sequentially, to ensure that we were eliciting associative recall. It remains to be seen whether bees that have experienced the colour and the scent of an object simultaneously can recall one of the object's attributes when the other is presented in isolation.

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Immobile plasticizer in flexible PVC

Plasticized poly(vinyl chloride) (PVC) is one of the most widely used polymeric materials in medical and related applications, and usually contains up to 40 per cent di-(2-ethylhexyl)phthalate (DEHP), which acts as the 'plasticizer' to impart flexibility to an otherwise rigid PVC[1]. The plasticizer can migrate from PVC-based devices and storage bags into physiological fluids, however, and has been detected in storage media such as blood, plasma, serum, drug solutions and fatty foods[2–4], as well as in the bodies of patients undergoing haemodialysis and transfusion[5]. This is a concern because DEHP is a lipid-removing liver carcinogen[6], and causes hepatic[7] and reproductive toxicity[8] in rodents, although opinion is divided on its toxicity in humans[9].

Attempts to prevent this migration have included coating, grafting or blending PVC with other polymers, glow-discharge treatment of the surface of PVC, prolonged ultraviolet irradiation, and photocrosslinking of dithiocarbamated PVC[10]. We have developed a surface-modification technique to prevent this migration, and show that plasticized PVC becomes extremely resistant to migration when treated with sodium sulphide in the presence of a suitable phase-transfer catalyst in water. The treatment should benefit the medical and related applications of flexible PVC.

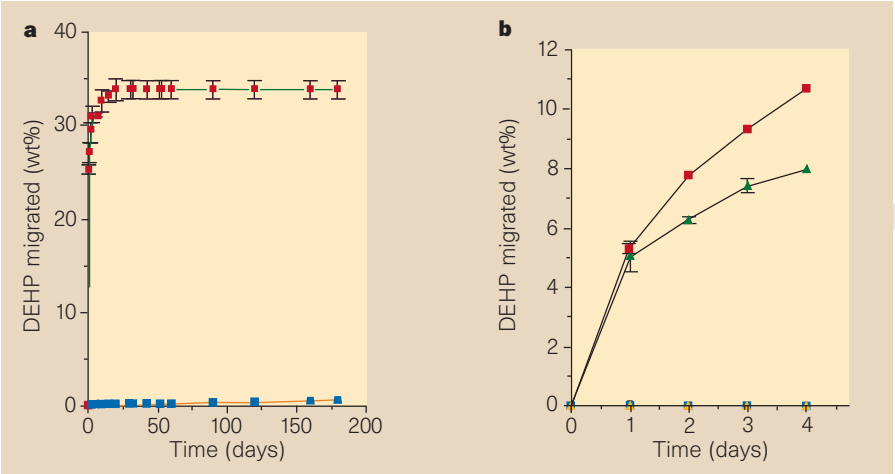

Figure 1 Surface modifications prevent migration of DEHP from PVC. **a,** Migration of DEHP from unmodified (red squares) and modified (blue squares) PVC tubes into petroleum ether at 30 °C. **b,** Migration of DEHP from unmodified (red and green symbols) and modified (blue and yellow symbols) PVC tubes into cotton-seed oil (squares) and poly(ethylene glycol)-400 (PEG400; triangles) at 70 °C.

The formation of dialkyl sulphide from an alkyl halide and sodium sulphide is well documented and proceeds readily in the presence of a suitable phase-transfer catalyst[11]. The chlorine atoms on PVC are labile and can be substituted by various other nucleophiles[12]. Our strategy was to substitute the chlorine on PVC using a dianion such as sulphide, which causes the polymer chains to crosslink. If crosslinking is confined mainly to the surface of PVC by reacting plasticized PVC in a solvent in which the polymer is insoluble, such as water, then such surface crosslinking should retard or prevent the diffusion of the plasticizer.

We therefore treated medical-grade PVC tubes (from Solmed, Denmark) with sodium sulphide (7.0 mol per litre) in the presence of tetrabutyl ammonium hydrogen sulphate (0.15 mol per litre) as the phase-transfer catalyst at 80 °C in water for 5 h, with occasional shaking. Specimens were then washed with plenty of water, sonicated for 1 min in a bath-type sonicator and dried to constant weight at 50 °C. X-ray photoelectron spectroscopy and elemental sulphur analysis showed that sulphur was present in the modified PVC specimens. The crosslinked network formed on the surface of PVC could be separated after treating it with tetrahydrofuran, causing only the uncrosslinked part to dissolve, along with other additives in flexible PVC.

The amount of DEHP that migrated into petroleum ether, a potential extractant for DEHP, over 6 months at 30 °C was determined spectrophotometrically from unmodified and surface-modified PVC tubes (Fig. 1a). Virtually no plasticizer migrated into this medium from surface-modified specimens, whereas unmodified PVC lost almost all its plasticizer in a day. Accelerated migration at 70 °C, followed by monitoring the change in weight gravimetrically, indicated that no migration occurred from the modified specimens into media of different polarities, such as cotton-seed oil and PEG400 (Fig. 1b).

Surface modification imparted a slight yellow colour to the tubes, causing optical transmittance to decrease by about 20 per cent in the 400–500 nm region of the spectrum. At 500–700 nm, the optical transmittance of the modified tubes was similar to that of the unmodified tubes (about 80 per cent).

When the surfaces of flexible PVC sheets were similarly modified, we found that plasticizer migration could be prevented completely, as it was in PVC tubes. However, modification led to a decrease in the stress (about 8 per cent) and strain (about 28 per cent) at the breaking point for PVC sheets. There was also significantly reduced adhesion of platelets and bacteria to the surface-modified sheets.

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