Plastics from renewable raw materials and biologically degradable plastics from fossil raw materials

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Plastics are an indispensable part of modern society. They are used in many different areas, in daily use, in technical applications and even in medicine. It is often forgotten that many modern developments would have been impossible without the use of plastics.

Plastics may have many advantages, but they are also the subject of environmental and political debate. The use of fossil raw materials, such as oil, and the dangers which can occur as a result of its extraction and transport have been criticized, as well as the disposal and recycling of plastics. The fact that some of the problems could be reduced by using renewable raw materials for the production of plastics has been overlooked. Particularly in recent times the interest generated by such products has increased, or rather, increased again. They are the subject of this section.

What are renewable raw materials?

Renewable raw materials are natural substances[1] which are used by mankind for purposes other than nutrition or foodstuffs. [1]. They can be agricultural, forestry, animal or microbial products. Examples of renewable raw materials which are used industrially are cellulose, starch, sugar, oils and fats. The philosophy of the renewable management of raw materials is that only amounts which do not upset the natural biological equilibrium are extracted, and thus no disruption of the biosphere results.

The variety of renewable raw materials and their different chemical structures leads to a wide range of applications. Table 1 shows some examples.

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[1] These do not include mineral oil, natural gas and coal, which are natural substances, but which were formed a long time ago.

Renewable raw material	Origin	Chemical / technical product	Application (example)
Cellulose	Wood, cotton	Cellulose ethanoate (acetate), cellulose ether	Sheets, films, filtration condensate, construction materials
Vegetable oils	*eg* rape	Rape seed oil Rape seed oil methyl ester	Lubricant Fuel
Sugar (saccharose)	Sugar cane, sugar beet	Saccharose derivates	Plastics
Starch	Wheat, potatoes, corn, starch	Physically or chemically modified starch (*eg* hydroxypropylstarch) alkylpolyglycoside	Pregelatinized starch, binders, adhesives, finishing agents, plastics Surfactants, detergents
Flax	Fibre flax (Flax)	Flax fibre	Fibre-reinforced materials
Latex	Rubber tree	Rubber	Car tyres
Wool	Sheep, goats *etc*		Clothes, insulating materials

Table 1 Examples of the application of renewable raw materials

The use of renewable raw materials to satisfy human needs has been happening for thousands of years. The technique of boiling soap from plant oils and wood ash was used by the Sumerians (2500 BC). The Egyptians had already discovered the method of dyeing using henna, a powder from the leaves of the henna shrub, in the 14th century BC, as had the people of Asia Minor in the 13th century BC, using alizarin from the madder plant.

The accumulation and decomposition of biomass are in equilibrium: 120 thousand million tonnes of carbon a year are bound by photosynthesis, while 60 thousand million tonnes are respired by plants in the dark and only 60 thousand million tonnes are converted to biomass in plants. These in turn are released into the atmosphere as carbon dioxide in winter as a result of decay processes. This is how the annual balance is worked out. This balance can be disrupted by natural disasters and by mankind. Around 2 thousand million tonnes of carbon dioxide are released into the atmosphere by deforestation and soil destruction, and five thousand million tonnes by the combustion of fossil fuels.

The total biomass of the earth amounts to 1841 thousand million tonnes, or 3.6 kg m^{-2} of surface area, according to estimates. Phototrophic plants, which use photosynthesis to produce energy, make up 99% of this figure. However, mankind uses only 3% of the biomass produced naturally (170 thousand million tonnes), by cultivation, harvesting and processing. This amounts to 2 thousand million tonnes of wood, 1.8 thousand million tonnes of grain and 2 thousand million tonnes of other natural substances (*eg* sugar cane, turnips, oily fruits).

This can be compared with a worldwide consumption of 7 thousand million tonnes of oil equivalent (mineral oil, natural gas, coal) for the production of energy. Only 7% is reprocessed by the chemical industry. In 1991, the German chemical industry covered 1.8% (10%) of its raw materials demand with renewable raw materials, and the trend is rising [2]. In the meantime, 10% of packaging chips are made from starch, and the proportion of biodegradable lubricants is over 30%.

Renewable raw materials have the big advantage over fossil raw materials that the sunlight required for their growth is available in unlimited amounts, and that the carbon dioxide released by their combustion corresponds to the amount bound by the plant during its growth. The chemical industry makes use of this advantage, as well as the ability of nature to synthesize new products. Thus, for example, soap can be made from vegetable oils in one step by an alkali ester cleavage. The basic molecular structure of the surfactant is already present and does not need to be developed via several reactions, as for example in the oxidation of alkanes to fatty acids.

However, even the cultivation and processing of renewable raw materials can cause environmental pollution, for example through the over-use of fertilizers and pesticides. Furthermore, the energy expenditure required for cultivation, harvesting and processing should not be forgotten. There are also products which are based on renewable raw materials which are not easily degradable or even toxic. As with any chemical product, this has to be carefully examined and taken into account.

What are plastics?

Plastics are materials which, from a chemical point of view, consist of organic macromolecules (there are some exceptions). Their production can be fully synthetic, *via* the polymerisation, polyaddition or polycondensation of small molecules, or partially synthetic, *via* the chemical conversion of macromolecular natural substances. The three different kinds of structure possible in plastics are described below.

Technical information: ways of producing plastics

The three different kinds of structure possible in plastics differ according to the type of chemical reaction by which the monomers are linked. This in turn depends on the type of monomer – see Figure 1

Polymerisation is used to link relatively small monomers to form a large macromolecule (a). The monomers contain either a carbon-carbon double bond, or they are heterocyclic. Polymerisation can be radical, cationic or anionic. For example, propene (propylene) can be radically polymerised to poly(propene).

In the case of polycondensation, two (usually different) monomers react with one another and a small molecule is cleaved off (b). Diols, diamines and dicarboxylic acids are suitable. For example, a diol and a dicarboxylic acid react to form a polyester and a molecule of water is cleaved off

Polyaddition links at least two different monomers in steps, without the cleaving-off of by-products (c). For example, polyurethanes can be formed from diisocyanate and a diol.

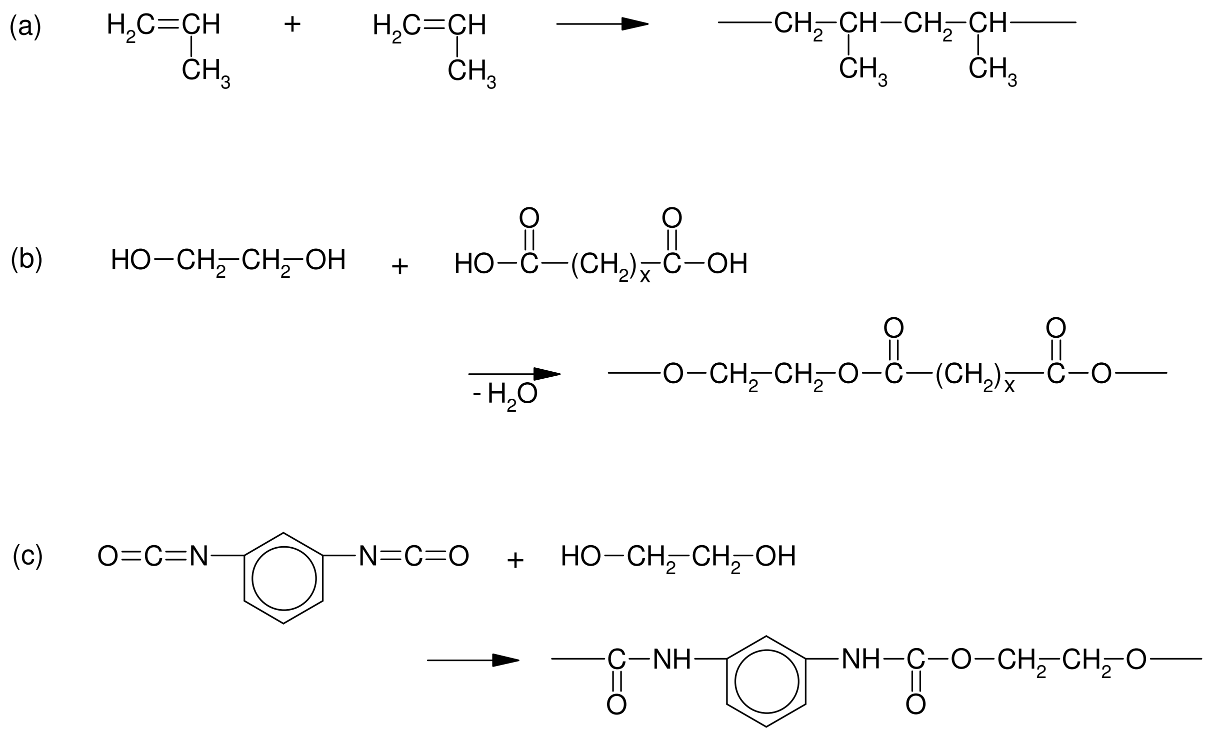


Figure 1 Production of plastics: polymerisation (a), polycondensation (b) and polyaddition (c)

The raw materials for fully synthetic plastics are today largely of petrochemical origin. In other words, they are based on crude oil and natural gas. Examples of plastics belonging to this category are poly(ethene) (polyethylene, PE), poly(phenylethene) (polystyrene, PS) and poly(chloroethene) (polyvinylchloride, PVC). It is also possible to extract raw materials for macromolecules from vegetable or animal raw materials. This will be discussed below. Furthermore, polymerisation can also be carried out using biotechnology.

The shape and order of the macromolecules are important characteristics of plastics:

- Thermoplastics have linear or linear / branched structures and are not cross-linked. They become soft when heated and can be melted. Examples are PE, PS and PVC.
- With thermosets the molecular chains are tightly woven and three-dimensionally cross-linked. They do not melt when heated, but are broken down at higher temperatures. Examples are Bakelite and certain polyurethanes.
- Elastomers are hard and rubbery plastics in which the macromolecules are loosely cross-linked in a three-dimensional structure. Rubbery elastomers can be deformed by stretching to many times their original length, but return to their original form when the stress is removed. The best-known example is rubber.

Thus the properties of plastics vary according to their molecular structure. Suitable synthesis methods can be used today to produce customized plastics. This is an important reason why they are so popular and commonly used.

Plastics from renewable raw materials

Plastics based on renewable raw materials are not a novelty. The first plastics which were used in large amounts were modified natural products. Examples include rubber based on natural rubber (1839), celluloid from cellulose (1865) and galalith which comes from casein in milk. (1897). Natural rubber is still an important product today. In the first third of the 20th century, polymers based on renewable raw materials were dominant. Then gradually plastics based on fossil raw materials began to take over, due to their ready availability and the fact that they created completely new possibilities in the world of chemistry.

Today the interest in plastics based on renewable raw materials has increased considerably. The aim here is to move away from petroleum-based plastics towards renewable raw materials, whilst at the same time trying to synthesize new products with special, desirable properties. For example, sugars are used as the alcohol components in the production of polyurethanes, and scientists are trying to better exploit raw materials, such as cellulose, which are available in large amounts. Products which are biologically degradable, *ie* which can easily be disposed of after use, are also gaining considerable interest. Only a few examples of the many possibilities will be illustrated here. We will start with the classic example, rubber, and extend the range from plastics based on cellulose, starch and 2-hydroxypropanoic acid (lactic acid) to polyurethanes made using castor oil.

Rubber

Rubber can be produced either synthetically, or from natural latex (or from mixtures of the two). Natural rubber is, today, an alternative to synthetic products, a fact which is highlighted by its proportion of only 30% of global rubber production.

Natural rubber is extracted from latex, the sap from the rubber tree (*Hevea brasiliensis*), which oozes out of the bark when the tree is damaged. Coagulation then produces solid natural rubber which is elastic and can be stretched considerably. If natural rubber is kneaded with sulphur and heated to around 400 K, rubber is then formed (vulcanisation) (Figure 2). These properties depend on the one hand on the sulfur content as well as on other additives, *eg* fillers such as soot and zinc oxide in the production of tyres.

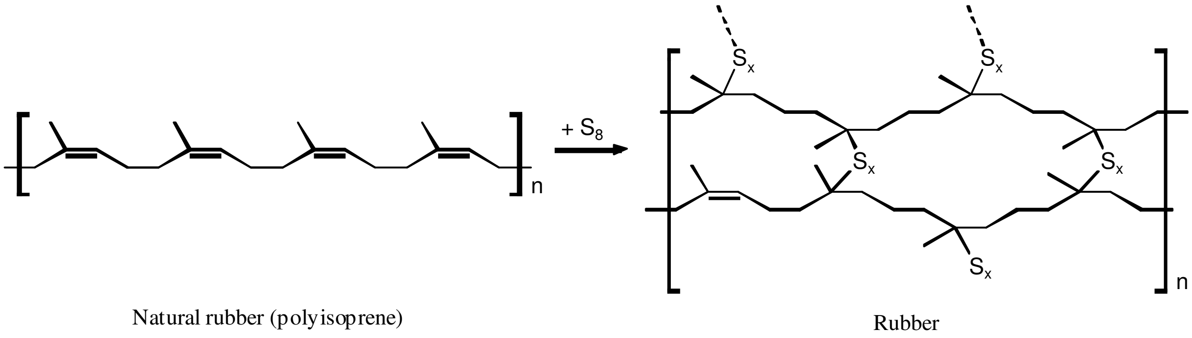


Figure 2 Vulcanisation of natural rubber (poly(isoprene)) with sulfur to rubber

Experiment: vulcanisation of natural rubber

In the following experiment we will be working with the natural latex concentrate Kagetex® FA [3]. The rubber dispersion is stabilized with ammonia (0.7 %) and has a dryness ratio of 61.5 %. Three types of rubber with different sulfur contents are produced [4].

Each group of students will need

- Eye protection
- Three aluminium dishes

- A glass rod
- A mortar and pestle
- Access to an oven or drying cabinet
- Natural latex concentrate liquid (*eg* Kagetex® FA)
- Sulfur (flammable)

Safety

- Wear eye protection
- Sulfur is flammable and its dust may be irritating to the eyes and respiratory system.

Method

Different mixtures with varying amounts of sulfur are set up as shown in Table 2.

Mixture	**Mass of latex / g**	**Mass of sulfur / g**	**Relative concentration of sulfur**
1	2.0	0.1	5
2	2.0	0.5	25
3	2.0	1.0	50

Table 2 Mixtures for the experiment on vulcanisation of rubber

The sulfur is ground in the mortar and mixed with the latex in an aluminium dish. The different mixtures are then left in the drying cabinet at 140 ^{0}C.

Disposal

The rubber waste can be disposed of with the household waste.

Observation

Elastic products are formed. The lower the sulfur content, the more elastic and soft the rubber is.

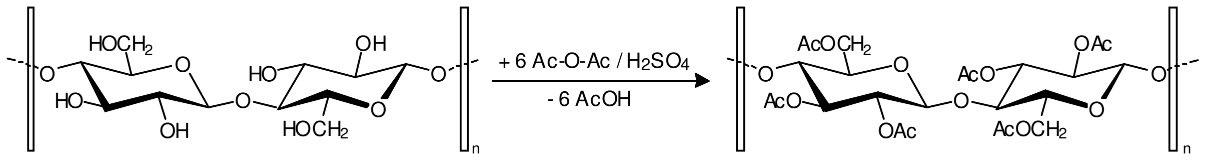
Evaluation

The degree of hardness of the rubber depends on the sulfur content. The sulfur reacts with the double bonds in the poly(isoprene) strands. Loose bonds are formed between the chains (vulcanisation). The more sulfur is added to the natural rubber, the higher the degree of intermolecular cross-linking and thus the hardness of the rubber produced.

Cellulose – not only for paper

Cellulose is a natural polysaccharide consisting of D-glucose molecules, which can be found as a structural substance in all plant cells. In industry, cellulose is extracted from wood using different extraction methods (wood contains 40-50% cellulose in addition to lignin and hemicelluloses). The largest part of world production is geared towards paper manufacture.

The free hydroxyl groups in cellulose can be esterified using ethanoic acid (Figure 3). The product, cellulose triethanoate (cellulose triacetate), is the basis of most photographic films. However, since this product has poor solubility, and thus is not suitable for other applications, a trick is required: some of the ester groups are cleaved hydrolytically with acid, so that a product with an average of 2.5 ethanoyl (acetyl) groups per glucose molecule is obtained. This plastic can be used many times and is used for the production of textile fibres as well as for buttons, handles and covers and as filtration condensate in cigarette filters.



Cellulose

Cellulose triacetate

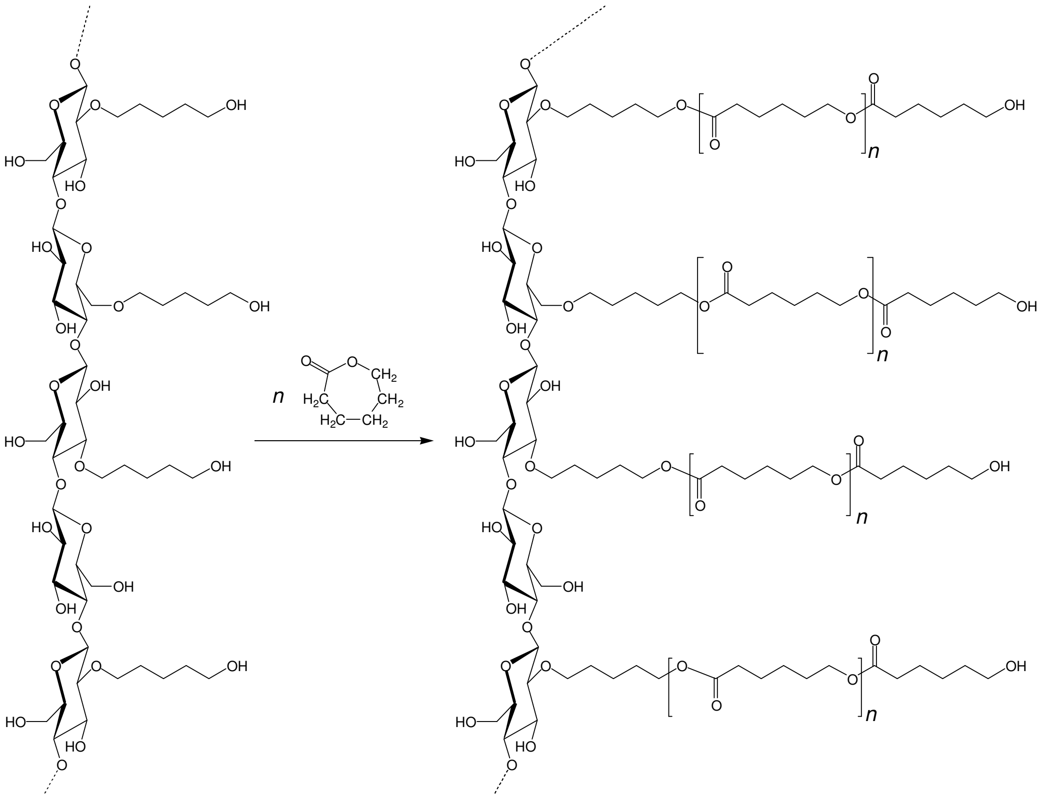
Ac = CH_3CO

Figure 3 The structure of cellulose triacetate made from cellulose

With new products, the aim is to produce materials which can be processed using conventional processes such as extrusion and injection moulding, in other words thermoplastically (they deform when heated), and which are biologically degradable. In the case of cellulose derivatives it seems that these two properties are irreconcilable. A new category of materials, cellulose esters, fulfils these requirements. As the name suggests, the free alcohol groups of the cellulose molecule are already partially esterified, as in ethanoyl cellulose (acetyl cellulose), in these compounds and in some cases also partially etherised.

The trick here is to attach large, biologically degradable side chains to the cellulose, to ensure that the long chains of the cellulose backbone are no longer so close together. Since these macromolecules can then collide with each other when heated – in contrast to cellulose, which is broken down – they are thermoplastic.

A by-product of this synthesis concept is the cellulosepolyhydroxyhexanoicacid ester. This synthesis works if ε-caprolactone – a cyclic ester derived from hexanoic acid (caproic acid) – is polymerized with cellulose to form poly(caprolactone).



The product is split by enzymes: the side chains are broken down by esterases and the cellulose by cellulases. In the case of the celluloseether ester a mixture of cellulases and esterases should be used for the enzyme test [5].

Viscose and rayon fibres are also produced from cellulose. The raw material is dissolved by treatment with carbon disulfide (CS_2) and then pressed through nozzles into an acid precipitation bath, thus cleaving the compound which is reformed, producing the textile fibres. Since the cellulose in this process is not changed chemically, when the whole process is considered, it is known as regenerated cellulose. It should be noted that hydrogen sulfide is produced in this process.

Starch – starting material for films and packaging materials

Starch, like cellulose, is a naturally-occurring polysaccharide consisting of D-glucose molecules, but with shorter molecular chains and a different chemical bond with the sugar units (Figure 4). In plants it serves as a carbohydrate reserve and is stored in the form of starch grains which vary from plant to plant. For example, corn grains contain 60-70 % and potatoes up to 20 % starch. The extraction of starch requires water and a series of grinding, washing, filtration and decanting steps.

Starch can be added to plastics in different amounts. For example, films and packaging can be produced from a mixture of starch and poly(ethene) (polyethylene). This reduces the weight for transport. However, the biodegradability of the poly(ethene) is not affected. Tests showed that the partial biodegradation of the starch changes the macroscopic film form (crack formation, brittleness, *etc*), but the degradation of the poly(ethene) over the course of 1-2 years was minimal (0.1%).

Even the starch in the poly(ethene) matrix is not always completely degradable. In contrast, oligomeric polyethylene waxes with low relative molecular masses (< 10 000) were degraded to a greater degree. This was to be expected, because the micro-organisms can only oxidize the free molecule ends, and there are very few of these in large molecules.

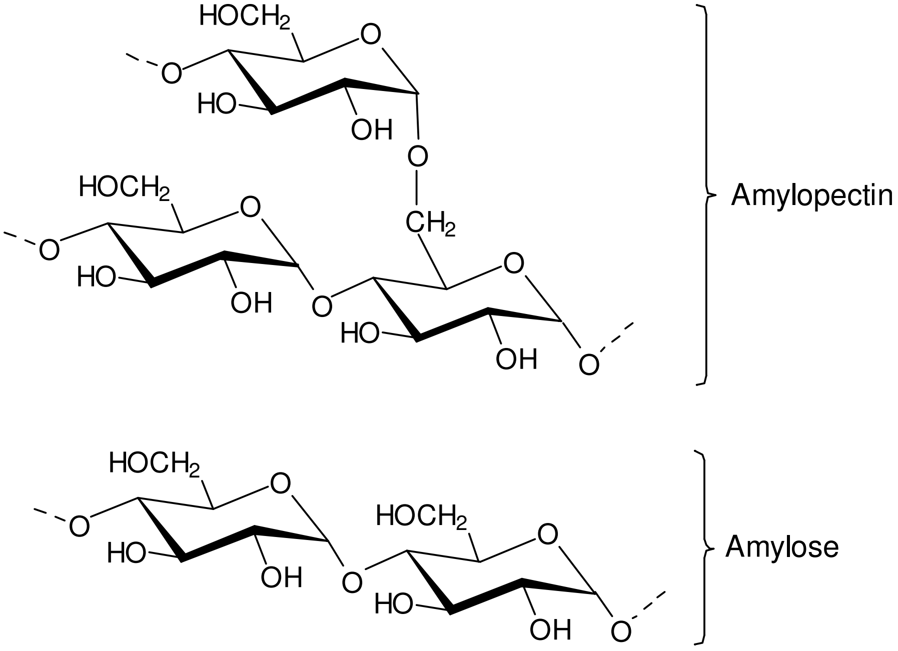


Figure 4: Section of a starch molecule (amylose and amylopectin)

The following experiment consists of two parts. First the extraction of starch from potatoes is described. A film can then be produced using the starch [4; 6].

Experiment: production of a film using starch

Part a: extraction of starch

Each group of students will need

- Eye protection
- Grater
- Tea strainer
- Mortar and pestle
- Two 400 cm^3 beakers
- Potatoes
- Distilled or deionized water

Safety

- Wear eye protection

Method

100 g of peeled and washed potatoes are ground with a grater. The mush is slurried with 100 cm^3 of water and poured through a tea strainer. This process is repeated twice. The beaker is left for five minutes until the starch is precipitated on the bottom of the beaker. The remaining water is decanted off. Another 150 cm^3 of water are added, stirred briefly and decanted again. This process is repeated again with 100 cm^3 of water.

Disposal

The potato and starch waste can be added to compost or disposed of with other household waste.

Observation

A white powder can be extracted from the potatoes.

Evaluation

The starch in potatoes can be extracted via a number of separation and purification steps. It is known as natural starch and is treated with cold water during the extraction process because starch does not dissolve in cold water.

Part b: production of a film

Each group of students will need

- Eye protection
- One 50 cm^3 round flask
- One reflux condenser
- One 25 cm^3 measuring cylinder
- Three 3 cm^3pipettes
- Magnetic stirrer with hot plate
- Oil bath
- Acrylic glass plate
- Drying cabinet
- Thermometer
- Spatula
- Natural potato starch (from Part (a) or a chemicals supplier)
- Propane-1, 2, 3-triol (glycerol) solution 50 %
- Hydrochloric acid 0.1 mol dm^{-3}
- Sodium hydroxide 0.1 mol dm^{-3} (irritant)
- Food dye (liquid)

Safety

- Wear eye protection

Method

Add 25 cm^3 of water to 2.5 g of potato starch, 3 cm^3 hydrochloric acid and 2 cm^3 proppane-1, 2, 3-triol (glycerol) solution. If you use the moist starch from Part (a), 4 g of potato starch are required. Heat for 15 minutes under reflux. The reaction is stopped by adding sodium hydroxide. The mixture can be dyed by adding 1 to 2 cm^3 of food dye. The hot, viscous mass is poured uniformly onto the acrylic glass plate and dried for two days at room temperature or for approximately 90 minutes at 100 °C in a drying cabinet. If the moist starch from Part (a) is used, the amounts should be adjusted to 4 g of starch.

Disposal

Waste can be added to compost or disposed of with other household waste. Neutralized liquid waste can be poured down the drain.

Observation

The initially highly viscous but later thin solution can be cast into a film. The clear film can then be removed form the glass plate.

Evaluation

Starch forms a film when it is dried from an aqueous solution. The reason for this is the intramolecular and intermolecular hydrogen bonds, in particular those between the long chains of the amylose molecules. However, the branched amylopectin, which makes up the larger part of the starch molecule, inhibits film formation. The reaction with diluted hydrochloric acid partially breaks down the amylopectin. This leads to improved film formation, but the product is brittle. For this reason propane-1, 2, 3-triol (glycerol) is added. Propane-1, 2, 3-triol retains water as a result of its hygroscopic properties. The bound water inhibits the formation of crystalline and brittle areas within the molecule. Thus water acts as a softener here as does propane-1, 2, 3-triol. The later is capable of slipping between the starch molecules and thus making the plastic softer.

Poly(2-hydroxypropanoic acid) (polylactic acid) – a biologically degradable plastic

2-hydroxypropanoic acid (lactic acid) can be obtained by the fermentation of glucose or maltose, or directly from milk or whey using suitable bacteria. This is added to drinks, but can also be used as the starting substance for a plastic, poly(2-hydroxypropanoic acid). It is possible to produce such different products as packaging materials or surgical thread from this polycondensate. The common characteristic of these applications is the biodegradability. Thus packaging made from this material decomposes on the compost heap, and surgical thread does not have to be removed after an operation, but is re-absorbed by the body. These plastics are also being considered for other areas of medicine: for example for the protection of broken bones it would be possible to use screws made of biodegradable plastic, which would then not have to be removed by a second operation.

When water is cleaved off from 2-hydroxypropanoic acid, an oligomer is formed - an ester consisting of 10 to 30 lactic acid units. This oligomer is in equilibrium with the corresponding dilactide – an ‘internal’ ester consisting of two molecules of 2-hydroxypropanoic acid. Poly(2-hydroxypropanoic acid) can be obtained by adding a suitable catalyst. In the following experiment only the formation of the oligomer [7] is shown.

Experiment: production of a plastic from 2-hydroxypropanoic acid (lactic acid)

Each group of students will need

- Eye protection
- Test tubes
- Test tube rack
- Bunsen burner
- Acrylic glass plate (approximately 15 cm × 15 cm)

- Boiling stone
- Microspatula
- Tin(II) chloride (irritant)
- 2-hydroxypropanoic acid (lactic acid)
- Cobalt chloride paper (dried)

Safety

- Wear eye protection
- Tin(II) chloride is irritating to eyes and skin, and is dangerous with oxidising agents such as nitrates and peroxides

Method

5 cm^3 of 2-hydroxypropanoic acid (lactic acid) are added to a microspatula load of tin(II) chloride crystals and a boiling stone in a test tube and heated for 10 minutes whilst stirring vigorously. The vapours emitted are tested with cobalt chloride paper. If an orange-brown colour occurs in the test tube, the hot solution is poured onto the acrylic glass plate.

Disposal

Plastic waste can be disposed of with other household waste.

Observation

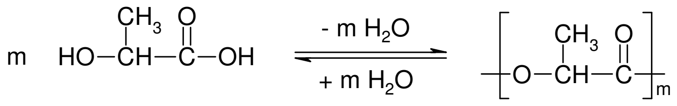
The solution applied to the acrylic glass plate solidifies and forms a yellow-brown slightly sticky mass. The cobalt chloride paper changes colour from blue to pink.

Evaluation

Cobalt chloride paper is used to test for water which, as a result of the temperature, escapes as steam from the test tube. The blue dry cobalt(II) chloride forms a pink-coloured hexahydrate when combined with water.

$Co^{2+} + 6H_2O \rightarrow [Co(H_2O)_6]^{2+}$

The reaction is an esterification in which the 2-hydroxypropanoic acid (lactic acid) is converted to oligomers with loss of water [8]. In general one molecule of alcohol reacts with one molecule of acid with loss of water to form an ester. The 2-hydroxypropanoic acid used is bifunctional. It consists of one hydroxyl and one carboxyl group which form an intermolecular bond.



$$m\ HO-\underset{}{\overset{CH_3}{CH}}-\overset{O}{\overset{\|}{C}}-OH \underset{+\,m\,H_2O}{\overset{-\,m\,H_2O}{\rightleftharpoons}} \left[-O-\overset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-\right]_m$$

Milchsäure

oligomere Milchsäure

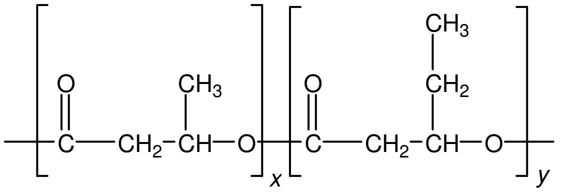
Labels: = Milchsäure = 2-hydroxypropanoic acid (lactic acid); oligomere Milchsäure = oligomeric lactic acid

The esterification is catalyzed by acid. The proton required for the first step of the esterification (protonation of the carboxyl group) is formed by the hydrolysis of tin(II) chloride with precipitation of a basic salt.

$SnCl_2 + H_2O \rightarrow Sn(OH)Cl + Cl^- + H^+$

Biopol – a thermoplastic which is completely biodegradable

The name Biopol stands for a group of polyesters based on hydroxybutanoic acid, which are formed by the fermentation of a sugar raw material by naturally occurring bacteria. Thus one has made use of nature here, for both the provision of the starting materials and the formation of the polyester. Their use is limited because of their cost.



$$-\left[\overset{O}{\overset{\|}{C}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-O \right]_x \left[\overset{O}{\overset{\|}{C}}-CH_2-\overset{\overset{CH_3}{|}}{\overset{CH_2}{\overset{|}{CH}}}-O \right]_y-$$

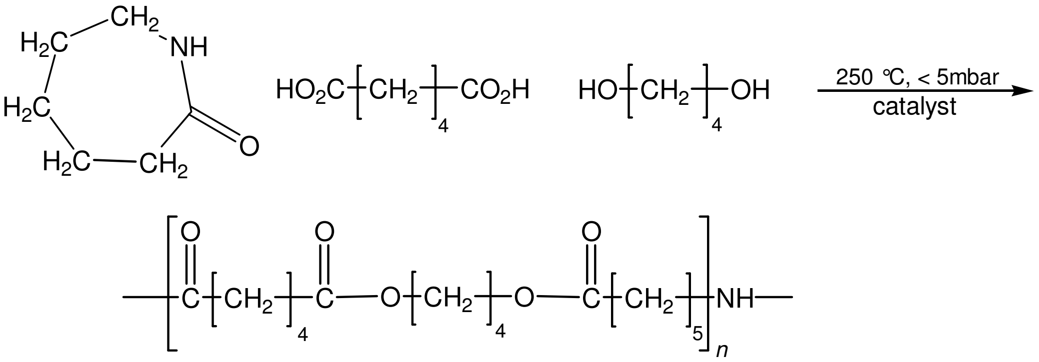
Biopol is thermoplastic, completely biodegradable and available in different forms with different physical properties. The plastic is used in the cosmetics industry for bottles and other containers. It is also used for caps for bottles, tubes and jars, Biopol-coated paper, cardboard organic waste bags and sacks as well as paper cups.

Biodegradable plastics – not only from renewable raw materials

Important biodegradable plastics, which have in part already found commercial use, are based partially or entirely on fossil raw materials. The raw material base can in some cases be varied. Depending on the price, renewable or fossil starting materials can be used for the synthesis. Examples include the polyesteramides and polyasparaginic acids developed by Bayer.

Polyesteramide ‘BAK 1095’ (Bayer):

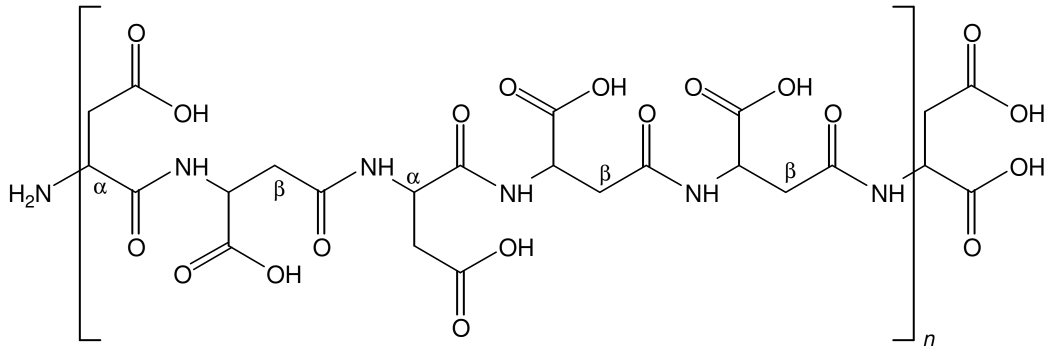
The starting materials are cheap monomers such as ε-caprolactam, hexanedioic acid (adipic acid) and diols (*eg* butane-1, 4-diol). These are combined in a typical polycondensation reaction in a condensation boiler. However because they are derived from crude oil these cannot be thought of as sustainable materials.



Depending on the process, the properties of the polyesteramides can be varied within certain limits whilst maintaining the same composition. The products are very easily degraded. After 50 days a film with a thickness of 200 µm is degraded by 95 % on a compost heap [7].

Polyasparaginic acid

Bayer AG has begun work on the development of a process for producing biodegradable polyasparaginic acids based on *cis*-butenedioic anhydride (maleic anhydride) derivatives [9].



In particular their use as detergent co-builders has attracted a lot of attention. These substances assist the washing process, partially binding calcium and magnesium ions, and have a dispersing effect. Since in Europe more than 2 million tonnes of detergent enter the environment after one use, biodegradable substances are urgently required here to reduce environmental pollution. The dispersing ability of polyasparaginic acids for calcium carbonate precipitates during the wash was investigated and excellent results were obtained.

Castor oil as a component of polyurethanes

Castor oil is extracted from the berries of the castor oil plant (*Ricinus communis*). As Figure 5 shows, this triglyceride contains a non-saturated acid as the acid component – ricinoleic acid -, which has a free hydroxyl group. The plastics chemist can use this group for the production of macromolecules. One possibility is to use ricinoleic acid directly as the alcohol component for polyurethanes.

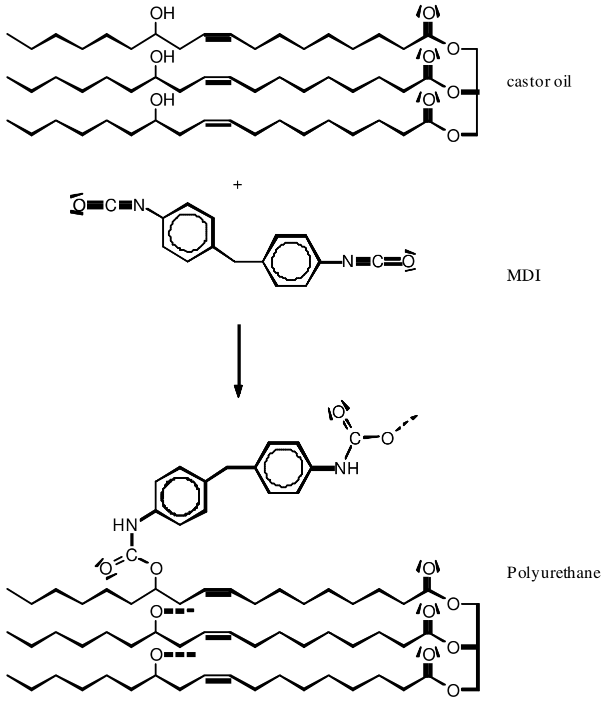


Figure 5 Structure of polyurethanes from castor oil and MDI

Polyurethanes are generally formed by the polyaddition of di- or poly-hydroxy compounds and isocyanates. Diphenylmethane-4, 4’-diisocyanate (MDI), for example, is used in large amounts in industry. In the following experiment this petrolic component is treated with castor oil. The reaction leads to a highly cross-linked, duroplastic polyurethane foam [4].

Experiment: production of a polyurethane foam based on castor oil

Each group of pupils will need

- Eye protection
- Test tube or demonstration tube
- Test tube rack
- Glass rod
- Spatula
- Bunsen burner
- Pasteur pipette
- Castor oil
- Diphenylmethane-4 ,4’-diisocyanate (MDI) toxic
- 1,4-Diazabicyclo [2, 2 ,2]octane (DABCO) toxic
- Distilled or deionised water

Safety

- Wear eye protection
- In view of the toxic nature of MDI and DABCO, teachers will probably wish to carry out this experiment as a demonstration

Method

4 g of castor oil, 3.3 g diphenylmethane-4, 4´-diisocyanate, a small spatula load of DABCO and six drops of water are mixed together in a test tube. The mixture is heated for 30 seconds, stirring all the time (until foam formation occurs). The test tube is then removed from the heat.

Disposal

The test tube with the fully reacted polyurethane can be disposed of with the household waste.

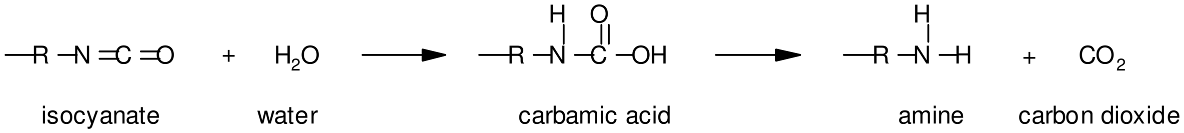
Observation

During heating a gas is released. The viscosity of the mixture increases. The reaction proceeds and does not require further heating. A yellow foam is formed which, after cooling, is hard and brittle.

Evaluation

The reaction of castor oil with isocyanate produces a plastic. The polymerisation is exothermic. DABCO acts as a catalyst, but the exact function will not be discussed in detail here.

The gas released during the polymerisation is carbon dioxide. It is formed by the reaction of water with the diisocyanate. Carbamic acid is formed as an intermediate product. The carbon dioxide leads to the formation of a foam which is fixed by the hardening of the polyurethane [10]. The amines react with excess isocyanate to form carbamide (urea) derivatives.



$$-R-N{=}C{=}O \;+\; H_2O \longrightarrow -R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-OH \longrightarrow -R-\overset{H}{\overset{|}{N}}-H \;+\; CO_2$$

Fibre-reinforced plastics

In addition to the plastics mentioned, which are either partially or completely synthesized from renewable raw materials, composite materials are also of considerable interest. Here different materials are combined with each other to achieve properties which the individual components do not possess. Fibre-glass and carbon fibre-reinforced materials are well-known examples, which are used for the production of yachts and moulded parts. The basic principle of their production is very simple: a mat of fibre-glass material, for example, is placed in a mould and soaked with liquid plastic. After the plastic has hardened, the workpiece can be removed from the mould.

In the last few years, tests have been run into how far natural fibres can replace fibre-glass and other reinforced fibres. This approach is not new, because, for example, the chassis of the economy car, Trabant, which used to be built in East Germany, was made from cotton fibres bound to a phenol resin. The aim in the development of modern techniques is to find ways of producing large numbers of pieces in a short period of time. In some cases this has already been achieved successfully. Today, some automobile parts, such as hat racks or door linings in the car interior, which are not subjected to heavy loads, are made from flax or sisal fibres. The fibrous material is pressed with plastic films in heated moulds – a fast and clean process.

Plastics made from renewable raw materials have many different properties and provide a variety of possible applications. Disadvantages at this time, are the higher cost in comparison with mass-production plastics based on mineral oil and the often lower availability of renewable raw materials compared with fossil raw materials.

The combination of renewable raw materials with fossil raw materials for the production of biodegradable plastics could therefore be the way ahead, in particular with a view to finding an answer (even a temporary one) to the question of economic feasibility. One thing is clear: this is an area of research which is likely to bring many new discoveries in coming years.

You can find more experiments related to the subject of plastics from renewable raw materials in Bader et al. [4; 11; 12] and Sommerfeld [6].

List of chemicals

Chemical	**Compound formula**	**CAS-Nr.**	**Hazard compound rating**
Ammonium ethanoate	$C_2H_7NO_2$	631-61-8	-
Cellulose triethanoate	$(C_{12}H_{16}O_8)n$	9012-09-3	-
Distilled water (aqua dest.)	H_2O	7732-18-5	-
Diazabicyclo[2, 2, 2]octane(DABCO)	$C_6H_{12}N_2$	280-57-9	toxic, Xn
Dichloromethane	CH_2Cl_2	75-09-2	slightly toxic, Xn
Diphenylmethane-4, 4’-diisocyanate	$C_{15}H_{10}N_2O_2$	101-68-8	toxic, Xn
Ethanoic acid	$C_2H_4O_2$	64-19-7	caustic, C
Ethanoic anhydride	$C_4H_6O_3$	108-24-7	caustic, C
Propane-1, 2, 3-triol	$C_3H_8O_3$	56-81-5	-
KAGETEX® FA	-	9006-04-06	-
Potassium hydroxide	KOH	1310-58-3	caustic, C
2-hydroxypropanoic acid	$C_3H_6O_3$	50-21-5	irritating, Xi
Sodium hydroxide	NaOH	1310-73-2	caustic, C
Castor oil	-	8001-79-4	-
Hydrochloric acid	HCl	7647-01-0	caustic, C
Sulfur	S_8	7704-34-09	inflammatory, F
Sulfuric acid	H_2SO4	7664-93-9	caustic, C
Starch	$(C_6H_{10}O_5)_n$	9005-25-8	-
Tin(II) chloride	$SnCl_2$	7772-99-8	toxic, Xn

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