Materials : A continuing journey

Curve, issue 29, October 2009, pp56-59

Jonathon Allen

If we think our cities are overcrowded, just try looking at soil. A single teaspoon of soil contains billions of micro-organisms that help breakdown, or *biodegrade*, organic matter. Bacteria, fungi, protozoa, nematodes, as well as worms, spiders and bugs all call it home and try to live in their subterranean paradise. Not that I've thought too much about the nematodes, and I don't care too much for creepy crawlies, and once I had a bad experiences with E.Coli in the form of food poisoning, but all of these soil dwellers have an important part to play in biodegradation and enrichment of the soil.

This harmony is often disturbed by humans and their waste – much of which is inorganic. Tin cans take around 50 to 100 years to degrade, a pair of shoes 25-40 years, cigarette buts around a decade, and glass around a million years. The organic matter we dispose of in rubbish tips doesn't tend to degrade that readily – there have been some reports of newspapers being excavated from tips decades after they were dumped, and they're still readable. In normal composting conditions paper should take only a few months to fully degrade; plastics typically take forever.

Whilst plastic is used for all manner of things, many of which are designed to last, over a third is used for packaging that, on the whole, is disposed of soon after purchase. Whilst plastic recycling is common, still far too much plastic is dumped. The plastics industry's response was the development of degradable plastics.

1st and 2nd generation of biodegradable plastics

The first generation of degradable plastics was based on modified commodity plastics (eg polyethylene, polypropylene and polystyrene), whereby an additive to the plastic helped speed up the degradation process. The polymer would degrade on exposure to either light (photodegradable), heat (thermodegradable), water (hydrodegradable) or by the action of micro-organisms (biodegradability). This last process utilised starch which was added between the long polymer chains through grafting or other bonding methods. When placed into soil, microbial action digested the starch, thus breaking the polymer into small, microscopic pieces.

The problem with this process is that the material just breaks down into smaller particles, and the polymer is still in the soil. As the polymer particles are so small, they have a large relative surface area that is hydrophobic (resistant to water) and can, according to the Algalita Marine Research Foundation, attract and store hydrophobic elements like PCB (polychlorinated biphenyl) and DDT (dichloro-diphenyl-trichloroethane) – both of which were banned in the 1970s due to their toxicity – in very high concentrations. These microscopic polymers fragments can leach out of the soil and into watercourses – indeed there is evidence that these are accumulating in the oceans where many marine creatures consume them. And we in turn may consume fish that may have been contaminated – we may have buried our rubbish only to find it may contribute to burying us!

The second generation of biodegradable plastics, largely derived from plant-based materials are designed to completely breakdown in a microbial environment. A number of standards, such as ASTM D6400, ISO 17088 and CEN EN 13432 help define what qualifies a biodegradable plastic as well as the test procedures in which to verify a material's biodegradability. The standards state that in order to qualify as a biodegradable plastic, complete biodegradation under composting conditions is required. This means that the material must be fully converted to carbon dioxide (CO_2), water and biomass within 180 days and compost at the same rate as natural materials such as leaves, grass and food scraps. The carbon should also be fully utilised by the micro-organisms that perform the degradation (this is measured by the amount of CO_2 and methane released in testing). The resultant compost must also be safe – that is it should have no impacts on plants nor contain traces of heavy metals in excess of defined thresholds. Further, in testing, 90% of the carbon in the plastic needs to be converted to CO_2, and less than 10% of the test material.

There has been a huge increase in the use of biodegradable plastics over the last decade, particularly in Western Europe, where legislation has helped mandate better environmental responsibility. Polylactide (PLA) and starch-based polymers were some of the first of the 2nd generation of biodegradable polymers, and captured a significant part of this burgeoning market. PLA is based on lactic acid that is typically derived from fermenting milk or cornstarch. It has similar properties to polystyrene – it is glossy and clear, but stiff and brittle – and can be processed like most thermoplastics.

Starch–based polymers, derived from foods such as corn, potatoes or rice, comes in a variety of forms depending on the starch content and how the material is processed. Plastified starch (50% starch) and thermoplastic starch (90% starch) have similar properties to polypropylene and can be moulded in the same ways and is used instead of traditional plastics for food packaging, rubbish bags, and disposable golf tees (just leave them in the ground to biodegrade). Whilst resilient to oils and alcohol, they degrade quickly in hot water. Foamed starch is produced using steam rather than a chemically-based reaction, making it an environmentally friendly alternative to other packaging foams – particularly expanded polystyrene. It has good insulating and shock absorbing characteristics, is antistatic, and biodegrades quickly.

A range of materials in the polyester group of polymers is of interest

Polyesters as a class of polymers can be formulated in different ways. Aromatic polyesters, such as PET (poly-ethylene terephthalate) have very good mechanical properties and have good chemical and biological resistance, hence PET is an excellent choice for drinks packaging. Aliphatic polyesters, however, lack these qualities, but in turn this means they can be biodegradable. Aliphatic polyesters have similar properties to polyethylene and polypropylene and can be moulded like other thermoplastics (injection moulding, blown film, extruded, foamed, etc.) In order to increase the rate of biodegradation, aliphatic polyesters can be coated with powdered coconut shell, which absorbs water in the soil making the plastic swell and thus increasing the area exposed to micro-organisms.

Aliphatic-aromatic copolymer blends the excellent properties of aromatic PET with the biodegradability of aliphatic polyesters. The resultant copolymer is a little more expensive than regular PET, and can be moulded in the same way and used for similar applications, but is designed to degrade by composting. Another blended polymer is polylactide aliphatic copolymer, or CPLA, which combines aliphatic polyesters with lactide. CPLA can be blended to exhibit the properties of a hard plastic like polystyrene or a more flexible material like polypropylene, and it has good operational stability up to about 200°C.

Polyhydroxyalkanoates, or PHAs for short, are polyesters produced by bacterial fermentation of sugars or lipids (naturally occurring fats, oils, and waxes). These materials exhibit quite varied characteristics, dependent upon the combination of the different monomers in this group of materials, ranging in melting temperatures from 40°C to 180°C and can be highly elastic, rigid or soft and sticky. Just to confuse matters, the most common PHA is PHB (poly-beta-hydroxybutyrate) which has similar properties to polypropylene. PHBV (polyhydroxybutyrate-valerate) is a blended copolymer which is tougher than PHB and is often used for packaging.

PHAs are biocompatible, meaning that they can be used in the body without causing inflammation. Polymers that are both biocompatible and biodegradable are of particular interest in medicine for a number of applications. For instance, biodegradable sutures and implants that, in time, dissolve and are naturally excreted by the body can help speed up recovery and save money, as the need for a second operation to remove them is negated. Keyhole surgery also makes use of biodegradable polymers that have shape-memory characteristics (see issue twenty-five of Curve) for self-tightening sutures or for stents (a mesh-like tube used to hold open an artery or other body tube in order to help clear it). Biocompatible biodegradable polymers are also used for sustained release of therapeutic drugs. A biopolymer can be dosed with a drug, implanted in the body, and as the polymer biodegrades, the drug is released. This allows doctors to specifically target a particular area of the body – a tumour for instance – thus reducing the frequency with which drugs may need to be given. A further application of this technique is to repair bone damage. Active bone morphogenetic proteins can be added to a biopolymer in the form of a bone-graft substitute – as the biopolymer degrades the proteins encourage the formation of bone in its place. Such materials include PLA, polycaprolactone (PCL) and polyglycolide (PGA).

Polycaprolactone (PCL) is derived from crude oil, and hence it has good resistance to water, oil, solvents and chlorine, and is used for a range of applications including fully biodegradable sutures, compostable bags, synthetic leather and fabrics. This material has a low melting point making it highly suitable for degrading in compost heaps as it degrades very quickly – at times too quickly: an attempt to make PCL bags in Sweden failed as the bags degraded before they were even used!

This last case presents an interesting and absurd paradox that perhaps should help us think about what we're doing. Whilst there are some fantastic applications of biodegradable materials, by far the most common is for disposable packaging and products. Call me old fashioned, or a miser, but I prefer the idea of re-using and re-cycling packaging.

This is a preprint copy of an article I wrote that appears in *Curve* magazine, Issue 29. For referencing the details are as follows:

"Materials: A continuing journey"
Curve, issue 29, October 2009,
pp56-59
ISSN 1446-4829