

Plastics conservation – Barbie™ and friends

Introduction

This material has been compiled (with permission) by Ted Lister from the book by Anita Quye and Colin Williamson, *Plastics collecting and conserving*, Edinburgh: NMS Publishing, 1999.

Teachers may find the above book a useful source of further reading if required.

Acknowledgements

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The resource

Three pieces of student material are presented:

- *A brief history of plastics;*
- *The decay and degradation of plastics;* and
- *Conservation of plastics.*

Each passage is set in a context of the collection, care, identification and display of plastic objects in museums and by private collectors. Many people think of objects made of plastic as 'throwaway' and do not consider them as collectable items or ones that might be found in museums. In fact there are increasing numbers of plastic objects in museums as well as in private collections and many are increasing in value. To give just one example, some Barbie™ dolls can change hands for thousands of pounds. It is also a misconception that plastics do not decay easily – many of them do, and this raises issues about how best to preserve them.

The issues examined in the passages include the chemistry of plastics, some of their history, ways in which plastics degrade, identifying different types of plastics and ways to store and display them to minimise deterioration.

Each piece consists of reading material for post-16 students (although *A brief history of plastics* may also be suitable for able pre-16 students) interspersed with questions to fulfil the following functions:

- as summative comprehension questions, *ie* for students to read the material and answer the questions to test their understanding;
- as formative comprehension questions *ie* to help students' understanding as they read the chapter; and
- as a way of highlighting that the chemical principles used by chemists in real life situations are the same as those learned in post-16 study.



Chemical nomenclature

The question of systematic names versus everyday names is particularly problematic with polymers, where everyday names are regularly used and recognised and systematic ones are often complex. In general, everyday names have been used in this publication with systematic ones in brackets where this is thought to be helpful, for example where the structure of the polymer is being discussed rather than the name being used simply to identify the material. In cases of doubt, we have erred on the side of simplicity and readability – Terylene is much more easily understood than poly(ethenediyl-1,4-benzenedicarboxylate)! Names that are registered trademarks, such as TeryleneTM, NylonTM and PerspexTM are spelt with a capital letter. Other names such as polyvinyl chloride (abbreviation pvc) and polythene (abbreviation pe) begin with a lower case letter.

Teachers' notes

Answers

A brief history of plastics

- Many answers are possible including a variety of polymeric materials. Non-polymer based materials that fit the definition could include clay, metals, glass *etc.*
 - Methods of shaping include carving, cutting, machining, forging *etc.*
- The kink occurred in the mid-1970s.
 - This follows the so-called Yom Kippur war between Israel and Egypt. Many oil-producing countries in the Middle East increased their crude oil prices in protest at the USA's support for Israel. This in turn increased the price of plastics (which are made from products obtained from crude oil) and thus reduced demand.
- Bois durci means literally 'hardened wood'.
- Vulcan was the Roman god of fire. The fire refers to the heat used to vulcanise rubber.
 - Ebony is a hard, black wood so that Ebonite resembled ebony.
- Elephants are relatively rare, they would have to be hunted, killed and the ivory imported. Only a relatively small amount of ivory is obtained from each elephant.
 - Many people consider hunting cruel, and elephants are becoming increasingly rare.
 - The ivory would have to be shaped into a perfect sphere.
- Carbon dioxide (and carbon monoxide), water, nitrogen oxides.
- The fibres have a much greater surface area exposed to oxygen in the air.
- Many possible answers, for example saucepan handles, parts in car engines such as distributor caps.
- A synthetic, thermoplastic condensation polymer.

The decay and degradation of plastics

- $350\,000\text{ J mol}^{-1}$
 - $350\,000 / 6 \times 10^{23} = 5.83 \times 10^{-19}\text{ J per bond}$
 - $v = 8.8 \times 10^{14}\text{ sec}^{-1}$
 - This is at the borderline between the violet and ultraviolet regions of the spectrum.
- Cross-links prevent polymer chains sliding past one another and prevent the material stretching and bending.
- Reactions normally slow down as the concentrations of the reactants decrease.
 - If one of the products catalyses the reaction, the rate of the reaction first

decreases, as explained above. Then, as the catalyst appears, it increases and decreases again as the reactants are used up, see Figure 1.

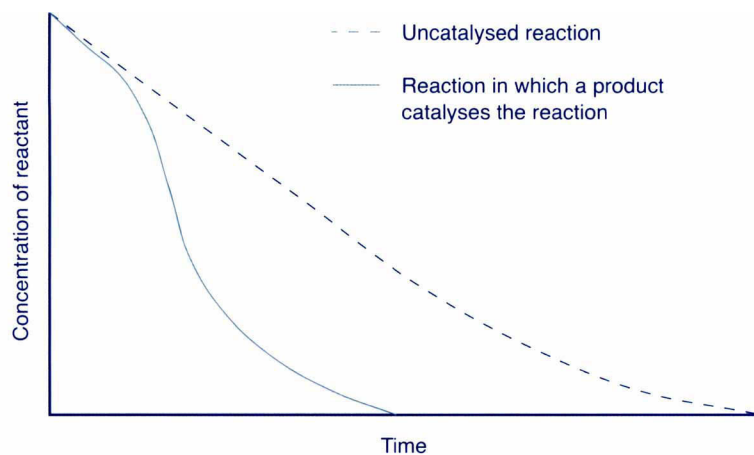


Figure 1

4. a)

- 'a few days'; disposable contact lenses,
- 'a few weeks'; carrier bag,
- 'a few months'; chocolate bar wrapper
- 'a few years'; washing-up bowl, toy, car bumpers
- 'many years'; electrical cable insulation, hip joint

Some variations are acceptable.

b) A chocolate bar wrapper must last long enough to allow for the distribution time and shelf life of the bar. Ideally, it would then decay to harmless products but in practice it will present a disposal problem.

5. a) It is heated.

b) This will speed up any reactions, such as chain breaking, which cause degradation.

6. Elimination.

7. A base.

8. a) Decolourisation of bromine solution.

b) In a solid, only the double bonds at the surface are exposed to the bromine solution.

c) See Figure 2.

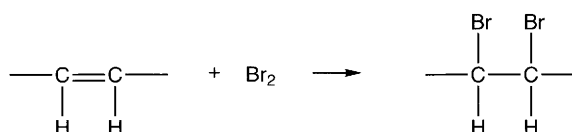
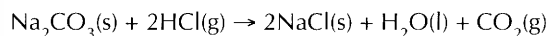


Figure 2

9. Hydrogen chloride gas will be unable to escape, its concentration in the case will rise and its catalytic effect will increase.

10. The sodium carbonate would react with the hydrochloric acid, thus slowing down the decay of the pvc.



11. See Figure 3.

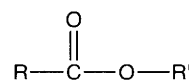


Figure 3

12. a) See Figure 4.

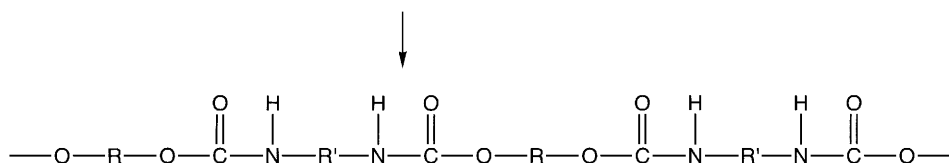
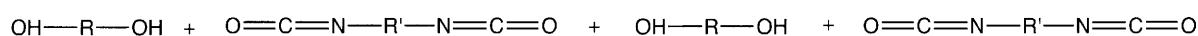
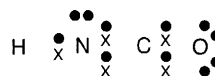


Figure 4

- b) A reactive site on each end of a chain is needed to make a polymer so that as each monomer adds onto the growing chain, further reaction is still possible.
- c) A triol allows a branched chain to form and thus leads to the possibility of cross-linking between chains.
- d) Cross-linking is likely to make the polymer more rigid.

13. a)



- b) See Figure 5.

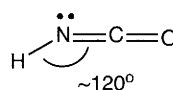
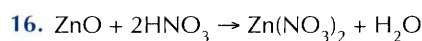


Figure 5

14. Foams have a large surface area exposed to oxygen in the air. Paint protects the polyurethane from oxygen in the air.

15. Water.



17. A smell of vinegar. This is the ethanoic acid released by the decaying polymer.

18. a) A strong acid, HA, dissociates completely into H^+ and A^- in solution. A weak acid dissociates only partly and an equilibrium exists the solution which contains mostly undissociated HA.

- b) Ethanoyl chloride.

Conservation of plastics

1. Displaying an object means that it is exposed to a light and to a variety of chemicals – oxygen and other gases in the air and water vapour for example. It will also be exposed to temperature changes and may be touched.
2. Look for sensible suggestions. The hinges in the joints may be made of metal. Hair could be made of Nylon and eyes of glass. Clothing could be made from a variety of materials both synthetic and natural, such as cotton.
3. a) 1.08 g cm^{-3} .
b) Polystyrene.
c) There may be other types of plastic with this density.

Many plastics contain additives such as fillers that affect the density.

Accuracy of measurement – a small inaccuracy in the measurement of mass or volume would result in a different value for density. Since many plastics have similar densities, this could result in a misidentification.

- d) Place the piece in a measuring cylinder part-full of water. Note the volume increase.
 - e) The density will be much less than for the non-foamed plastic – see the Table in the question.
4. a) Nitric acid. Ethanoic acid (acetic acid).
b) Both these plastics are long chain hydrocarbons. Wax candles and paraffin are made from shorter chain hydrocarbons that could be produced by breaking the longer chains.
c) Carbon dioxide. It is acidic.
d) Carbon monoxide.
 5. a) See Figure 6.

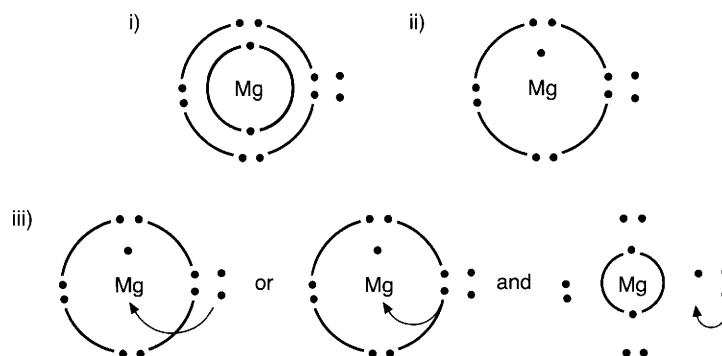


Figure 6

- b) Two: (i) directly from shell 3 to shell 1 and (ii) indirectly – from shell 2 to shell 1 and then from shell 3 to shell 2. There are therefore three frequencies in the spectrum.
6. This is a difference of $20 \text{ }^\circ\text{C}$ and would reduce reaction rates fourfold, thus quadrupling the life of the object.
 7. a) 1.66×10^{-9} .

- b) 6.6×10^{-10} .
- c) The first is approximately 2.5 times larger than the second.
- d) This supports the rule (if only as a rule of thumb) because the rule would predict the first to be twice as big as the second.
8. a) The increased surface area compared with a solid lump will increase the rate of reaction of the iron with the oxygen.
- b) iron + oxygen \rightarrow iron(III) oxide
- $$4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$$
- c) Volume of case = $1 \times 0.5 \times 0.5 = 0.25 \text{ m}^3 = 250 \text{ dm}^3$
 Air is 20% oxygen, so the case contains 50 dm^3 of oxygen
 From the equation, 3 moles ($3 \times 24 = 72 \text{ dm}^3$ at room temperature) of oxygen react with 4 moles ($4 \times 56 = 224 \text{ g}$) iron.
 So 155.6 g of iron is required.

The main assumption is that at room temperature the volume of 1 mole of gas is 24 dm^3 . Other assumptions are that the case has no leaks and that the volume of contents of the case can be ignored.

Practical work

The following experiment is about identifying plastics according to their density. An alternative version of this experiment is given in K. Hutchings, *Classic Chemistry Experiments*, London: Royal Society of Chemistry, 2000, pp27–32. The student sheet is available at http://www.chemsoc.org/networks/learnnet/classic_exp.htm (look at files 11-20).

Experiment – Identifying plastics according to their densities

This experiment could be done as a class experiment or a demonstration.

Materials will float in liquids that have a greater density than they do. For example, polythene (density about 0.9 g cm^{-3}) will float in water (density 1.0 g cm^{-3}) but pvc (density about 1.2 g cm^{-3}) will not.

Solutions of salt (sodium chloride) have greater densities than pure water. Pure water has a density of 1.0 g cm^{-3} while a saturated salt solution has a density of about 1.3 g cm^{-3} .

One way of comparing the densities of plastics is to see whether or not they float in salt solutions. Take small pieces of the following plastics: polythene, polyester, pvc, phenolic, Perspex, polystyrene. Place them in a 250 cm^3 beaker and almost fill the beaker with tap water to which one drop of washing-up liquid has been added. (The washing-up liquid is to prevent bubbles sticking to the plastic pieces. These would tend to make them float.) You should find that the polythene floats, because its density is less than that of water. Now add salt, a large spatula full at a time. Stir after each addition to dissolve the salt. Continue until you have added about 70 g of salt. You should notice that the various plastics begin to float one by one as the density of the salt solution increases. In which order do the plastics start to float? What does this tell you about the densities of these plastics?

Small samples of the required plastic materials can be obtained as follows:

- polythene – bread bags, bin liners, carrier bags, food bags (either high or low density polythene is suitable for this experiment);

- polyester – fizzy drinks bottles (the transparent body of the bottle, not the black base);
- pvc – cooking oil or shampoo bottles;
- phenolic – electrical fitting such as plug sockets (normally dark-coloured);
- Perspex™ – Perspex™ sheet sold in DIY shops, car rear light lenses; and
- polystyrene – disposable cups from drinks machines (not expanded ones) translucent plastic egg boxes (not expanded ones).

Some further suggestions for sourcing plastic samples are given in K. Hutchings, *Classic Chemistry Experiments*, London: Royal Society of Chemistry, 2000, p28, and *Nuffield Co-ordinated Sciences, Teachers' Guide*. Harlow: Longmans, 1988, p214. The former also includes a table of densities of various plastics.

A brief history of plastics

The word 'plastic' means literally 'able to be moulded'. A more modern definition is 'a material that can be moulded or shaped into different forms under pressure and/or heat'. By these definitions, clay, for example, is plastic. Nowadays when we use the word plastic we usually mean one of a group of synthetic (man-made) materials such as polythene, pvc, Bakelite™, Nylon™ etc. All these materials are polymers – large molecules made up of many smaller molecules (called monomers) chemically bonded together. These materials are also plastic in the original sense in that they can be moulded into shape (although some of them require additives to make them easily mouldable). This ability to be moulded is one of the main advantages of plastic materials. Some types can be moulded only once and then retain their shape until they are destroyed, others can be remoulded several times.

- Q1.** a) Think of as many materials as you can which fit the definition of a plastic: 'a material which can be moulded or shaped into different forms under pressure and/or heat'. Which ones on your list are synthetic polymers?
- b) What other methods are there for shaping materials other than moulding them into shape?

Many synthetic polymers are of relatively recent origin – most of them have been developed in the last 50 years and none is much more than 150 years old. Compare this with metals, which have been used by mankind for over 5000 years and materials such as wood and stone, which have been used for over 2 million years.

The use of plastic materials has increased enormously in the last 50 years (Figure 1).

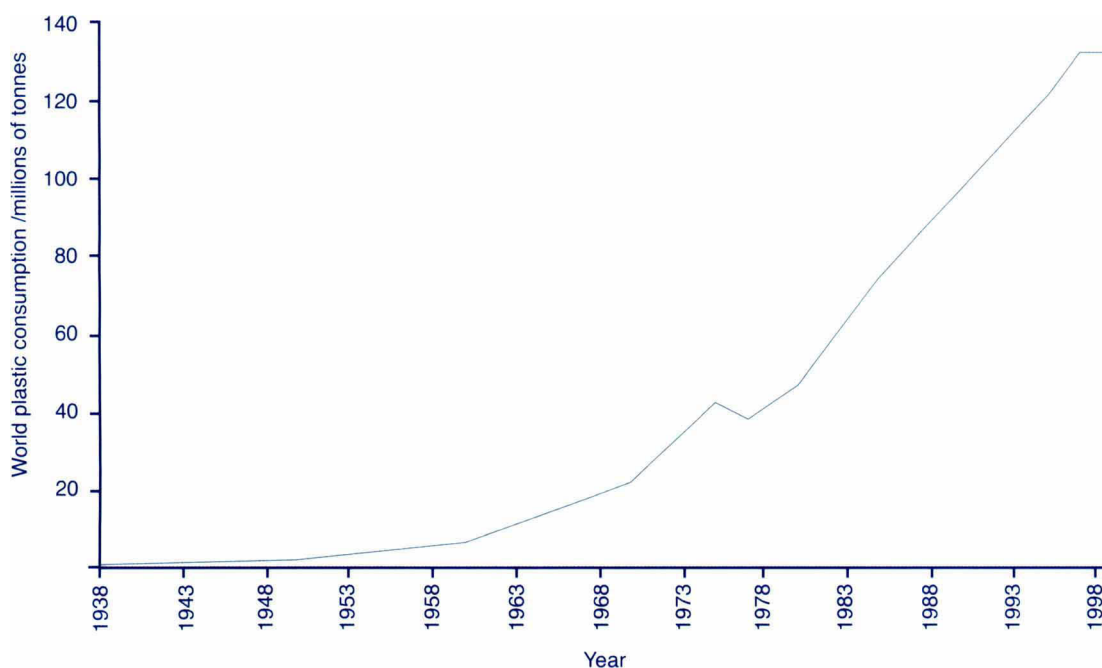


Figure 1 World plastic consumption during the 20th century

- Q2.** Look at the graph in Figure 1. There is a significant kink in plastics production.
- a) Use the graph to work out the approximate date of this kink.
- b) A world event around this date caused this sudden drop in plastics production. Find out what this was.

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Sources of polymers

Polymers themselves are not new. Cellulose is a polymer made from sugar monomers. It is found in plants and has been around as long as the plants themselves. Rubber is another polymer from a plant source, the rubber tree, Figure 2. This time the monomer is a molecule called isoprene (methylbuta-1,3-diene). The formulae of cellulose and of rubber are shown in Figure 3.



Figure 2 Natural rubber is the sap of the rubber plant

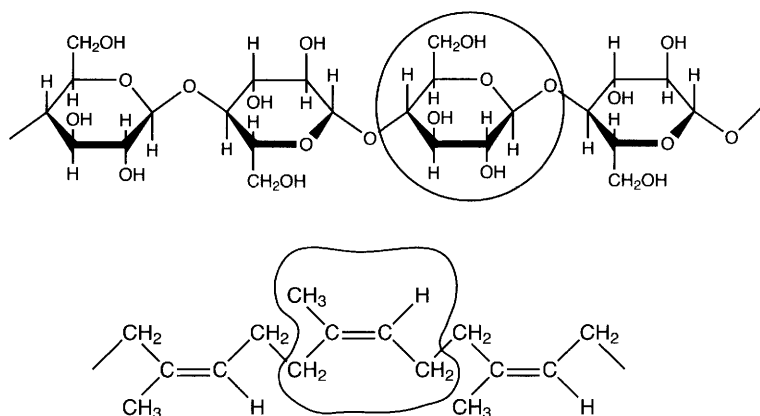


Figure 3 Parts of the polymer molecules of cellulose (top) and rubber (bottom) with the monomer units ringed

Rubber can be moulded and is therefore a plastic; it can be used as it is, although it is usually treated chemically to make it harder. Cellulose, on the other hand, cannot be moulded as it is. It can, however, be treated chemically to convert it to a form which can be moulded. Treating cellulose, obtained from cotton, with nitric and sulfuric acids converts the cellulose into a form that can be moulded into shape. This new form is an example of a modified (or semi-synthetic) polymer. This polymer is called cellulose nitrate by chemists and has the trade name Celluloid™.

So there are three types of polymer:

- natural polymers such as rubber, which can be used with little or no chemical treatment;
- natural polymers which need chemical treatment to make them useful – these are called modified (or semi-synthetic) polymers; and
- synthetic (man-made) polymers that are made from raw materials such as products from crude oil which are not themselves polymers.

Natural polymers

Not surprisingly, the first polymers to be used by mankind were natural polymers. Some examples include:

- animal horns and hooves – these can be softened in boiling water so that they can be shaped;
- beeswax – taken from beehives – this can be softened or melted by heating, and hardens on cooling;
- shellac – this is a substance, given out by some insects, that can be melted and moulded; and
- bois durci – the protein albumen, found in blood and egg white, mixed with powdered wood and made into a mouldable polymer.

Some of these polymers have been used for up to 2000 years. Some examples are shown in Figure 4.

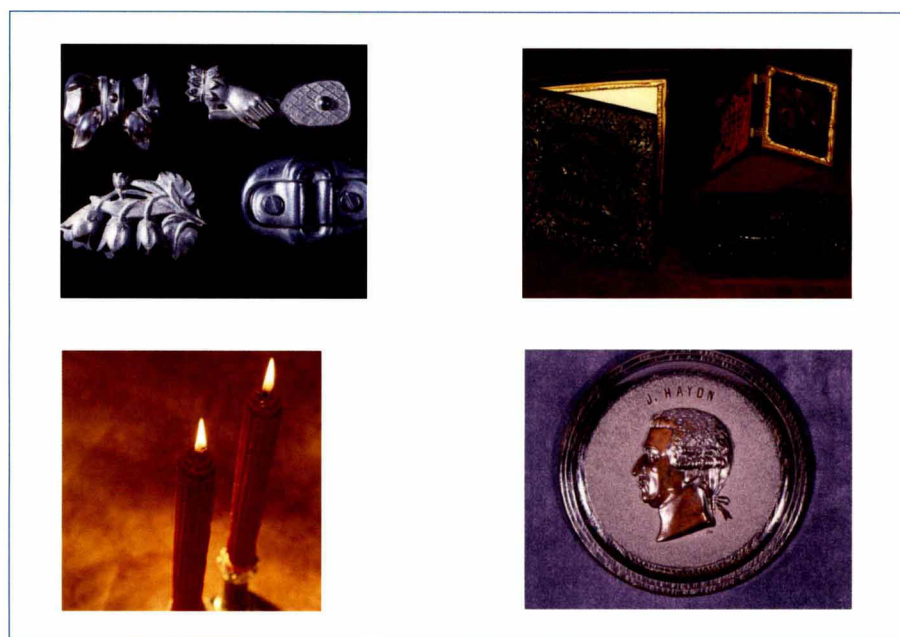


Figure 4 Clockwise from top left: horn brooches, shellac cases, Bois Durci plaque of the composer Haydn, beeswax candles

(Photographs courtesy of Smile Plastics Ltd and Photodisc.)

- Q3.** Bois durci was developed by a Frenchman, Francois Charles Lepage. Use a French dictionary to help you work out what 'bois durci' means. Hint: the word 'durci' comes from the verb durcir, which is linked to the word dur.

Modified polymers

As chemical understanding and techniques developed, it became possible to use chemistry to change the properties of natural polymers to tailor them to particular uses. One of the first examples was the vulcanisation of rubber which was discovered in about 1840 by Thomas Hancock in the UK and Charles Goodyear (who gave his name to the Goodyear tyre company) in the USA. Natural rubber is soft and sticky. Hancock and Goodyear found that heating it with sulfur made rubber much harder, but that it still retained its flexibility. The new material was much more useful for making articles such as soles for shoes. The more sulfur that was added, the harder the rubber became.

Adding 30% sulfur produced a hard, black material called 'Ebonite' or 'Vulcanite' which was used for making items such as combs, brooches and parts of pens. It was also used as an electrical insulator. Some examples are shown in Figure 5.



Figure 5 Vulcanite bracelets, vulcanite pipes. Vulcanite is also known as ebonite

- Q4. a) Find out about the Roman god Vulcan. Suggest why the above process is called 'Vulcanisation'.
- b) Find out about ebony, which is a type of wood. Suggest why the modified rubber polymer was sometimes called Ebonite.

Hancock and Goodyear's discoveries were made largely by trial and error. We now know that natural rubber is made up of long chain molecules rather like strands of cooked spaghetti. When natural rubber is stretched, these molecules can slide past one another and when the stretching stops, they stay in their new positions. Reaction with sulfur forms chemical links (called cross-links) between the chains so that they can no longer slide past each other, see Figure 6. If there are just a few of these links, the material tends to pull back to its original shape when stretched, making it elastic. More links make it impossible to stretch the material at all, and it is hard. So, depending on the number of cross-links, rubber can vary from a consistency like chewing gum, to an elastic material like a rubber band, to a hard and rigid material.

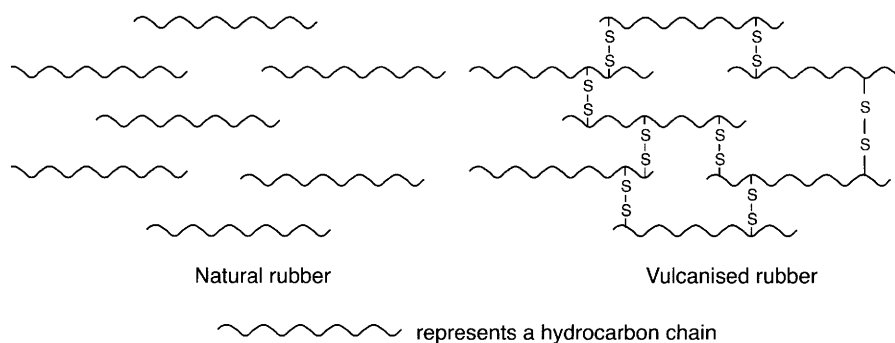


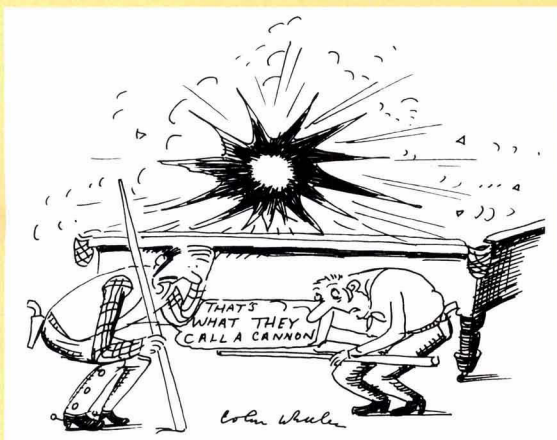
Figure 6 The vulcanisation of rubber

In the 1840s, the idea that substances were made up of small particles called atoms and molecules was new and few scientists really accepted it. Certainly the idea of long chain molecules was not accepted until about 100 years later following the work of a German chemist called Hermann Staudinger.

Great balls of fire!

Before synthetic plastics appeared on the scene, the only materials available were natural ones. This meant that quite ordinary objects had to be made from materials that we would now consider to be very expensive and inappropriate. For example billiard balls had to be made from ivory, one source of which is the tusks of elephants. Chemists then began to treat natural materials with chemicals to improve their properties. An example of this was the treatment of cellulose with nitric and sulfuric acids to form cellulose nitrate (a semi-synthetic polymer). One of the first uses of cellulose nitrate plastics was to make billiard balls.

- Q5. a)** Why would billiard balls made from ivory be expensive?
- b)** Why would many people nowadays consider that it would be inappropriate to make billiard balls from elephant ivory?
- c)** What manufacturing problem would have to be overcome when making billiard balls from ivory?



One problem with cellulose nitrate is that it is unstable and flammable. In fact chemically it is very similar to the explosive, guncotton. So it presented a significant fire risk. It has even been suggested that the energy of a collision between two balls on the table could set off a minor explosion. This has led to a story (probably apocryphal) dating from the late 1800s about a letter to a manufacturer of billiard balls from a saloon owner in Colorado, USA. This is supposed to have said that the saloon owner did not mind the explosions so much but that as soon as one occurred, every man in the saloon instantly pulled a gun! This, of course was the era of the American "wild west".

Fibres could also be made from cellulose nitrate. They were used as a substitute for silk called Chardonnet silk, after its inventor, Hilaire de Chardonnet. This material also suffered from flammability problems; a joke from the 1890s (which would nowadays be considered politically incorrect) suggested that the ideal present for a mother-in-law was a dress made from Chardonnet silk, and a match.

- Q6.** The elements that make up cellulose nitrate are carbon, hydrogen, oxygen and nitrogen. Suggest the products formed when cellulose nitrate burns in air.
- Q7.** Cellulose nitrate fibres can be ignited by touching them with a lighted match but billiard balls made of the same material cannot. Explain this.



Because cellulose nitrate is so flammable, chemists searched for a substitute. One approach was to react cellulose with other acids. One acid that (indirectly) produced a useful plastic was acetic acid (now called ethanoic acid). The resulting polymer is called cellulose acetate (cellulose ethanoate) and is still used in Rayon fabrics.

Synthetic polymers

The first completely synthetic polymer was Bakelite™, named after its inventor, the Belgian-born American chemist Leo Baekeland who first produced it in 1909. He made it by reacting two chemicals together, phenol (then obtained from coal) and methanal (then obtained from wood). These two chemicals both consist of small molecules that become linked together in the reaction. So Baekeland had actually made a polymer from scratch rather than changing one that had already been made naturally. In the case of Bakelite™ the molecules were linked not so much in chains, as in a network – chains held together by links between them. This meant that Bakelite™ could be moulded into shape before the chemical reaction started but, once made, there were so many links between the chains that it could not be softened by heat and re-moulded. This type of plastic, which can be moulded only once (when it is first made) and cannot then be re-moulded, is described as thermosetting.

Q8. Suggest some everyday uses that require a material that does not soften when it is heated.

Bakelite™ was used for a variety of objects such as ashtrays, the cases of radios and even coffins, see Figure 8. Similar polymers are still used for making electrical sockets, because they are good electrical insulators.



Figure 8 Objects made from Bakelite™

Synthetic thermoplastics

In the 1930s, some new types of synthetic plastic began to be made which had distinctly different properties to those of Bakelite and other thermosetting plastics. They soften (and can be moulded) when heated, and harden when cooled, a cycle which can be repeated over and over again. These plastics are described as thermosoftening or thermoplastic, which literally means 'heat mouldable'.

The first of these was polyvinyl chloride now called poly(chloroethene) by chemists but normally known by its initials, pvc. This polymer is made from the monomer vinyl chloride (chloroethene). The formula of chloroethene is C_2H_3Cl or $CH_2=CHCl$. The = sign means that there is a double bond between the two carbon atoms. This monomer can be made to link together in long chains, Figure 9.

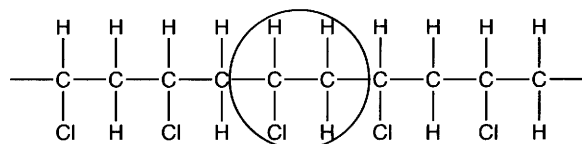


Figure 9 Part of the pvc molecule with the monomer unit ringed

The simplest formula (called the empirical formula) of the polymer is the same as that of the monomer – C_2H_3Cl . Nothing has been added or taken away, the monomers have just linked together. This type of polymer is called an addition polymer – the name stressing that the monomers have just added together.

There are now many addition polymers of this type known and used. Their monomers all have a carbon-carbon double bond and a general formula of $CH_2=CHX$, where X can stand for a variety of atoms or groups of atoms. For example in polythene (poly(ethene)), X is a H atom, in polypropylene (poly(propene)), X is a CH_3 group and in polystyrene (poly(phenylethene)), X is a ring of six carbon atoms, five of them with hydrogens attached.

A few years later, a different type of thermoplastic was developed. One of the first examples was the material now known as Nylon™, developed for the Du Pont company in the USA by a team led by the chemist Wallace Carothers. Nylon™, and other polymers of the same type are made from two different monomers, which we can call $H-X-H$ and $HO-Y-OH$ where X and Y represent chains of carbon and hydrogen atoms. When the monomers react together, an H from $H-X-H$ and an HO from $HO-Y-OH$ react together to form a molecule of water, HOH or H_2O , and X and Y are joined with a covalent bond, Figure 10.

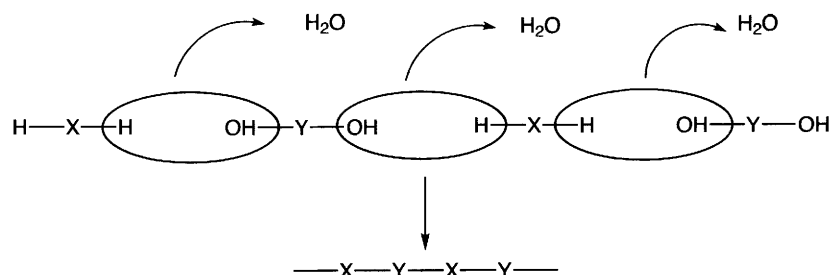
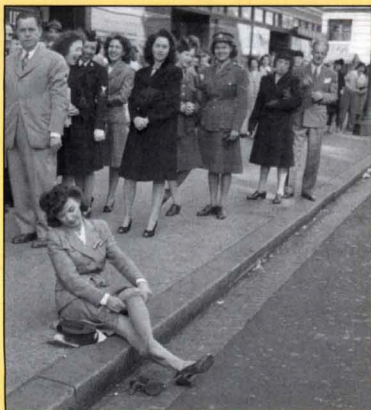


Figure 10 Making Nylon™

The technical name for two (or more) molecules joining together and eliminating a small molecule as they do so is 'condensation' so polymers like this are called condensation polymers. The molecule that is eliminated is often water but may be another small molecule such as hydrogen chloride (HCl).

What's in a name?

Nylon is a trade name rather than a proper chemical name. There have been many stories about the origin of the name – one of the most common being that it was derived from New York London, the two headquarters of the Du Pont company. The truth seems to be that it was simply a word dreamed up by Du Pont's advertising department and that the polymer could just as easily have been called Nulon. The word Nylon was thought to trip off the tongue easily and sounded a little like Rayon, which is the trade name for cellulose acetate and was also used to make clothing fibres.



Systematic chemical names are rarely used for plastics. This is because they are often too long for everyday use and too cumbersome to trip off the tongue. For example the systematic name of Terylene™ is poly(ethenediyl-1,4-benzenedicarboxylate)! Incidentally, although Terylene™ is a trade name, it does have a chemical history. The non-systematic name of one of the monomers from which Terylene™ is made is terephthalic acid (benzene-1,4-dicarboxylic acid).

Nylon™ was developed to replace silk for making stockings

Summary

We have seen three ways of classifying plastics:

1. Natural, modified (semi-synthetic) or synthetic describes the origin of the polymer.
2. Thermoplastic (thermosoftening) or thermosetting describes how the plastic reacts to heat.
3. Addition or condensation describes the type of chemical reaction used to make the polymer.

All three classifications can be used to describe a single material. For example rubber is a natural, thermoplastic, addition polymer. Bakelite is a synthetic, thermosetting, condensation polymer.

- Q9.** How would you describe Nylon™ in the same way that rubber and Bakelite are described above?

The decay and degradation of plastics

Although people often think that they last forever, plastics do decay over a period of time as chemical changes occur which affect their structures. Different plastics decay in different ways and at different rates, so it difficult to talk about the decay of plastics in general. However, most plastics have in common the fact that they are organic polymers based on long chains of carbon atoms linked by covalent bonds. There may be cross-links between these chains and there may also be side groups attached to the chains.

The factors that lead to decay of polymers are the same for most types of plastic. They include:

- light;
- oxygen from the atmosphere;
- moisture from the atmosphere;
- additives, such as fillers or plasticisers, from within the plastic itself; and
- mechanical stress, such as being stored under pressure.

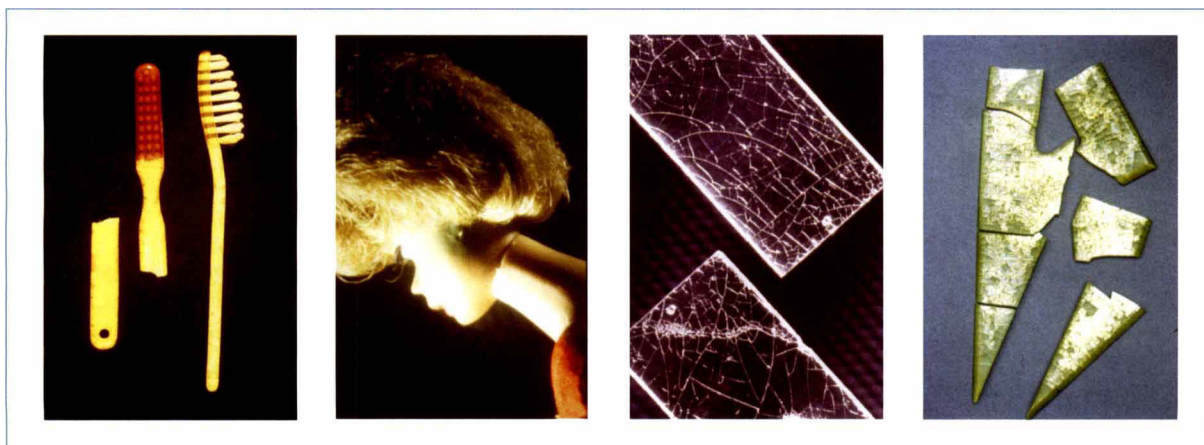


Figure 1 Decay of plastics: cellulose nitrate tooth brushes, a Barbie™ doll, Perspex labels, cellulose nitrate set square
(Pictures courtesy of Smile Plastics and the National Museum of Scotland.)

These lead to a number of general types of chemical change within the polymer molecules.

1. Shortening of the polymer chains
If bonds within the polymer chains are broken, a polymer with shorter chains can be formed. This will normally have properties that are less useful than those of the original polymer – solid polymers may start to crumble, for example.
2. Cross-linking of the polymer chains
Chemical changes that form new bonds between the existing polymer chains will normally lead to the polymer becoming less flexible and more brittle.

3. Chemical changes to the side groups in polymers

These can often lead to the release of small molecules such as water or acids. The loss of these changes the structure of the polymer. The released molecules themselves can often bring about further changes or, in some cases, catalyse the reaction that produced them in the first place.

The effect of light on polymers

Light can cause polymer chains to shorten (this involves bond-breaking) and can also make cross-links form between chains (this involves bond-making). You may find it difficult at first sight to see how the same factor can cause both these changes.

When light energy breaks a carbon-carbon bond, the bond breaks homolytically, that is, one of the two shared electrons in the bond goes to one of the carbon atoms and the other goes to the other carbon atom, so that each has an unpaired electron (shown in equations by •). This is because both carbons have exactly the same electronegativity (electron-attracting power). If a carbon-hydrogen bond is broken, the same thing happens because hydrogen and carbon have almost the same electronegativity. The two situations are shown in Figure 2.

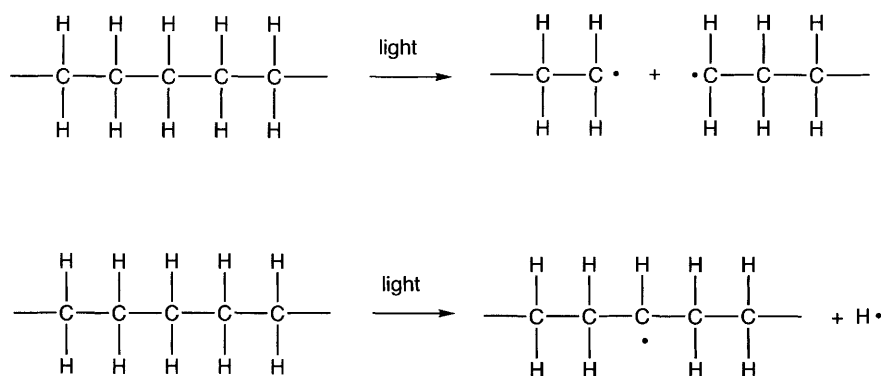


Figure 2 Bond-breaking caused by light

Species with unpaired electrons are highly reactive and are called radicals. They will react with almost anything to form a more stable species with paired electrons. Two radicals formed by breaking C-H bonds may come together and form a covalent carbon-carbon bond. This forms a cross-link between the chains, Figure 3. The radicals formed by the breaking of a C-C bond may react with some other species, possibly a hydrogen atom from elsewhere in the polymer. This will lead to two shorter chains, Figure 4.

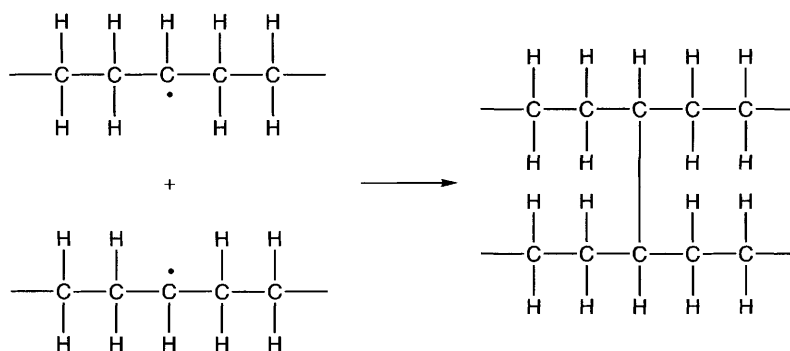
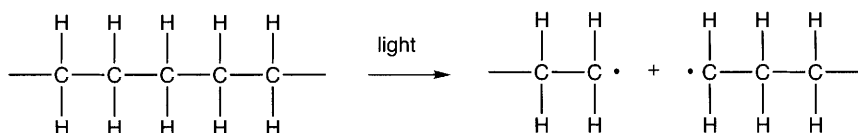


Figure 3 Two radicals may form a cross-link

Step 1



Step 2

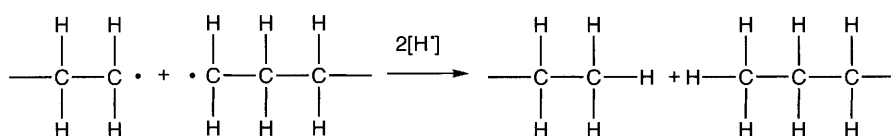


Figure 4 Chain shortening

- Q1.** Does visible light have enough energy to break chemical bonds? This question shows you how to find out. The bond energy of carbon-carbon single bonds is about 350 kJ mol^{-1} . A quantum of light energy (a photon) has an amount of energy, E , given by the equation $E = h\nu$, where h is Planck's constant, $6.6 \times 10^{-34} \text{ Js}$, and ν is the frequency of the light.
- What is the energy of C-C bonds in J mol^{-1} ?
 - What is this energy in J per bond? The Avogadro constant (the number of molecules in a mole) is 6×10^{23} .
 - Use $E = h\nu$, to find the frequency of light that has just sufficient energy to break a carbon-carbon bond.
 - Use a reference book or database to find in which region of the electromagnetic spectrum this light lies.
- Q2.** Explain why cross-links between polymer chains will lead to the material becoming less flexible. A diagram might help.
- Q3.**
- What happens to the rate of most chemical reactions as time goes on? Explain your answer.
 - What happens to the rate of a reaction in which one of the products is a catalyst for the reaction? Explain your answer. You may find that it helps to sketch graphs of concentration of reactant or product against time as part of your answer.

It is possible to add materials called stabilisers to some plastics to slow down their decay. However, many objects made of plastic are not designed to last for long and so it is often not cost-effective for manufacturers to use these.

- Q4.** Plastics can be used for:
A washing up bowl, disposable contact lenses, a carrier bag, the insulation on electric cables used for house wiring, a chocolate bar wrapper, a toy, a plastic hip joint, a car bumper.
- a) For each of the plastic items in the list, estimate how long they are designed to last. Select from:
- 'a few days';
 - 'a few weeks';
 - 'a few months';
 - 'a few years'; and
 - 'many years'.
- b) Explain your answer for the chocolate bar wrapper by describing what would happen if the material did not last long enough, and what would happen if it lasted too long.

We will look in a little more detail at how four common plastics decay.

Polyvinyl chloride, pvc (poly(chloroethene))

Like many plastics, pvc materials are made of more than just the polymer. The basic polymer is shown in Figure 5, but commercial materials have a number of additives.

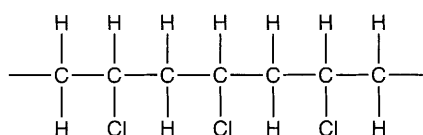


Figure 5 Part of a pvc molecule

These include plasticisers to increase the flexibility and stabilisers to help prevent the polymer degrading when it is moulded during manufacture and later. Plasticisers are small molecules that lie between the long chain polymer molecules and act like a lubricant, making it easier for the large molecules to slide past one another. Pvc plastics can be made with a wide range of flexibility. This is shown by the wide variety of objects that are made from pvc. This includes drainpipes, shoes, 'vinyl' records, hospital blood bags and hosepipes.

Stabilisers work in a variety of ways – some of them are molecules that react with the free radicals formed when ultraviolet light causes bond-breaking and prevent them causing further reaction.

- Q5.** a) What is done to pvc during manufacture to make it soft enough to be moulded?
- b) Why is this treatment likely to make it degrade?

The main long-term degradation reaction of pvc is the loss of hydrogen chloride, HCl. This is an acidic gas that dissolves in water to form hydrochloric acid. The loss of HCl can be brought about by ultraviolet light and/or high temperatures. It results in the formation of carbon-carbon double bonds in the polymer chain – one for each molecule of HCl lost, Figure 6.

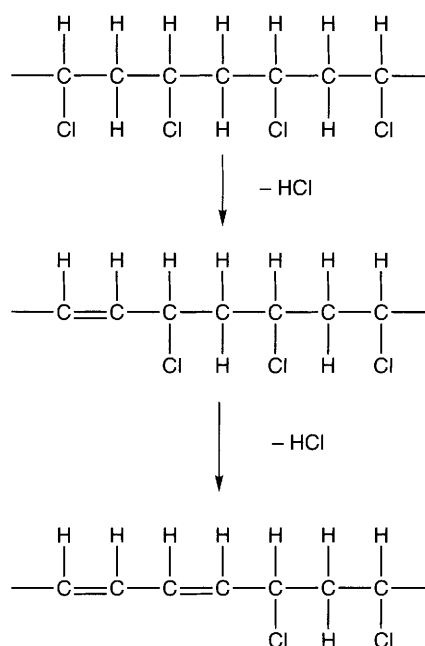


Figure 6 Loss of hydrogen chloride from pvc

- Q6. Classify the reaction by which pvc degrades as one of the following types: substitution, addition, oxidation, elimination, reduction.

The acidic hydrogen chloride acts as a catalyst for the degradation of pvc, so that once started it will tend to speed up. The polymer resulting from this reaction may have an arrangement of alternating double and single bonds, Figure 6. This is described as a conjugated system. Conjugated systems tend to absorb visible light, *ie* they are coloured. So one effect of this type of degradation is to make the polymer yellow and eventually darken in colour. The doll shown in Figure 7 shows the effect clearly. The head and hands of the doll, which have been exposed to light, have darkened while the body and legs, normally covered by clothes, have not.



Figure 7 The exposed parts of this doll have darkened in colour

- Q7. Since hydrochloric acid catalyses the degradation of pvc, suggest what sort of substance might be added to pvc to act as a stabiliser.

Did you know? The molecule β -carotene, Figure 8, is responsible for the orange colour of carrots and the pink of flamingos' feathers. It has a conjugated system of 11 alternating double and single bonds. It absorbs blue light and therefore reflects the red and yellow, so it looks orange.

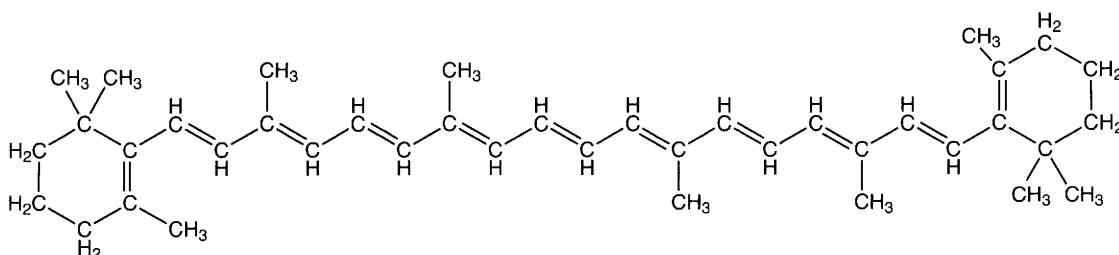


Figure 8 β -carotene

- Q8. a) Give a simple chemical test for a compound containing carbon-carbon double bonds. This test is usually carried out on a solution of the compound under test.
- b) Why might it be more difficult to carry out on a solid sample of plastic?
- c) Write an equation to explain the test and its result.
- Q9. Why might a pvc doll that was already degrading deteriorate more quickly if kept in a sealed case than if stored in a well-ventilated room?
- Q10. A museum conservator wished to display a pvc object in a glass case to prevent damage caused by the public handling it. She suggested that placing a small dish containing sodium carbonate in the case might help to prevent degradation of the plastic. Explain why this might help and give any chemical equation(s) relevant to the protection process.

Another way in which pvc objects degrade is by loss of plasticiser molecules. These molecules are often liquid esters. It is sometimes possible to see beads of plasticiser on the surface of pvc and this is called 'weeping'. Loss of plasticiser may make the plastic shrink and become more rigid, both of which may cause it to crack.

- Q11. Draw the functional group of an ester.

Polyurethanes

The polyurethanes are another versatile group of polymers. They contain the urethane group -NHCOO- that is formed by the reaction of an isocyanate (an -NCO group) with an alcohol. See Figure 9.

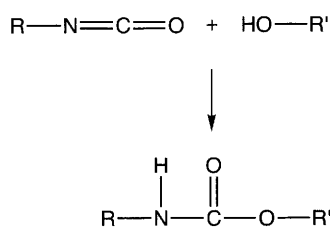


Figure 9 Formation of a urethane link

- Q12.** To form a polyurethane, two monomers are used, a diol and a di-isocyanate.
- Give an equation for this reaction using HO–R–OH to represent the diol and O=C=N–R'–N=C=O to represent the diisocyanate and showing at least two molecules of each monomer.
 - Explain why a diol and a diisocyanate are needed to make a polymer.
 - Suggest what might happen if a small amount of a triol were added to the reaction mixture.
 - What effect might this have on the property of the resulting polymer?
- Q13.** Isocyanic acid, H–N=C=O is the 'parent' of the isocyanates. Draw a dot-cross diagram to show the bonding in this molecule and predict its shape.

Polyurethanes can be made to have a wide variety of properties making them suitable for many uses – from foams for cavity wall insulation and furniture fillings to fibres such as Lycra used in swimwear. The differences are partly explained by differences in chain lengths of the R groups in the monomers.

Foams, such as the padding behind the dashboards of cars and the filling of cycling helmets are made by introducing a gas into the liquid polymer during manufacture before it sets. This produces a honeycomb-like structure of tiny bubbles looking rather like the inside of a Crunchie[®] bar.

Polyurethanes degrade by oxidation, which causes them to discolour and then weaken. This is a particular problem with polyurethane foams and less of a problem with polyurethane items that have been painted.

- Q14.** Explain why the information in the sentence above is consistent with the decay of polyurethane being caused by oxygen in the air.

Cellulose nitrate

This is one of the oldest synthetic plastics. In fact it is only partly synthetic. It is made by reacting a natural polymer, cellulose (a poly-sugar or polysaccharide found in wood and cotton) with nitric and sulfuric acids. Some of the –OH groups on the cellulose molecule are converted to nitro groups (–ONO₂), Figure 10. Cellulose nitrate is the plastic from which old movie films were made and its degradation is a cause of serious concern for film historians as original copies of classic films become unviewable.

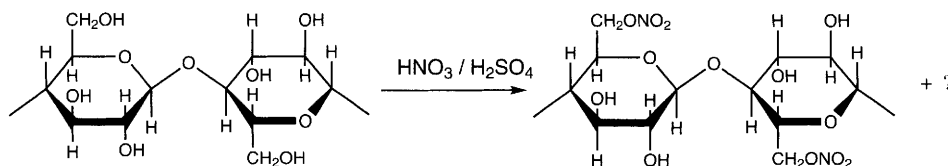


Figure 10 Formation of cellulose nitrate

- Q15.** Complete the equation above for the nitration of cellulose by working out what small molecule is eliminated, *ie* what does the question mark in the equation represent?

Changing the number of –OH groups per sugar molecule that are nitrated changes the properties of the final plastic.

Did you know? The nitration of cellulose has to be carefully controlled because the percentage of the –OH groups that are nitrated affects the properties of the polymer that is produced. This is about 11% in cellulose nitrate for plastics, and 12% for making film. Nitration of about 13% of the –OH groups produces the explosive guncotton.

Both light and moisture cause cellulose nitrate to decay by loss of the nitrate groups. The $-OH$ groups of the original cellulose re-form, and nitrogen oxides are given off. These react with oxygen and moisture in the air to form nitric acid. The acid has two effects. Firstly it acts as a catalyst for further loss of nitrate groups. Secondly it reacts with the main polymer chain, breaking it down into shorter chains and, ultimately, individual sugar molecules. The latter effect is similar to the acid-catalysed hydrolysis of starch, a molecule that is also a polysaccharide.

Interestingly, some cellulose nitrate objects contain zinc oxide used as a filler and as a white pigment. This method was often used to make imitation ivory. The zinc oxide reacts with any acidic degradation products of the polymer and thus prevents the two effects described above. It therefore acts a stabiliser as well as a filler and a pigment.

Q16. Write an equation for the reaction of zinc oxide with nitric acid.

Cellulose acetate (cellulose ethanoate)

This polymer, Figure 11, is related to cellulose nitrate. It is produced from cellulose by reaction with ethanoic anhydride (acetic anhydride). (Ethanoic anhydride is used rather than ethanoic acid because it reacts in the same way as the acid but more vigorously.) Cellulose acetate breaks down in a comparable way to cellulose nitrate, ultimately producing ethanoic acid in moist conditions. Ethanoic acid is a weak acid, but it acts on the polymer in a similar way to nitric acid.

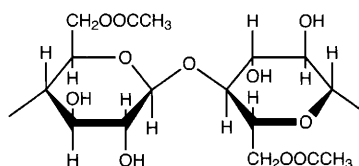


Figure 11 Cellulose acetate

- Q17.** A conservator might smell a cellulose acetate object that she suspected was beginning to degrade. What sort of smell would she be expecting? Explain your answer.
- Q18.** Ethanoic acid is a weak acid and will not react as readily with cellulose as will a solution of the same concentration of nitric acid, which is a strong acid.
- Explain carefully the difference between strong and weak acids.
 - Ethanoic anhydride is used as an alternative reagent to ethanoic acid for making cellulose acetate. It reacts more readily with the $-OH$ groups of cellulose than ethanoic acid but produces the same product. Suggest another alternative reagent with similar reactivity to ethanoic anhydride.

Other reactions of decay products

Except as an academic exercise, the decay of plastics cannot be considered in isolation. An object may not be made of just one plastic – it may contain two or more types of polymer and/or it may contain other materials such as metals. A doll is a good example. The body may be made of one polymer and the hair of another. It may have jointed limbs with metal hinges and it may be dressed in a variety of other materials. It may be stored in packaging made of yet another type of plastic. All these materials may interact with one another.

Did you know? Collectors of many objects that were sold in packaging usually like to collect the packaging too. Barbie™ dolls are now becoming collectors' items. They fetch much higher prices if they are still in the original packaging.

So, for example, acid decay products from a plastic may react with the metal parts of the joint, or vapours given off by one plastic may react with another plastic in the same museum display case. This clearly has implications for the storage and display of plastic objects and means that museum conservators need to be able to identify different types of plastic and to understand the chemistry of the decay processes that take place in these plastics. Without this knowledge, it would be easy to do more harm than good. 'Commonsense' might suggest that storing a plastic object in a sealed container might keep it from harm. However, if the object is made from, say, pvc, this would keep hydrogen chloride gas given off by the object in contact with it and thus catalyse further decay.

- Q1.** Suggest some ways in which the need to display a plastic object to the public might clash with the need to conserve it.

Despite the popular misconception that they last forever, plastics do decay and deteriorate. One complicating factor is that plastic is not a single material - there are about fifty basic types whose properties can be tailored in various ways to give many thousands of materials with different properties. Many of these tailoring methods involve adding other substances to the base polymer from which the plastic is made. This leads to many more possible chemical reactions by which the material might decay. The situation is further complicated by the fact that many objects will be made of more than one type of material (both plastic and non-plastic).

- Q2.** The main body of a Barbie™ doll is made from pvc. Suggest what other materials might be used in making the rest of the doll and its clothing. Try to suggest what material might be used for what part.



Figure 2 Barbie™ dolls

Identifying plastics

Some of the ways in which plastics decay are discussed in *The decay and degradation of plastics*. Before knowing how to care for a plastic object, it is essential to know as much as possible about what type of plastic it is made from and what additives (fillers, pigments, stabilisers etc) it contains. How this is done will vary depending on the circumstances and the type of object. For example, an individual collector will not have access to the same facilities for testing as will a national museum. Another issue is that some methods of testing require a sample of the material to be taken from the object (destructive testing) and some do not (non-destructive testing). The size of the required sample will vary from method to method. How acceptable this sampling is may depend on the size of sample required in relation to the size of the object.

Identifying a plastic is very much a case of detective work, with many techniques being used to give clues. Except for some instrumental techniques, it is rare that a single method will give a definitive answer. Often a particular method will rule out certain plastics rather than positively identify the actual material.

Outward appearance

Important clues can come from simply feeling or looking at the object, often with the aid of a magnifying glass. Many objects will have markings such as trademarks, patent numbers and registration marks, Figure 3. These may identify the manufacturer and give an idea of the date of the object. Collectors may then be able to check records and find out that a particular manufacturer made this type of object at that date out of a certain type of plastic. The date of manufacture can also be used to rule out certain plastics that had not then been developed or come into regular usage. For example Nylon did not come into use until about 1940, so objects reliably dated as being significantly older than this cannot be made of Nylon. Even an object without markings can be dated by its style and design – the Art Deco style, Figure 4, came in in the 1920s, for example. However, some care is needed – an Art Deco object could not have been made *before* the 1920s but it could be a newer imitation.



Figure 3 A manufacturer's mark on a plastic item



Figure 4 Objects in the Art Deco style

Colour, and transparency, can help to identify plastic types. Relatively few types of plastic can be made into wholly transparent mouldings and a number of types can only be opaque. Table 1 gives some general guidelines although they need to be used with care – the thickness of a sheet or moulding can affect transparency, for example as can colourants and fillers.

Transparent when moulded*	May be either transparent or opaque	Always opaque
Perspex™	Cellulose nitrate	Phenol-formaldehyde
Cast phenolic	Cellulose acetate	Urea-formaldehyde
Polyester	pvc	Vulcanised rubber
Polystyrene	Polypropylene	Bois durci
Polycarbonate	Polythene	Vulcanite
		Shellac

* Addition of pigments can make these appear opaque.

Table 1 Transparency and opacity of some plastics

Colour can also be helpful, if only in ruling out possibilities – phenol-formaldehyde is almost always in dark shades, for example. Surface finish may also give an indication of plastic type – for example, acrylics, polystyrene and cellulose esters can be highly polished, whereas the surface of polythene is much less glossy.

Finally the method of manufacture may help. It is often possible to determine the method by which a plastic object has been moulded from tell-tale markings. Certain plastics are made by only a limited range of techniques. So this can give clues as to what material an object might or might not be made from. For example, injection moulding involves forcing molten plastic under pressure into a mould. This leaves behind a small 'tail' of plastic, called a sprue, where the filling hole was. When this is removed, it leaves a small surface imperfection (see Figure 5).

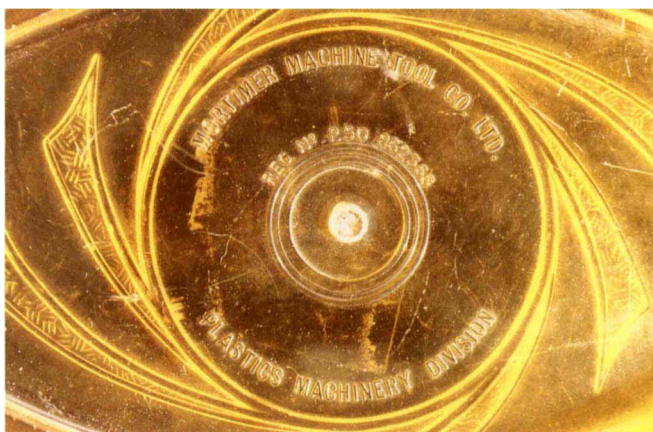


Figure 5 The injection moulding mark on a plastic object

Objects made from casein and from cellulose nitrate were never made by injection moulding so the appearance of this type of mark in a moulding would rule out these types of plastic.

Physical tests

Physical tests are ones in which no chemical change is involved. Two useful ones for helping to identify plastics are measurements of hardness and of density. Perhaps the simplest hardness test is to see if the plastic can be marked by thumbnail. Plastics that can be marked include: polythene, polypropylene, polyurethane, pvc (with plasticiser) rubber and gutta percha. This is clearly a 'low-tech' test that could be applied by a collector at an antique fair, say.

The density of a material is the mass of 1 cm³ of it. If the density of a plastic can be measured, it can be compared with the known densities of plastics given in reference books. Care is needed in interpretation as different additives can affect the density considerably.

- Q3.** Density is defined by the equation density = mass / volume. A plastic chess piece was weighed and found to have a mass of 7.0 g and a volume of 6.5 cm³.
- What is its density?
 - Which of the plastic types shown in the Table below might it be made from?

Plastic	Density / gcm ⁻³
Expanded polystyrene	0.02–0.06
Polypropylene	0.89–0.91
Low density polythene	0.91–0.93
High density polythene	0.94–0.96
Polystyrene	1.04–1.11
pvc	1.20–1.55
Polyethylene terephthalate	1.38–1.40

- Why is this method not reliable for making a positive identification of the plastic?
- Suggest a method of finding the volume of the chess piece.
- Some plastics are made into foams. An example is expanded polystyrene, used as a packing material. What effect will this have on the density of the plastic?

One of the simplest physical tests that can be carried out on plastics is measurement of melting or softening points. Plastics can be divided into thermosetting and thermoplastic (see *A brief history of plastics*). Thermosetting plastics, such as Bakelite, do not melt at all – when heated they remain solid until they begin to decompose chemically. Thermosoftening plastics, such as polythene, do melt, but rather than melting completely at a particular temperature, they tend to soften gradually over a range of temperatures. This is because a sample of polythene, say, is not a pure substance, but a mixture of many molecules with a range of chain lengths and therefore different melting points. The following plastics soften when placed in boiling water: pvc, polythene, polystyrene, cellulose nitrate, cellulose acetate, vulcanite.

Chemical tests

Traditional chemical tests tend to be destructive and are therefore not used by collectors unless it is possible to take a sample of the object without damaging it. The most used chemical test is to heat a small sample in a small test tube containing a piece of moist indicator paper, measure the pH of any fumes and note their smell. Tables 2 and 3 indicate the results found with some plastics. Some of the smells, of course, are difficult to recognise and describe unless they have been experienced before.

Safety note

Burning plastics and smelling any fumes produced can be dangerous. It should not be tried without the close supervision of a chemistry teacher.

Plastic	Smell
Casein	Burnt milk or hair
Cast phenolic	Phenol or carbolic soap
Cellulose acetate	Vinegar, burning paper
Cellulose nitrate	Camphor, then nitrogen oxides
Gutta percha	Burning rubber
Melamine formaldehyde	Fishy
Nylon™	Burnt hair, celery
Pet (Polyetheneterephthalate)	Burnt raspberry jam, sweet
Phenol-formaldehyde	Phenol or carbolic soap
Poly(methylmethacrylate) (Perspex™)	Sweetish, fruity
Polythene	Wax candles, paraffin
Polypropylene	Wax candles, paraffin
Polystyrene	Marigolds
Polyurethanes	Stinging
Pvc rigid	Hydrochloric acid, chlorine
Pvc plasticised	Hydrochloric acid + aromatic
Urea-formaldehyde	Formaldehyde (methanal), fishy, ammonia
Vulcanite	Burning sulfur/rubber

Table 2 Smells associated with burning plastics

pH 1-4 acidic	pH 5-7 neutral	pH above 8 alkaline
Cellulose acetate	Polythene	Nylons
Cellulose nitrate	Polystyrene	Phenol formaldehyde
Pet	Perspex™	Urea-/thiourea-formaldehyde
Polyurethane	Polycarbonate	Melamine-formaldehyde
Polyester	Silicones	
Pvc	Epoxies	
Vulcanised fibre		

Table 3 pH of vapours given off by heated plastics

- Q4. a) Suggest what acidic gases are given off on heating
- cellulose nitrate
 - cellulose acetate.

- b) Suggest why both polythene and polypropylene produce a smell of wax candles and paraffin when heated.
- c) The method for this test suggests gentle heating to avoid the samples burning. What gas are all the plastics likely to give off if they burn in a plentiful supply of air? Is this gas acidic or alkaline?
- d) What gas are they likely to give off if they burn in a limited supply of air?

Instrumental tests

These have a number of advantages over simple chemical and physical tests. They can often give more definite results that are easier to interpret and they normally require only a small sample – often no more than a few milligrams, the size of a printed full stop. In some cases, no sampling at all is required. However, the instruments themselves are expensive and require an experienced chemist to operate them and interpret the results.

Infrared (IR) spectrometry

This is probably the most useful single instrumental method for identifying plastics. It involves shining a beam of infrared (heat) radiation of a range of frequencies through a sample and onto a detector, Figure 6. Chemical bonds in the sample will absorb radiation at the exact frequencies at which they vibrate. So after the beam has passed through the sample, some frequencies will be missing – which ones will depend on the chemical bonds present in the sample. The results are presented as a graph of the intensity of the radiation detected after passing through the sample against the frequency of the radiation (often presented in wavenumbers in cm^{-1} (1 / the wavelength of the radiation in cm)). A dip in the graph (confusingly, this is usually referred to as a peak) shows that radiation has been absorbed at this particular frequency.

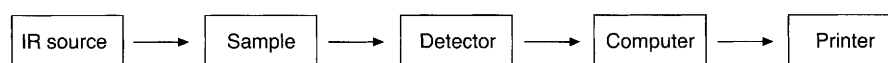


Figure 6 (a) Flow diagram of an infrared spectrometer



Figure 6 (b) An infrared spectroscopy instrument
(Picture reproduced by courtesy of Perkin Elmer.)

This technique allows the bonds present in the sample to be identified (for example the N–O bond present in, say, cellulose nitrate) absorbs infrared radiation of frequency approximately 1650 cm^{-1} . The infrared spectrum can also be used a ‘fingerprint’ to identify samples by matching – two samples with identical spectra are almost certain to be the same. Museums analysts are building up collections of IR spectra of known

samples of different plastics to be used as references to compare with the spectra of unknown samples. The use of this technique is shown in Figure 7. This shows the IR spectrum of a sample taken from a trinket box next to that of a known sample of cellulose nitrate. The similarity is obvious even without computer matching techniques. The third spectrum is that of a sample of tortoiseshell, another material from which the box might have been made judging by appearance alone. This spectrum is quite different. The absorption at about 1650 cm^{-1} represents the vibration of the N–O bond in the nitro group.

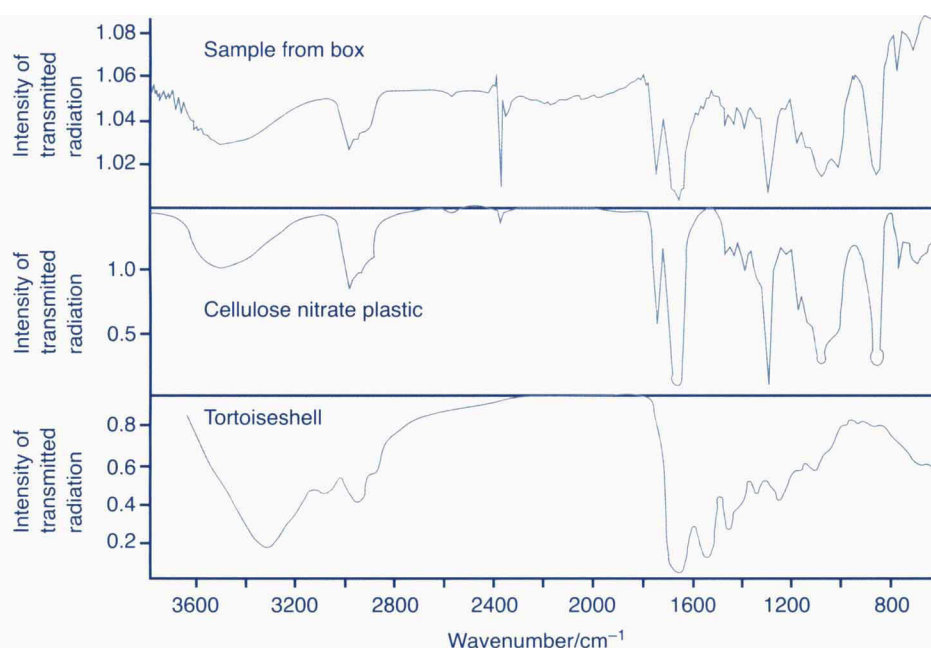


Figure 7(a) Identifying plastic by matching the infrared spectrum



Figure 7(b) The box from which the samples were taken

Gas Chromatography – Mass Spectrometry (GCMS)

This method is really two techniques in one. The gas chromatograph separates the different components in the plastic sample and the mass spectrometer helps to identify them. A solution of the sample in an organic solvent is made and it is injected into a column, a long, thin spiral tube of silica coated internally with an alkane. A stream of inert gas carries the sample through the column and the more volatile (easily vaporised) components are carried through more quickly than the rest. So the various components of the original plastic come out of the column separately. A chromatogram is produced showing how much of each component is present in the original mixture, see Figure 8.

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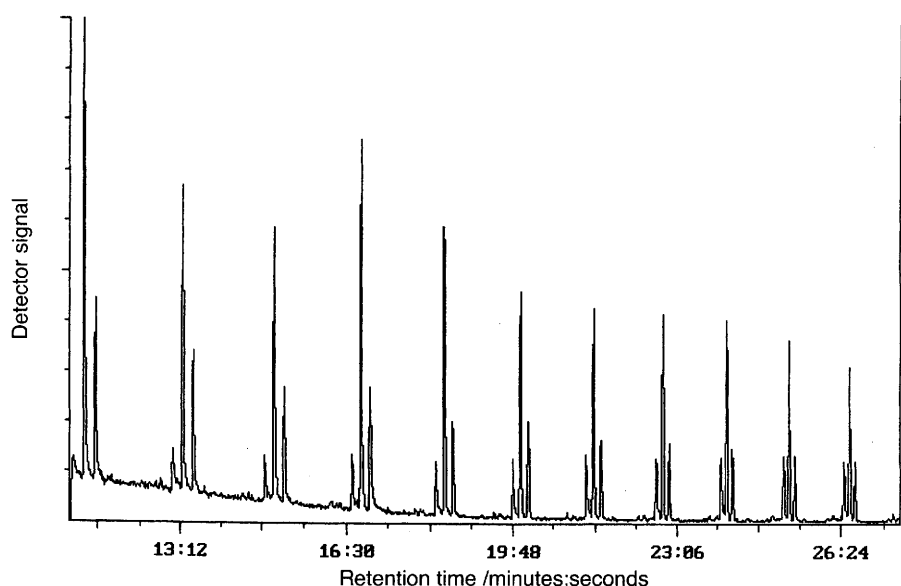


Figure 8 A gas chromatogram of poly(ethene) obtained by heating the plastic. Each trio of peaks represents components of different chain length

(Picture reproduced by courtesy of the Tate Gallery conservation department.)

As it comes off the column, each component is fed directly into a mass spectrometer. Here it is converted into positive ions, most commonly by bombardment in an electron beam. The extra energy given to these ions by the electron bombardment makes them break into fragments. Some of these are charged and fly through the spectrometer, accelerated by electric and magnetic fields. The end result is that the fragments are separated by mass. So each component of the original plastic produces a mass spectrum that can be used as a fingerprint to identify it, see Figure 9.

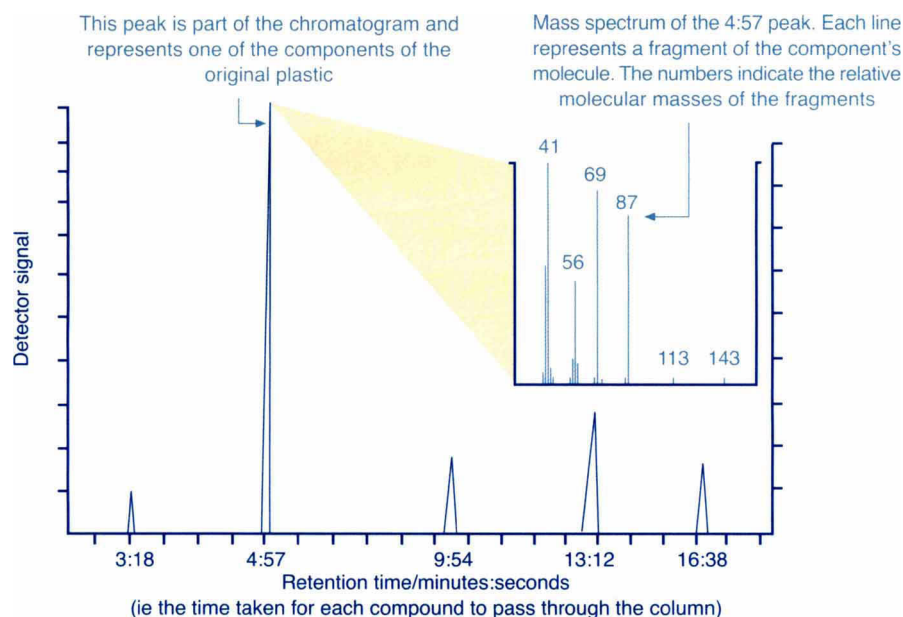


Figure 9 A typical result from GCMS on a sample of plastic

Other techniques

Chromatography

Other chromatographic techniques are used – these all work on the same basic principle of separating mixtures on the basis that some components are carried faster through a stationary medium than others.

X-ray diffraction

X-ray diffraction can be used to identify inorganic fillers in plastics. Here a beam of X-rays is fired at a sample and the resulting diffraction pattern is recorded on photographic film, see Figure 10. It is possible to work out from this pattern the actual positions of the atoms in the sample. However, for identifying materials in plastics, the diffraction patterns can simply be compared with those of known samples.



Figure 10 Example of a diffractogram pattern

(Reproduced by permission of the EPSRC National X-ray crystallography service.)

Electron microscopy

Scanning electron microscopy works by firing a beam of electrons at a sample and observing the scattered electrons. It can show the surface at magnifications much higher than optical microscopes. Energy dispersive X-ray spectroscopy is a development of this technique that can identify the elements present in a sample and their amounts. Some of the electrons in the beam have sufficient energy to knock out inner electrons from atoms in the sample. Electrons from outer shells drop into the inner shell to fill the gap and, in doing so, give out X-rays. The frequencies of these X-rays are different for different elements and so the elements in the sample can be identified. If the object to be examined is fairly small, sampling is not needed as the whole object can be fitted into the sample chamber of the instrument.

- Q5.**
- Draw diagrams to show (i) the electron arrangement of a magnesium atom (ii) the electron arrangement when an electron from the innermost shell has been removed (iii) an electron from an outer shell falling into the inner shell to fill the gap.
 - How many possibilities are there for the process of an electron from the outer shell falling into the inner shell to fill the gap to take place? Therefore, how many different frequencies of radiation could be expected?

More detailed information on these techniques can be found in B. Faust, *Modern Chemical Techniques* (1995) and R. Levinson, *More Modern Chemical Techniques* (2001), published by the Royal Society of Chemistry.

Case studies

The two cases that follow give some indication about how firstly a private collector, and secondly a museum might go about identifying what a plastic object could be made from.

The individual collector

A collector at an antique fair noticed an interesting amber-coloured decorative box. Simply by looking at its appearance and style and comparing it with similar objects she had seen before, she guessed that it was a trinket box dating from around 1900. This suggested that it was probably made from cellulose nitrate, as this substance was commonly used for making this type of article at that time. The colour supported this conclusion as cellulose nitrate can easily be coloured with pigments.

She picked up the box to look for any manufacturer's markings to confirm her conclusions but there were none. At the same time, she noticed that the box felt heavier than she would have expected if it were made of cellulose nitrate and also that it had moulding lines indicating that it was certainly moulded, and not carved from a natural material.

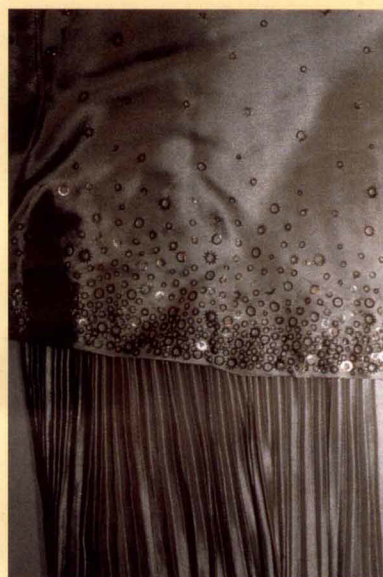
Slightly puzzled, she rubbed the box vigorously with her handkerchief to warm its surface. Sniffing gently, she noticed a faint odour similar to carbolic soap or TCP antiseptic. This was phenol, which strongly suggested that the box was made from a phenol-formaldehyde plastic such as Bakelite™. This would explain its heaviness. A quick scratch with her thumb left no mark. This is what would be expected for Bakelite™. Perhaps the box was a later copy of a turn-of-the-century piece?

The box was certainly a puzzle but she decided that any further tests to identify the plastic would require a sample to be taken, which the seller was unlikely to agree to, so scratching her head she moved on to the next stall.

A museum

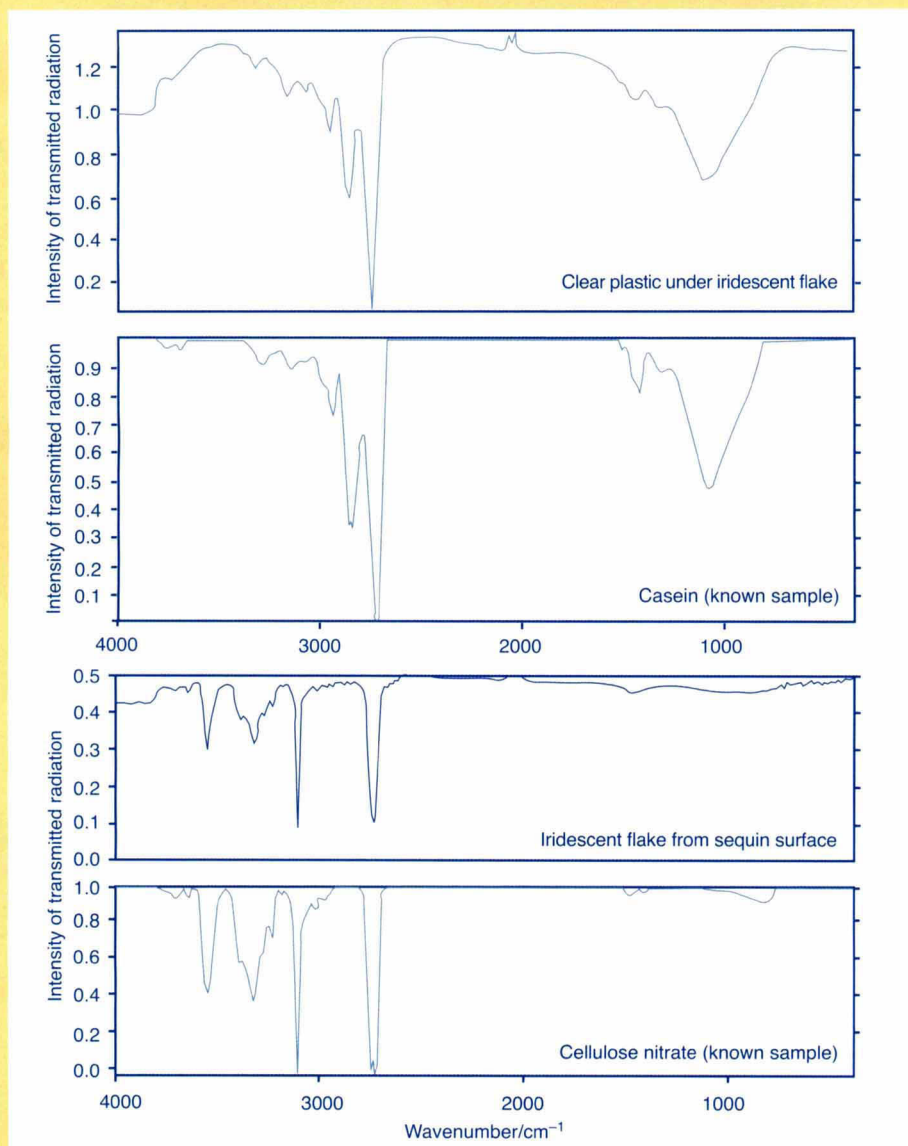
One special dress in the National Museums of Scotland collections was created by couturier Norman Hartnell, who has designed for Her Majesty Queen Elizabeth II. This finely pleated, sequin-covered, silky, low-cut dress was made in 1938-39, but a recent conservation examination found that some sequins were disintegrating.

Box continued...



The Norman Hartnell dress with detail showing sequins

Samples, the size of printed full-stops, were analysed in the museum by infrared spectrometry to identify what the sequins were made from and therefore possible causes for the deterioration. Analysis revealed that the iridescent bronze-coloured sequins were composed of two man-made plastics: cellulose nitrate applied as a thin layer over casein, a plastic derived from milk protein. The identification was done by running the spectra of the samples and matching them with a computer database of spectra of known plastics.



Deterioration could now be explained – these two plastics are incompatible because they behave differently towards moisture. Cellulose nitrate is moisture-sensitive and so it should be stored and displayed in a low-humidity environment. However casein benefits from more humid environments to prevent it from dehydrating and cracking. Inappropriate storage conditions used in the past have caused the two layers to separate as the different plastics contracted or expanded by different amounts. Because the best conditions for each plastic are different, the best compromise has been to maintain stable, average relative humidity (50%) at 20 °C with regular checks on the sequins to see if they continue to deteriorate or, hopefully, stabilise.

Caring for plastics

Here again there may be a difference in requirements between the private collector and a museum. Many private collectors will want objects in their collections to look as new, while museums will often be more concerned to preserve the object from long term damage or deterioration. The difference is often that between so-called passive and active conservation. Passive conservation concentrates on finding conditions for storage and / or display that minimise deterioration while active conservation involves cleaning, repair and restoration.

Passive conservation

We have seen that it is not always easy to identify plastic materials with certainty. This is especially true of modern materials that often contain a complex blend of additives (pigments, fillers, stabilisers, plasticisers *etc*) as well as the basic polymer. Fortunately, many passive conservation measures are applicable to most types of plastic. These include storage at low temperature, away from high levels of light (especially ultraviolet light, present in daylight) and moisture and, for some materials, in the absence of oxygen.

All chemical reactions go more slowly at low temperatures so low temperature storage will slow down all decay reactions. A rough rule of thumb applicable to many reactions is that a temperature drop of 10 °C will halve the reaction rate. Refrigerated storage is not likely to be practical for the private collector and would also create difficulties for items on display. However some archives of cine film, made from cellulose nitrate, which is particularly prone to decompose, are stored at low temperatures.

Q6. How will storing an object at 5 °C (roughly the temperature inside a fridge) rather than at 25 °C (the temperature of a warm room) affect the lifetime of a plastic object?

Q7. Reaction rates are governed by the Arrhenius equation

$$k = Ae^{-E_a/RT}$$

where k is the rate constant and is proportional to the reaction rate, A is a constant, E_a is the activation energy for the reaction, R is the gas constant, $8.3 \text{ JK}^{-1} \text{ mol}^{-1}$, and T the temperature in kelvin. The expression $e^{-E_a/RT}$ gives the fraction of molecules that have enough energy to react at that temperature T .

- The activation energy for a typical reaction is about 50 kJmol^{-1} . Using this value of E_a , calculate a value of $e^{-E_a/RT}$ at 25 °C. Remember to convert the temperature to kelvin first and also to convert kJmol^{-1} to Jmol^{-1} . You will need to use the e^x button on your calculator.
- Now repeat the calculation for a temperature of 15 °C (10 °C lower).
- How do the two fractions compare?
- Does this explain the rule of thumb given above?

Storage away from light will help to prevent free radical reactions caused by ultraviolet light breaking bonds in the plastic, see *The decay and degradation of plastics*. Glass absorbs ultraviolet light to some extent, so both window glass and the glass of a display case will help to reduce UV. It is also possible to use special types of glass or film coatings that absorb ultraviolet better than normal glass. Objects in storage can easily be kept in the dark, but this is clearly not possible for items on display. However, you may have noticed that many museum galleries do have subdued lighting (as well as being kept cool).

A number of plastics decay by oxidation – polyurethane is one example discussed in *The decay and degradation of plastics*. The obvious solution to this problem would seem to be to display items in a sealed environment filled with an unreactive gas such as nitrogen or one of the inert gases. However the need for 100% effective sealing makes this impractical. Moreover, a number of plastics give off acidic gases when they decay and these would tend to build up in a sealed environment. In some cases, such as those of cellulose nitrate and cellulose acetate, these gases can catalyse further reaction and may also affect other materials in the same case. So sealed cases are generally avoided. The effect of storing a cellulose nitrate object in a sealed bag is shown in Figure 11.



Figure 11 The part of this cellulose nitrate fan that has been kept in a sealed bag has clearly deteriorated more than the exposed part

One solution is to use a scavenger, a chemical that reacts with the substance we want to get rid of – in this case oxygen. Some museums use a commercial product called 'Ageless'[®], originally developed for prolonging the shelf life of foods, which also decay by oxidation. Ageless[®] contains finely powdered iron that reacts with oxygen and can reduce the concentration of oxygen to as low as 0.01%.

- Q8.**
- Why is powdered iron used in Ageless[®]?
 - Write a word and a balanced symbol equation for the reaction of iron with oxygen assuming that the product is iron(III) oxide.
 - Use the equation to calculate how much iron would be needed to remove all the oxygen from the air contained in a sealed display case 1 m x 0.5 m x 0.5 m. State what assumption you are making in your calculation.

The case of moisture is not quite so straightforward. In some cases of polymer degradation, water acts as a reactant – the decay of cellulose acetate and cellulose nitrate are examples. So storage in dry conditions makes sense. In other cases, such as casein and some polyesters, which are described as hygroscopic, the plastic itself absorbs water from the atmosphere. If this type of plastic is stored in too dry an atmosphere, it can lose water and begin to crack. The conservator must select and maintain the most suitable water vapour content for the storage atmosphere. The water vapour content of the atmosphere is called the relative humidity – it is the ratio, expressed as a percentage, of the amount of moisture in a sample of air to the maximum amount of moisture that air can hold at that temperature. A relative humidity of between 30% and 50% is recommended for storing most plastics, rising to 60% for hygroscopic ones. Controlling humidity can cause a conflict. We have seen that plastics are best stored in a well-ventilated place to prevent build-up of acidic gases. However, changing the air will make it difficult to keep the humidity constant.

Silica gel is often used to remove excess moisture from the atmosphere. This is a material based on sodium silicate that has many pores throughout its structure in which water molecules can be trapped. When it becomes saturated with water, it can



be regenerated by being heated in an oven. A cobalt salt-based indicator is often added, this turns from blue to pink when the gel can absorb no more water.