POLYMER COMPOSITES

Swell properties and swift processing

Carbon nanotubes have great potential as polymer additives, but they are difficult to process. A mixture of nanotubes in a polypropylene melt exhibits enhanced electrical conductivity and an unusual flow force that simplifies processing.

MATTEO PASQUALI is at the Department of Chemical Engineering, MS 362, Center for Nanoscale Science and Technology, Rice University, 6100 Main St, Houston, Texas 77005, USA.

e-mail: mp@rice.edu

Carbon nanotubes (CNTs) can be thought of as sheets of graphite rolled up to form a closed cylinder. Single-walled CNTs are formed by a single sheet, and multiwalled CNTs consist of several of these sheets rolled up one inside the other. These materials display remarkable properties[1] that make them particularly attractive as additives to commodity polymers, which have poor electrical and thermal conductivity. For example, a small amount of well-dispersed CNTs can boost the electrical and thermal conductivities of materials that would otherwise be insulators, and also provide mechanical reinforcement. Unfortunately, one major problem of working with CNTs is their difficult dispersion into polymers, or at least this is what was thought until now. On page 564 of this issue, Kharchenko and colleagues show that CNTs can be dispersed well into polypropylene (PP) — an inexpensive commodity polymer[2].

The findings of this study are manifold and interesting because they point to the possibility of obtaining macroscopic rods of a polymeric material with advanced properties while at the same time simplifying the extrusion process. Indeed, the electrical conductivity of PP containing just a small percentage of CNTs increases by over six orders of magnitude. However, this was to be expected. What is surprising is that in the liquid phase, the mixture of CNTs and molten polymer displays an odd flow phenomenon known as 'negative first normal stress difference' (negative N_1).

To understand this concept, let us take a step back and talk about the flow behaviour of liquids. When classic (structureless) liquids such as water or oil are sheared between two parallel plates, the only force acting on the plates is tangential to the plates. Complex fluids — liquids with microstructure such as polymer melts, polymer solutions, emulsions or suspensions — can behave quite differently. When sheared between two plates, they can develop an additional force that is perpendicular to the plates. Such force is due to the difference between the normal stress perpendicular and parallel to the flow direction, termed 'first normal stress difference'; in most complex fluids this is a positive normal stress difference[3] that pushes the plates apart (Fig. 1a). This is the same force that is responsible for other curious phenomena observed in everyday life outside the laboratory. One of these is dough climbing up a rod during stirring rather than forming a dip, which is what normally happens when stirring water. For polymer scientists, a classic manifestation of this phenomenon is the swelling of polymer melts when they are extruded from dies. When the polymer exits the die, the compressive cross-stream stresses that were accumulated during the flow push the polymer outwards (see Fig. 1a, right); this causes shape distortion, complicating the design of extrusion dies and limiting the speed of the process.

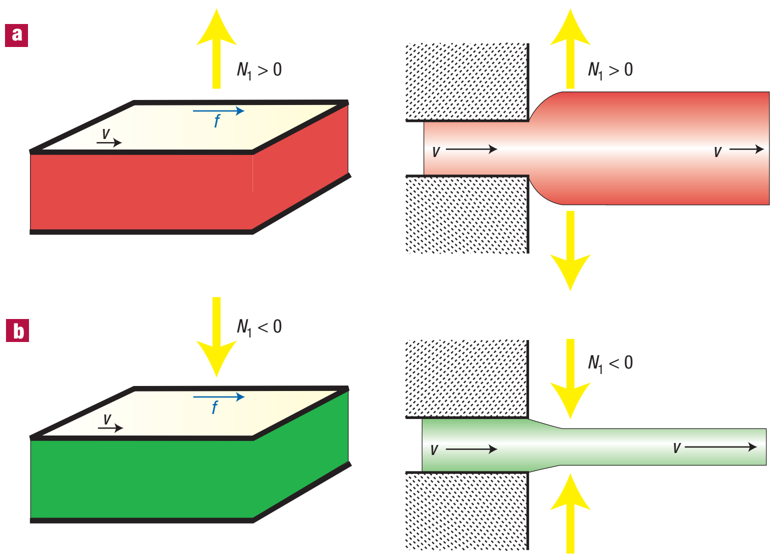

Figure 1 First normal stress differences and die swell properties. **a**, Generally, when polymer melts are sheared between parallel plates (one stationary, the other moving with velocity v), they develop tensile stresses along the flow direction and compressive stresses in the cross-stream direction. The difference of these stresses N_1 is positive and it induces a net force (f) that pushes the plates apart (left). In the related extrusion flow (right), the polymer melt is sheared inside the die; this causes compression across the flow lines, and the polymer swells when it exits the die. This can yield an irregular extrudate shape and limit the processing speed. **b**, When a mixture of few percent of CNTs in a polymer melt is sheared, it develops compression along the streamlines and tension in the cross-stream direction[2] ($N_1 < 0$); this unusual effect yields a net force f that pulls the plates together (left). When such a mixture of nanotubes and polymer is extruded (right), the mixture contracts on exiting the die because of the tension across the streamlines. This effect may lead to easier processing of polymer–nanotube and polymer–fibre composites.

A few complex fluids display the opposite effect when sheared between plates: they develop a tension across the flow direction that draws the plates together — that is, a negative N_1 (Fig. 1b). Liquid-crystalline polymers, such as the precursors of the Kevlar and Zylon high-performance fibres, are the best known class of liquids to display such negative N_1 (ref. 4), although the phenomenon has been observed occasionally in concentrated suspensions[5], emulsions[6], and also in liquid-crystalline dispersions of single-walled CNTs[7] as well as in dispersions of multiwalled CNTs in a low-molecular-weight solvent[8]. The origin of negative N_1 is not clear, although it has been linked with flow-induced phase separation and striping in the direction perpendicular to the flow plane in a few cases[6,8].

As positive N_1 is related to die swell in extrusion, negative N_1 is related to a contraction of the fluid exiting the die. This had been demonstrated in the case of highly concentrated suspensions[5] (above 50% solids), but had never been brought to bear in practical applications. Now, Kharchenko and co-workers[2] have shown that this rare effect can be induced at will by adding a small amount of multiwalled CNTs to a common polymer, and that this can be exploited to eliminate die swell. Thus, CNTs can be used as processing aids while at the same time improving the final properties (in this case the electrical conductivity) of the solid material: this is unusual, because good properties and easy processing do not often marry together.

The work of Kharchenko *et al.*[2], together with other recent reports of negative N_1 (refs 5–8), will surely generate practical as well as theoretical interest. On the practical side, it is possible that similar effects may be obtained by dispersing fibres other than CNTs in polymers, which will impact the field of fibre-reinforced composites. It will be interesting to find operating windows for the extrusion of polymer–fibre composites that show negative N_1. This could be done by checking if processing instabilities, such as the surface fracturing of a polymeric extrudate, are delayed or eliminated by controlling the extent of the negative N_1, as recent work suggests[9], and by determining whether high extrusion speed can degrade electrical properties by aligning the CNTs and disrupting the CNT network. On the theoretical side, the cause of negative N_1 in several classes of complex fluids ultimately needs to be explained and related to the fluid microstructure, and possibly other variables such as the strength of the flow and the presence of confining surfaces. Of course, such theoretical understanding will also be invaluable in designing optimal formulation and processes for soft nanostructured materials.

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MATERIAL WITNESS

Faux food to the rescue?

Told that I wanted to study chemistry, my school careers adviser suppressed an expression of panic to suggest that there were opportunities for chemists in frozen foods. My father was not a scientist of any sort, but he discerned with disdain that food science wasn't exactly at the cutting edge of research, a judgement with which I concurred.

But now I wonder. In a recent essay (http://www.prospect-magazine.co.uk/start.asp?P_Article=12702), political analyst Michael Lind argues that all the world's predicted future population of 9 million might achieve the living standard of developed nations without despoiling our planet. Indeed, Lind thinks that it may be possible for such a global society to coexist with larger areas of wilderness than are preserved today.

Lind's Panglossian arguments invite copious criticism; but how does he propose to realise this miracle anyway? New technology is the main answer. "Sometimes", Lind says, "there really are technical fixes." The owner of a ranch in Texas, Lind makes agriculture one of his primary concerns. How will we feed 9m people especially as greater affluence is accompanied by an increased meat intake? "A pasture and a cow", Lind admits, "is an extremely inefficient way to convert soil, water and sunlight into a steak."

What's the alternative? "I would rather eat a nutritious pork chop from a laboratory test tube than from a pig which had spent its life drugged in a tiny cage caked with its own waste", Lind argues. By making meat artificially, we would liberate masses of land that can revert to wilderness.

It is a truly Baconian vision, in which food is made "entirely from raw materials and artificial energy in a subterranean food factory". Nigel Calder, former editor of *New Scientist*, talked in his book *The Environment Game* (1967) about "nourishing but unpalatable primary food produced by industrial techniques". But Calder envisaged this as animal feed, not for human consumption. For us, it would have to be palatable too.

Nonetheless, the image this invokes is of trays of 'astronaut food', with all the right nutrients but frankly as appealing as baby food. That is where the materials expertise of food scientists enters. There is now plenty of research showing how the texture of food affects the sensory experience — the pleasure — of eating it. (See, for example, *J. Agric. Food Chem.* 50, 5149; 2002.) Clever engineering of processed foods could make bland, 'plastic' cheese and meat substitutes a thing of the past.

I am not sure I'll ever be a convert: I take Lind's point that free-range livestock is potentially (if not inevitably) wasteful of land, but I do wonder whether he has tasted the difference between a free-range and a battery-reared chicken. On the other hand, as a lapsed vegetarian I do feel some eagerness for food scientists to perfect the texture of *faux* sausages and bacon. It should not be hard to make food substitutes nutritious; the greater trick will be to make these things acceptable to food snobs. Food scientists may be unglamorous, but chefs are today's rock stars. Which of them will be first to make a gourmet dish from artificial meat?

Philip Ball