COMBINATORIAL MATERIALS SCIENCE

Reaching beyond discovery

Whatever you are trying to make, the choice of materials is often bewildering. Novel combinatorial approaches allow you to reduce the time and costs necessary to optimize results, while stimulating the quest for deeper fundamental knowledge.

ERIC J. AMIS **is at the Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland, USA.**

e-mail: eric.amis@nist.gov

What do shampoo formulation, sensor optimization and catalyst scale-up have in common? Certainly not much at first glance. But a recent symposium* at the 2003 Fall Meeting of the Materials Research Society (MRS) in Boston, highlighted how the same novel approach for combinatorial and high-throughput experimentation is being used to accelerate the development of these and other areas of materials science. By using these so-called Combi approaches, materials scientists can now test hundreds of combinations of materials and processing conditions in only one day, compared with the weeks or months typical of traditional methods. Although the promise to deliver faster, cheaper and better results has been driving the adoption of the Combi methodology in new product development for the past decade, it is now clear that the tools and paradigm are also being adapted to basic research in a number of elegant applications[1].

Catalysis has been the predominant application of combinatorial methods in materials science[2] with nearly every major chemical company investing in the methodology. Although there have been reports of remarkable successes in discovery and optimization[3], nagging questions remain concerning the ability to consistently scale-up from the high-throughput reaction conditions. There is no roadmap to reproduce performance on the scale of a pilot plant for a catalyst originally identified in the bottom of one element of a microreactor array. Although there are indications of promising results, published reports are rare[4]. In one example, reported at the MRS meeting (Donald Whisenhunt Jr, GE Global Research, Schenectady, New York, USA), a system optimized using arrays of 25-μL non-stirred homogeneous catalysis reactions was scaled up to a conventional one-gallon vigorously stirred, gas-purged continuous reactor that ran for 6–8 hours at a time. The small-scale reactions had successfully rank-ordered the catalyst packages.

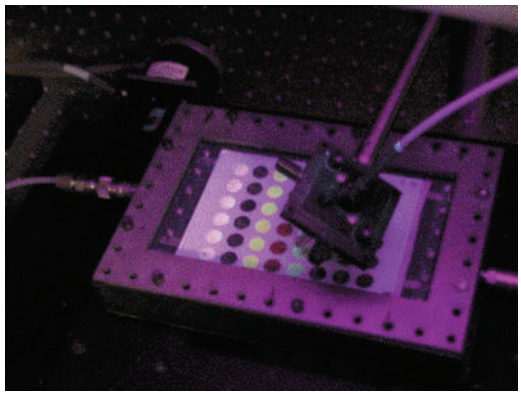

Figure 1 Sensor array testing. The sensing ability of organic thin-film formulations is evaluated with an optical scanning probe that measures their reflectance or fluorescence and relates these properties to the film performance. The films in this array are formulated to be responsive to environmental parameters such as the composition of chemical vapours that flow over them.

Interesting spin-offs are on the horizon as the tools developed for high-throughput combinatorial measurements are adapted to process measurements and to the development of sensors. At first glance it seems strange to translate measurement methods designed for the microscale and apply them to manufacturing scales. The point is quite different[5]. Both library optimization and process monitoring require a diversity of non-destructive tools and high-throughput measurements. More importantly, because the high-throughput screening and optimization can be used to interrogate vital process variables (for example, mixing, temperature, time), it will be possible to apply an established knowledge base to understand and use the on-line process measurements. This natural extension of the Combi paradigm has another twist in some work reported on sensors.

Optimized sensors require a highly synergistic combination of material composition and morphology, operating environment, dynamics of the interaction with the analytes and interferents, and ageing kinetics[6]. For example, solid-film sensors for analysis of chemicals in water at trace concentrations can consist of multicomponent materials containing a sensor reagent, a surfactant, an internal buffer and a polymer-binding matrix. All components of this 'sensor formulation' are dissolved in a common solvent or mixture. The present optimization process of such compositions is very labour-intensive and time-consuming. These multidimensional optimizations constitute the perfect challenge for the Combi methodology. They require the

*Combinatorial and Artificial Intelligence Methods in Materials Science, Materials Research Society Fall Meeting, Boston, Massachusetts, USA, 1–5 December, 2003.

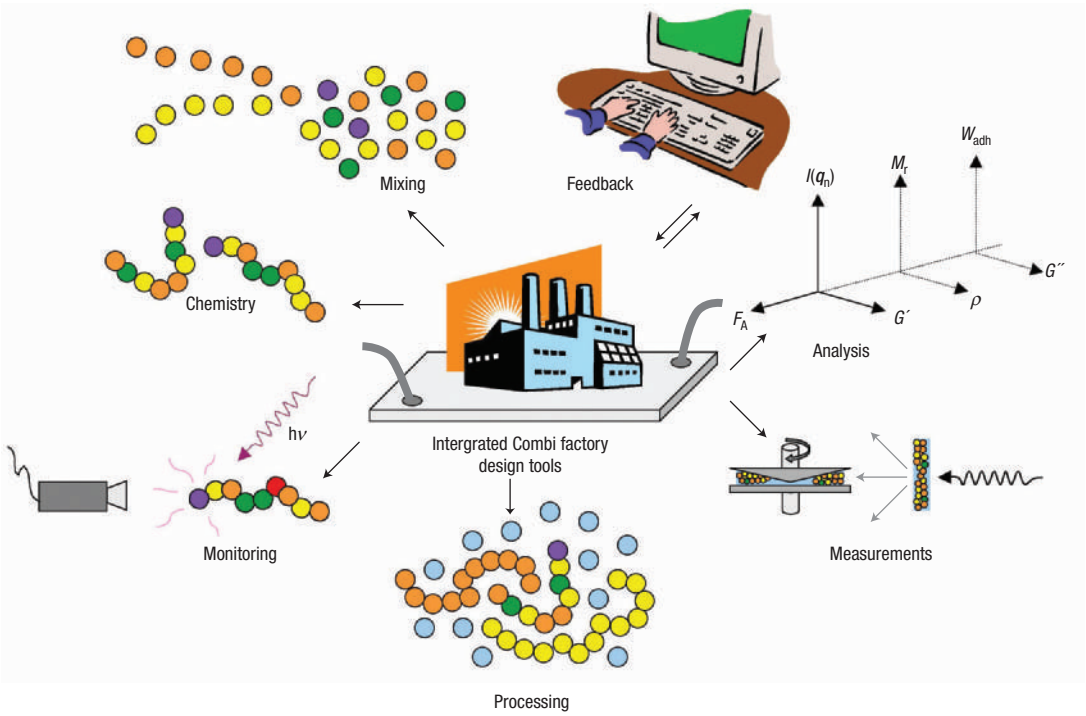

Figure 2 An integrated Combi factory. In a conceptual design, a factory for combinatorial and high-throughput experimentation melds the models of lab-on-a-chip with plant-on-a-chip to provide a complete synthesis, processing and analysis platform. Whether this is implemented with integrated robots or fluidics modules, the advantage of the Combi design is that it reduces the cost of extensive experimentation.

identification of the best compositions to match multiple key criteria, including low detection limits, adequate dynamic range of measurements and immunity to interferences. Testing of the sensor materials involved the use of automated equipment (shown in Fig. 1) designed for array libraries. The combinatorial design of experiment required a multilevel screening. First, the response of sensor reagent candidates to elevated concentrations of analyte species was evaluated in the presence of other needed formulation components. Second, solid films were made from the best-responding sensor reagents to identify candidates that maintain their ability to respond even in the form of a solid film. Finally, the 'lead' solid-film compositions were further tested in detail against all analyte concentrations and interfering species. Not only does the Combi methodology efficiently optimize the formulation, it also provides the means to more fully understand and characterize the performance.

Optimization of polymer formulations stands out as a huge opportunity to apply combinatorial and high-throughput methodology. Even if we only consider solutions and suspensions, the applications range from paints, adhesives and lubricants to foods, cleansers and personal care products. Although the optimization considerations vary, and the relevant figure of merit is usually complex, the underlying issues are similar. Success depends on complex interactions between multiple constituents, some in minute quantity and others of questionable purity, and often the technology available involves a fair amount of art and critical experience. As with catalysis, there have been numerous applications of Combi for paints and coatings by industrial researchers. Much of the work in this area focuses on significantly increasing experimental throughput with automated sample handling, robotics and alternative testing protocols[7].

A different approach to the problem (Kathryn Beers, National Institute of Standards and Technology, Maryland, USA) adopts concepts from microfluidic technology to construct an integrated Combi factory (illustrated in Fig. 2) for systematic investigations of polymer formulations. The platform differs from the typical lab-on-a-chip microfluidics biological assay systems in two important aspects. First, unlike dilute solutions, polymer formulations are often highly viscous or viscoelastic. This is handled by increasing channel dimensions. Second, to ensure their wide applicability, these constructs are designed to accommodate organic solvents and resist elevated temperatures. Another design feature is that devices for various functions interconnect as modules that can dose, mix, process, test and characterize simultaneously for multiple components, processing conditions and desired test characteristics[8]. Coupling analysis modules with processing modules could provide simultaneous interrogation of relevant on-line properties such as viscosity, film forming, self-assembly, morphology, stability and so on.

As in other applications, Combi is not a magic bullet, and its most challenging aspects mirror those of the traditional experiments. But the undeniable power of the Combi methodology comes from reducing the costs (time and materials) of experimentation. Thus it allows us to ask questions we would never have the nerve to ask in a traditional study.

References

1. Amis, E. J., Xiang, X. D. & Zhao, J. C. *Mater. Res. Soc. Bull.* **27**, 295–300 (2002).
2. Archibald, B. *et al.* in *Handbook of Combinatorial Chemistry. Drugs, Catalysts, Materials* Vol. 2 (eds Nicolaou, K. C., Hanko, R. & Hartwig, W.) Ch. 2, 885–990 (Wiley-VCH, Weinheim, Germany, 2002).

3. Kirsten, G. & Maier, W. F. *Appl. Surf. Sci.* published online 16 september 2003, (doi:10.1016/S0169-4332(03)00911-5).
4. Bricker, M. L., Gillespie, R. D., Holmgren, J. S., Sachtler, J. W. A. & Willis, R. R. in *High Throughput Analysis: A Tool for Combinatorial Materials Science* (eds Potyrailo, R. A. & Amis, E. J.) Ch. 26, 581–609 (Kluwer Academic/Plenum, New York, 2003).
5. Potyrailo, R. A. *Trends Anal. Chem.* **22,** 374–384 (2003).
6. Potyrailo, R. A. *Macromol. Rapid. Commun.* **25,** 77–94 (2004).
7. Schmatloch, S. *et al. Macromol. Rapid Commun.* **25,** 95–97 (2004).
8. Watts, P. & Haswell, S. J. *Curr. Opin. Chem. Biol.* **7,** 380–387 (2003).

PHOTONICS

Shrinking optical fibres

Optical fibres: great for long-haul telecommunications, but can the same concept be used to 'conduct' light on the microscopic scale? Recent research would indicate not only that we can, but that it is a superior solution.

PETER DOMACHUK AND BENJAMIN J. EGGLETON

ARC Centre of Excellence for Ultrahigh-bandwidth Devices for Optical Systems (CUDOS), School of Physics, University of Sydney, Sydney, New South Wales 2006, Australia.

e-mail: domachuk@physics.usyd.edu.au; egg@physics.usyd.edu.au

The 1990s were a time of great success for optical communication technologies based on light-guiding fibres[1]. This, however, was only the first step towards all-optical networks. Many believe the next technological step in achieving high-bandwidth optical communications systems lies in the miniaturization of optical signal processing devices: the creation of so-called photonic chips. These are analogous to the development of the chip-based solid-state circuit using transistors, which revolutionized electronics during the 1970s. One of the major hurdles in this miniaturization has been the poor performance of optical waveguides formed by conventional microfabrication techniques[2]. Developed by the microelectronics industry, such techniques tend to create structures that have considerable surface roughness, which, although not a problem for electrons, causes optical scattering that significantly degrades the performance of photonic devices[3]. Writing in *Nature*, Limin Tong and colleagues present an approach for making miniaturized waveguides with exceptionally smooth surfaces and uniform diameters that not only addresses these problems, but is readily accessible to the average university laboratory[4].

Rather than trying to adapt techniques developed for making computer chips, Tong and colleagues instead borrow from those developed for making conventional optical fibres. Previous attempts to scale down the size of optical fibres have used either gas flames or high-power lasers to melt silica fibres so that they may be drawn down to submicrometre diameters[5]. In the case of laser heating, the amount of power required to bring about a molten state of the silica is prohibitive. And although a simple gas flame can easily deliver enough energy to the silica, turbulence and convection caused by uneven heating of the silica and the atmosphere surrounding it severely limits the uniformity of the nanometre-scale fibres that are drawn. To overcome such problems, the authors use a flame to melt their fibres not in free space, but whilst wrapping them closely around the end of a second tapered sapphire fibre. This acts as a local heat-sink that provides a very stable thermal environment and allows silica nanowires with diameters ranging from 50 to 1,100 nn to be drawn with unprecedented uniformity — down to a mere 0.002% per unit length. An added bonus of these nanowires, as with conventional silica optical fibres, is their great flexibility. At these dimensions, the tensile strength of silica is very high, and this property is amply demonstrated by the authors with the knotting and twisting into coils of these

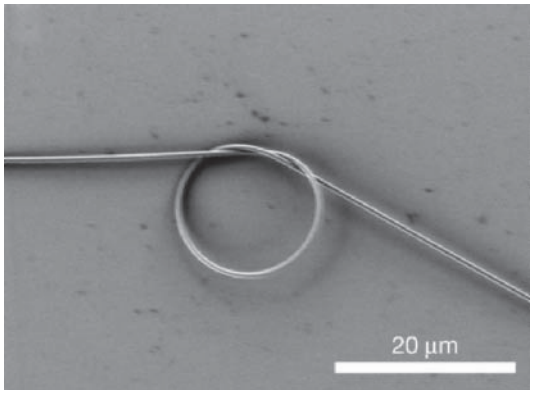

Figure 1 Tong and co-workers demonstrate the flexibility and robustness of their silica nanowires by literally tying them in knots. This scanning electron micrograph shows a 15-μm diameter micro-ring made with a 520-nm-diameter silica wire (from ref. 4).