to the surface; the component with the lowest surface energy tends to migrate to the surface, thereby minimizing the total energy of the system. This means that in many materials containing a mixture of additives, the hydrophobic components, for example, segregate to form a thin coating at the surface, which then becomes more hydrophobic than the bulk. Even different end or side groups can provoke this segregation — it can occur in a film that consists of just polymer chains, where, for instance, fluorinated side chains can become enriched at a surface. In some cases, however, it has been shown that entropic forces may overcome enthalpic ones, and that the 'wrong' component — seen from the enthalpic viewpoint — migrates to the surface. This is the case when enthalpic contributions are not very strong, and this effect is used in the work of Mackay *et al.* for crosslinked PS nanoparticles and PS polymer. Although translational entropy is lost when the nanoparticles segregate to the substrate interface, as well as enthalpic contact energy between nanoparticles and polymer, this is countered by the gain in conformational entropy provided by moving the linear PS chains away from the substrate and replacing them with nanoparticles. The stabilization of the polymer–nanoparticle bilayer by crosslinking also changes polymer molecular weight and architecture, contributing to the driving force for surface segregation. The process can then be repeated on top of the stable crosslinked layer. The authors obtain well-ordered multilayers composed of several polymer–nanoparticle bilayers, each about 10 nm thick. By tuning the polymer and nanoparticle surface functionalization, they also bring enthalpic effects into play to produce other nanostructured layers. This is a very fine example of dedicated design of nanostructured self-assembled materials by control of interactions during preparation.

As nanoparticles can carry many different functions and can be chemically activated or loaded, this approach has great potential for application. Relatively straightforward applications could use the specific properties of the nanoparticles to alter the properties of the surface, for instance hardening for scratch resistance, changing the wetting behaviour or exposing a catalytic component for bioreactions. More complex applications could depend on particular distributions of nanoparticles in a multilayer film, which could vary from layer to layer. This is needed for antireflection coatings, brilliant colour effects or waveguiding applications. The work by Mackay and colleagues suggests that length scales and distributions in such composites can be controlled by film thickness, kinetics, concentration and multilayer formation where different layers can contain different nanoparticles or polymer components.

Mackay *et al.* observe a particular effect that is of direct interest for applications. They anneal a system comprising a layer of poly(methylmethacrylate) (PMMA) on top of or under a layer of PS. When the pure polymers are used, the top polymer layer dewets into droplets on a smooth layer of the other polymer. If the top layer contains nanoparticles, however, their segregation to the polymers' surface stabilizes the top polymer against surface rupture and dewetting. This works with either the PMMA layer or the PS layer on top, indicating the generality of the phenomenon. Dewetting in everyday applications causes problems in particular for the stability of very thin films, and results in the formation of holes and finally segregated droplets on the surface. This work shows promise therefore for reducing these effects in multilayer assembly and thin-film coating applications.

References

1. Sommer, J.-U. & Reiter, G. *Ordered Polymeric Nanostructures at Surfaces* (eds Julius Vancso, G. & Reiter, G.) 1–36 (Advances in Polymer Science series vol. 200, Springer. Berlin/Heidelberg, 2006).
2. Sydorenko, O., Tokarev, I., Minko, S. & Stamm, M. *J. Am. Chem. Soc.* **125,** 12211–12216 (2003).
3. Warren, S. C., Disalvo, F. J. & Wiesner, U. *Nature Mater.* **6,** 156–161 (2007).
4. Balazs, A. C. *Nature Mater.* **6,** 94–95 (2007).
5. Krishnan, R. S. *et al. Nano Lett.* **7,** 484–489 (2007).

MATERIAL WITNESS

Rollobots

Spirit, the redoubtable Martian rover, has spent the past year driving on just five of its six wheels. In February, the Rover's handling team said it had perfected the art of manoeuvring with one wheel missing, but the malfunction raises the question of whether there are better ways for robots to get around. Walking robots are becoming more efficient, thanks to a better understanding of the 'passive' mechanism of human locomotion; but a single tumble might put such a robot out of action permanently in remote or extraterrestrial environments.

So a recent survey of rolling robots provided by Rhodri Armour and Julian Vincent of the University of Bath (*J. Bionic Eng.* **3,** 195–208; 2006) is timely. They point out that spherical robots have several advantages: for example, they'll never 'fall over', the mechanics can all be enclosed in a protective hard shell, the robot can move in any direction and can cope with collisions, uneven and soft surfaces.

But how do you make a sphere roll from the inside? Several answers have been explored in designs for spherical robots. One developed at the Politecnico di Bari in Italy aims to use an ingenious internal driver, basically a sprung rod with wheels at each end. It's a tricky design to master, and so far only a cylindrical prototype exists. Other designs include spheres with 'cars' inside (the treadwheel principle), pairs of hemispherical wheels, moving internal ballast masses — the Roball made at the Université de Sherbrooke in Québec, and the Rotundus of Uppsala University in Sweden — and gyroscopic rollers like Carnegie Mellon's Gyrover.

But Armour and Vincent suggest that one of the best designs is that in which masses inside the sphere can be moved independently along radial arms to shift the centre of gravity in any direction. The Spherobot under development at Michigan State University and the August robot designed in Iran use this method, as does the wheel-shaped robot made at Ritsumeikan University in Kyoto, which is a deformable rubber hoop with 'smart' spokes that can crawl up a shallow incline and even jump into the air.

Although rolling robots clearly have a lot going for them, it might give us pause for thought that nature very rarely seems to use rolling. There are a few organisms that make 'intentional' use of passive rolling, being able to adopt spherical shapes that are blown by the wind or carried along by gravity: tumbleweed is perhaps the most familiar example, but the Namib golden wheel spider cartwheels down sand dunes to escape wasps, and woodlice, when attacked, curl into balls and roll away. Active rollers are rarer still: Armour and Vincent can identify only the caterpillar of the Mother of Pearl moth and a species of shrimp, both of which perform somersaults.

Is this nature's way of telling us that rolling has limited value for motion? That might be jumping to conclusions; after all, wheels are equally scarce in nature, but they serve engineering splendidly.

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