic soy protein in which the polyester forms the continuous phase and the thermo-

plastic protein forms the dispersed phase (see Figure 1). The polyester imparts the desired water resistance, processability, and mechanical properties (300–700% elongation to break), while the protein imparts melt elasticity (for processing), enhanced biodegradability, and reduced cost. Thermoplasticization of the soy protein is done by blending it with glycerol and modified soybean oil in a twin-screw extruder. Both operations, the protein plasticization and the reactive blending, can be combined into a single operation by using two extruders in a T configuration, thereby producing protein–polyester resin continuously in a one-step process. The developers anticipate that their process will be both cost-effective and relatively easy to scale up for commercialization.

The thermoplasticization of soy protein is necessary in order to obtain good mechanical properties for the protein–polyester blends. Plasticization of the soy protein using glycerol under the high shear and heat conditions present in an extruder causes denaturing (unfolding) of the proteins and exposes functional groups that can interact with the polyester physically and/or chemically. This results in enhanced mechanical properties for the protein–polyester blends: tensile strength of 13.4 MPa (1941 psi) and 1500% elongation to break, compared with 8.6 MPa (1240 psi) and 470% elongation to break for the unplasticized protein–polyester blend.

Several resin compositions, from 20% protein to 40% plasticized protein in the protein–polyester blends, have been prepared using reactive extrusion processing. Silicone oil was added to improve flow and processability. These resins have been extrusion-cast into films. Their properties (measured by the ASTM D882 Standard Test Method for Tensile Properties of Thin Plastic Sheet, ≤ 25 mm) are comparable to LDPE (low-density polyethyl-

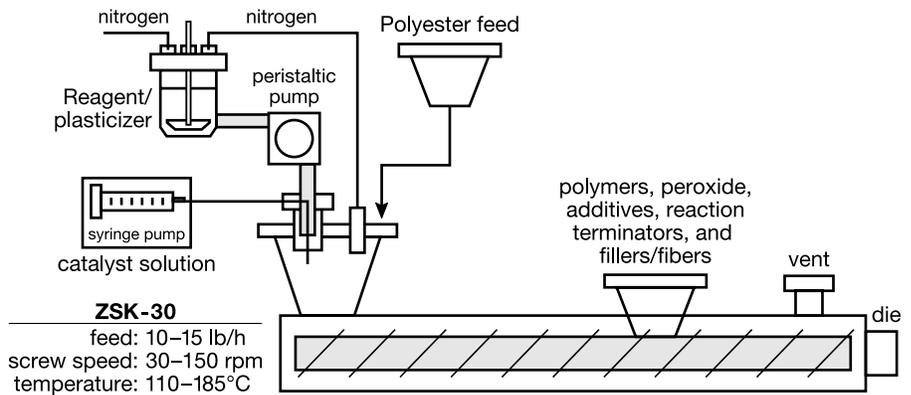


Figure 1. Schematic illustration of the reactive extrusion process for preparing thermoplastic protein–polyester blends.

ene), the material of choice for agricultural film and compost bags. A 30-protein: 70-polyester film composition has a tensile strength of 21.4 MPa (3098 psi) and 200% elongation to break. In comparison, LDPE films used in compost-bag applications have tensile strengths of about 13.8 MPa (2000 psi) and elongations to break of 250–600%. The developers note that since the tensile strength of the base of one recently developed copolyester resin is 19 MPa (2755 psi), the thermoplastic soy protein has enhanced the tensile strength while the elongation remains close to 200%, which is an acceptable range for agricultural and compost-bag applications. The addition of silicone oil was found to aid processing without degrading mechanical properties; increasing the protein component decreased the mechanical properties.

The protein–polyester resin blend can also be injection-molded using standard machinery. However, the tensile strengths of the molded products are lower than that of the extrusion-cast film, but have high elongation values. During

the film-extrusion process, the material undergoes orientation and crystallization, resulting in the observed higher tensile strengths. Products injection-molded from the protein–polyester blend could be biodegradable replacements for such LDPE injection-molded products as seedling containers and erosion stakes.

Opportunities

A company has been formed, BioPlastic Polymers & Composites LLC, to commercialize these soy-based biocompatible polymers. Joint applications, R&D, and licensing are available.

Source: For the technology, contact Prof. Ramani Narayan, Dept. of Chemical Engineering, A2527 Engineering Building, Michigan State University, East Lansing, Michigan 48824-1326, USA; tel. 517-432-0775, fax 517-432-1105, e-mail narayan@pilot.msu.edu, and URL www.msu.edu/user/narayan. For commercialization, contact BioPlastic Polymers & Composites LLC, 4275 Conifer Circle, Okemos, MI 48864, USA; tel./fax 303-265-9072. □

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