



26 NOVEMBER 2018

## PLASTIC FROM POTATOES, RUBBER FROM RICE

PROFESSOR ANDREW ABBOTT

In the modern world the pace of change can be bewildering and society often seeks to address complex issues with simplified messages. One such issue that is all too common in the media is our use and misuse of plastic. Plastics have become one of the largest man-made materials after concrete and steel and on a par with aluminium.

The annual production of plastics has increased from around 5 million tonnes in the 1950s to nearly 335 million tonnes today. To put that into perspective if we were to melt that into a single block it would cover Hyde Park to approximately the height of the Shard. One tonne of plastics is approximately 1 m<sup>3</sup> and could make 20,000 two litre drinks bottles or 120,000 carrier bags. Plastic has led to our consumer society; it has helped us with our busy lives, but it has also resulted in a throwaway society. Plastics makes up around 7% of the average household dustbin and we use about 7% of crude oil to make plastic.

The range of plastics that we use may seem large but there are only 7 or 8 polymers which make up about 90% of our plastic use. To make a polymer we need a building block called a monomer which need to react at a minimum of two points to make a chain (if it reacts at 3 or 4 points then cross-linking can occur and a more rigid polymer is produced). The table below shows the most common polymers together with their monomers, what they are used for and their approximate annual scale of production.

These are the most common polymers because the monomers are the easiest to chemically manufacture. The importance of polymers in society can be judged from that fact that 7 of the top chemicals produced worldwide every year are monomers.

Since 1950s about 8.3 bn tonnes of plastic have been produced but during that time only 7% of plastic has ever been recycled. Of the 8.3 bn tonnes only 2.5 bn tonnes is still in use meaning that 5.8 bn tonnes was used once and of that 4.9 bn tonnes has been discarded with only 0.7 bn tonnes which has been incinerated.

Polymer	Monomer		Scale / 10 <sup>6</sup> t p.a.
High Density Poly Ethylene		Rigid plastics	80
Low Density Poly Ethylene		Flexible plastics e.g. bags	55
Polypropylene		Bottle tops	50
Poly Vinyl Chloride		Window frames	18
Polystyrene		Rigid plastics	15
PET Polyester		Plastic bottles	28
Nylon	$\text{HOOC}(\text{CH}_2)_4\text{COOH}$ $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$	Strong fibres, ropes	36
Polybutadiene		Rubber	17



Of 275 metric tonnes of plastic waste produced each year it has been estimated that between 4.8–12.7 million of mismanaged plastic waste end up in the oceans. That seems a lot and in absolute terms and it clearly is but it equates to 2-5% of all plastic thrown away. It has been estimated that 20 countries are responsible for 83% of the plastic in the world's oceans. Media is full of reports calling for plastics to be banned but as with most technological issues this is impossible and would result in far more problems that it would solve.

Think of all the vital and lifesaving roles plastics play in healthcare, transport, electronics, and electrical applications (what would we use for electrical insulators?) building and construction, clothing and food production. Our biggest challenge with plastics is in waste management. It is probably our social misuse of plastic that is the root cause of many of our environmental issues.

It has been estimated that 20 countries are responsible for 83% of the plastic in the world's oceans. This is due, in part, to less economically developed countries having the infrastructure to deal with refuse collection but also to export of plastic refuse from countries claiming that it is for recycle. Packaging is the major use of plastic accounting for about 36% of plastic made. It is important for maintaining sterile products and for extending food product shelf-life but equally there is a need for a re-design of many products to use less packaging.

So the media is full of calls for bioplastics which can degrade in the environment. The aim of this presentation is to look into these calls and see if we could genuinely make plastics from potatoes and rubber from rice. You and I and the trees around us are polymers and in fact it has been estimated that nature could make the mass of polymers that humans make in about 1.5 days by photosynthesis. Of all of the organic carbon in the biosphere about 85% is in the form of carbohydrates, most of which is in the form of cellulose, starch and lignin. We clearly use this in the form of wood for construction and as natural fibres like cotton, flax and hemp. Cellulose can be difficult to process due to its low solubility but it can be modified to give fibres such as rayon or chemically modified to make cellulose acetate which is used in some wrapping materials e.g. Cellophane. All cigarette filters for example are made out of cellulose acetate however although they degrade faster than synthetic polymers they can still persist in the environment for between 18 months and 10 years depending on the conditions and given that 18 bn cigarettes are smoked each day, that is a lot of persistent litter.

There are several polymers which are described as bioplastics or biodegradable and these are based around simple organic molecules such as lactic acid. Polylactic acid (PLA) is derived from starch by fermenting in to form the lactate then chemically modifying it and the polymerising it. While this certainly is a polymer obtained from a renewable resource, when the metrics are calculated for the waste produced and the energy consumed in the process it could be argued that if it is incinerated at end of life polyethylene is far greener to produce than PLA.

An alternative to cellulose is the use of starch. Starch alone cannot form films with satisfactory mechanical properties as can be seen when it forms around the top of a pan when boiling potatoes. Starch is also hygroscopic in nature so is unsuitable for high-moisture and liquid food products. One way around the brittle nature of starch is to add plasticisers and the most commonly used one is glycerol which is a waste product from making soap and biodiesel. These plastic films are not very strong, but they are good for one use packaging and they are starting to be used as packaging for sending magazines through the post.

Many plastics which are labelled as either “biodegradable” or “decompose faster than conventional plastics” are composites of starch and biopolymers. These can aid the breakdown of plastics which can limit the impact of plastics but still result in small fragments of particles of plastic which can be ingested by aquatic creatures.

So can plastics be made directly from biomaterials which degrade in a reasonable timescale and do not leave a residue, like starch? Starch is made up of two forms of the same molecule, amylose (linear) and amylopectin (branched). The different plant sources of starch result different amounts of amylose (typically 10-20%) and amylopectin (80-90%). Flour is largely made of starch and as most people will know that the type of flour used in baking changes the consistency of the product that you make. An extreme version of making a material from starch is salt dough. This consists of 2 parts flour, 1 part salt and 1 part water. Thoroughly mixing these three components and making the resulting dough into a shape, followed by slow drying, results in a very rigid structure. This has been used for hundreds of years for making folk art to adorn the house. The salt binds to the starch



molecules and makes a rigid structure. The salt also keeps the free water content low and ensures that the material is preserved.

The thought process carried out in our group was what happens if the salt used is a liquid (not a solution)? Salts are generally thought of as crystalline solids but a class of salts known as ionic liquids have been intensively used over the past 20 years. If the salt used was fluid would this hold the starch together in a less rigid structure so that a flexible plastic could be produced? While most ionic liquids are toxic and very expensive, we have developed a range of fluids made up by complexing a B-vitamin with simple organic molecules, many of which are found in nature. These so called deep eutectic solvents are easy to make on a large scale and can be made so that they are biodegradable. Initial experiments showed that mixing this with starch could produce a transparent plastic which has similar mechanical properties to polyethylene. While the material is fully compostable and fully recyclable the issue remains whether it is more important to use starch for making plastic or for feeding an ever-expanding population.

Plastics are actually mixtures of polymers with other materials such as carbon black or chalk which is why many plastics are black or white; they use a low-cost filler to bulk them out. This is economically helpful but from a recycling perspective it makes regenerating materials of the same composition very difficult. This is one of the reasons that so little plastic is recycled.

A widely used example of a composite material is synthetic wood such as medium density fibreboard, plywood or chipboard. These use a thermoset resin made from urea and formaldehyde (UF). There are concerns over the use of formaldehyde as it is a known carcinogen and urea-formaldehyde does not easily biodegrade. The difficulty in finding a replacement for UF is cost; there are almost no cheaper alternatives which could be used. Mixtures of DESs with starch were found to make an appropriate resin with which to stick together wood fibre and because the thermoplastic starch can be remelted unlike UF which is a thermoset, the resulting wood board is not only biodegradable but it is also recyclable. The importance of this is that there is a lot of wooden panelboard which is used for short duration applications such as retail and construction. An additional property of these materials is that they can be injection moulded to make different shapes and we have demonstrated that wood can be thermally formed into different shapes. The properties of thermoplastic starch also make the boards easier to saw, glue and drill.

The process has been scaled up to make more than fifty 1m x 1m x 1.8 cm boards which have been used to make furniture and point of sale items however, in this first incarnation of the technology the stumbling point is the economics again.

In an endeavour to improve this we returned to nature to see how wood fibres are stuck together in trees. Trees photosynthesize carbohydrates from CO<sub>2</sub> and water. These carbohydrates polymerise through a variety of pathways to produce starches, cellulose, lignins and a variety of low molecular mass oligomers (a small number of monomers joined together) to produce the main fibres and a range of saps and sticky substances to stick them together. To some extent that is the same process as we use when we bake and make products like flapjacks.

Through working with carbohydrate manufacturers we were able to test a variety of low value product streams as potential resins for sticking fibres together. Not only did this process produce products which are comparable with UF but the economics of the materials are comparable with current technology. The boards are recyclable and fully biodegradable.

It is important in future to design new materials for their expected life expectancy. If a plastic bottle will have a shelf life of less than 1 month, why does the packaging material have to last for 450 years? Why do we persist in having products where the packaging persists in the environment? Can we design materials where more of the mass comes from waste? The problem with this is ensuring supply of feedstocks of a known quality. There may also be a public reticence to use materials with a given provenance. For example, selling writing paper made from recycled bank notes may be easier than material made from recycled toilet paper.

In conclusion, plastics themselves are not inherently bad, we just need to consider how we use them and more importantly how we dispose of them. More materials must be designed for recycling and better degradation in the



environment. It would be good if we could embrace the importance of efficient incineration as a way of removing plastic from the environment and for recovering heat and power. Better education required on the properties of materials and what terms such as recyclable, compostable and biodegradable actually mean and they should not just be seen as words to clear the conscience of the user when they dispose of them.

Biomaterials can be part, but certainly not all, of the answer. Smarter products and packaging need to be developed and our use of throw-away items must be seen as an exception rather than a rule.

© Professor Andrew Abbott, 2018