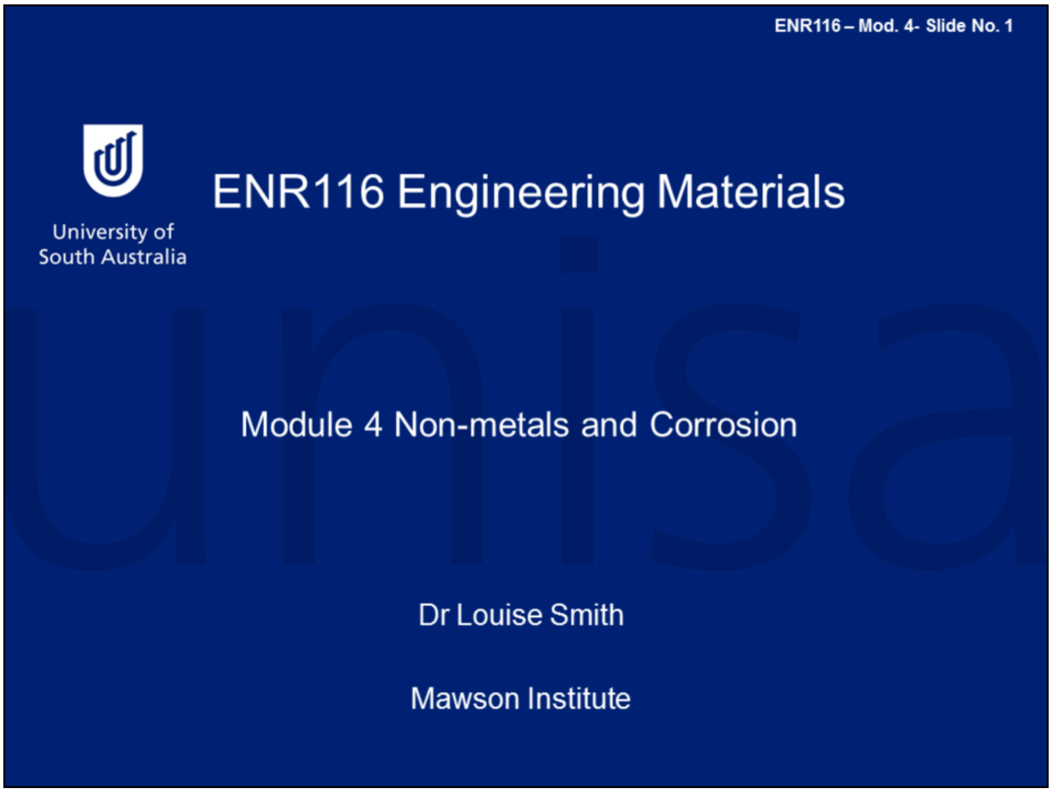

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ENR116 Engineering Materials

Module 4 Non-metals and Corrosion

Dr Louise Smith

Mawson Institute

Welcome to Module # and *name* of *Unit name*

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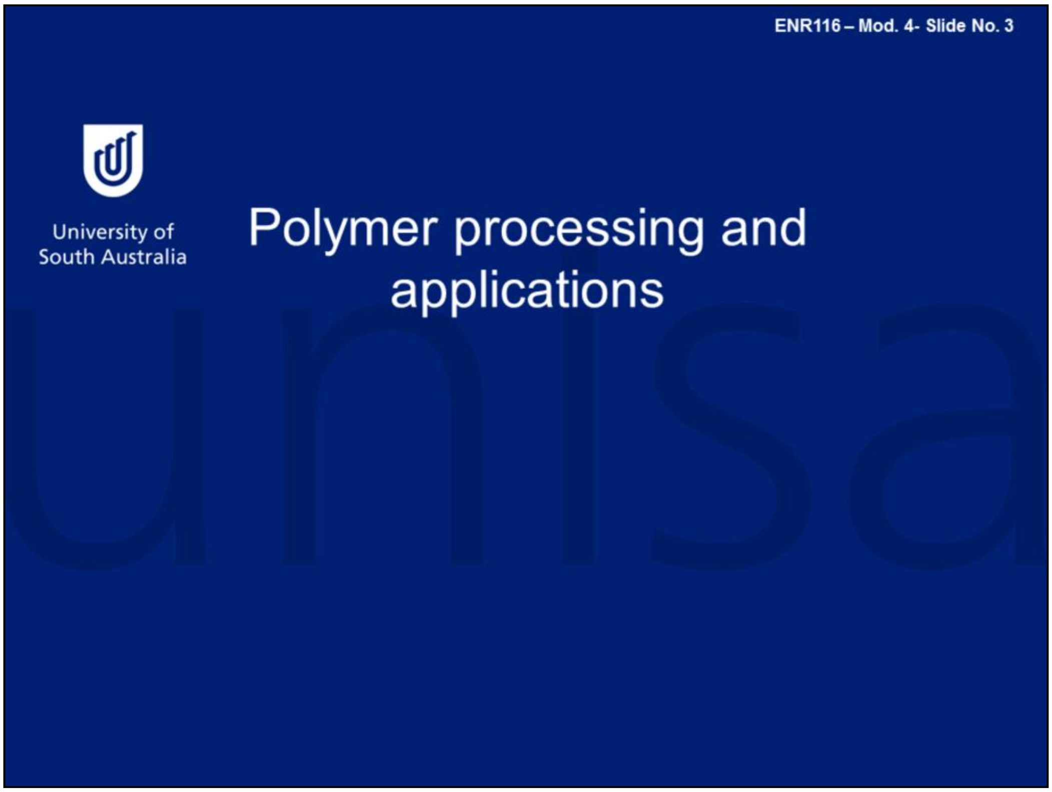

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Polymer processing and applications

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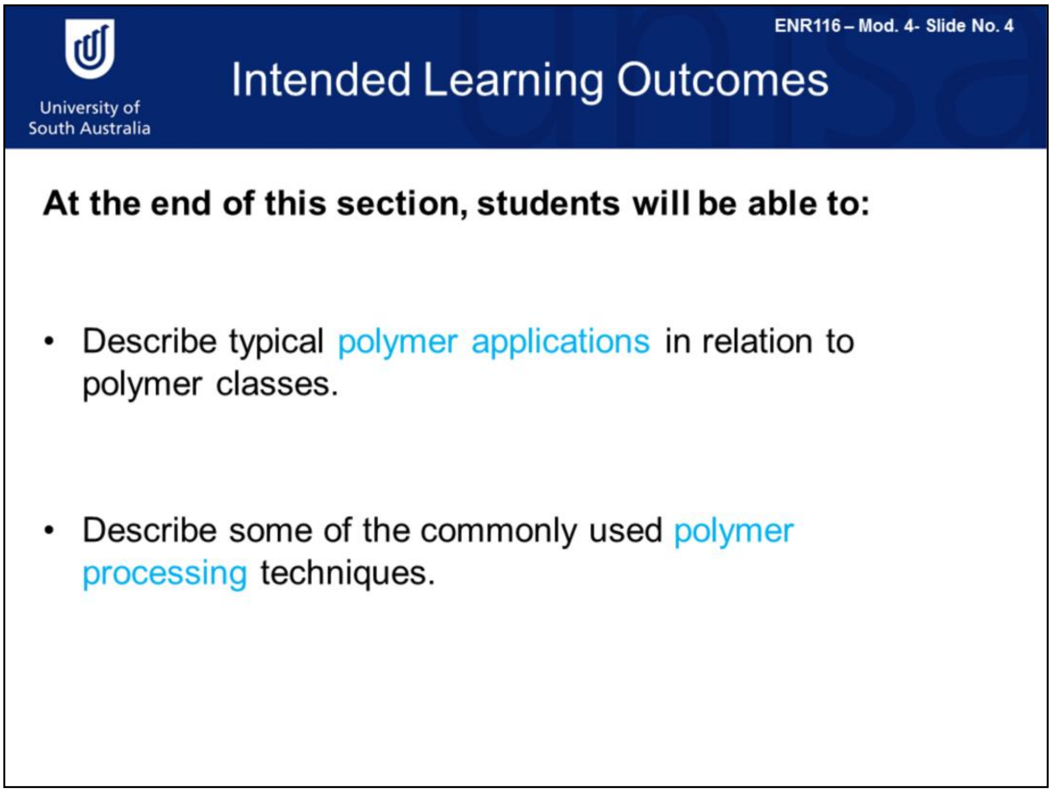

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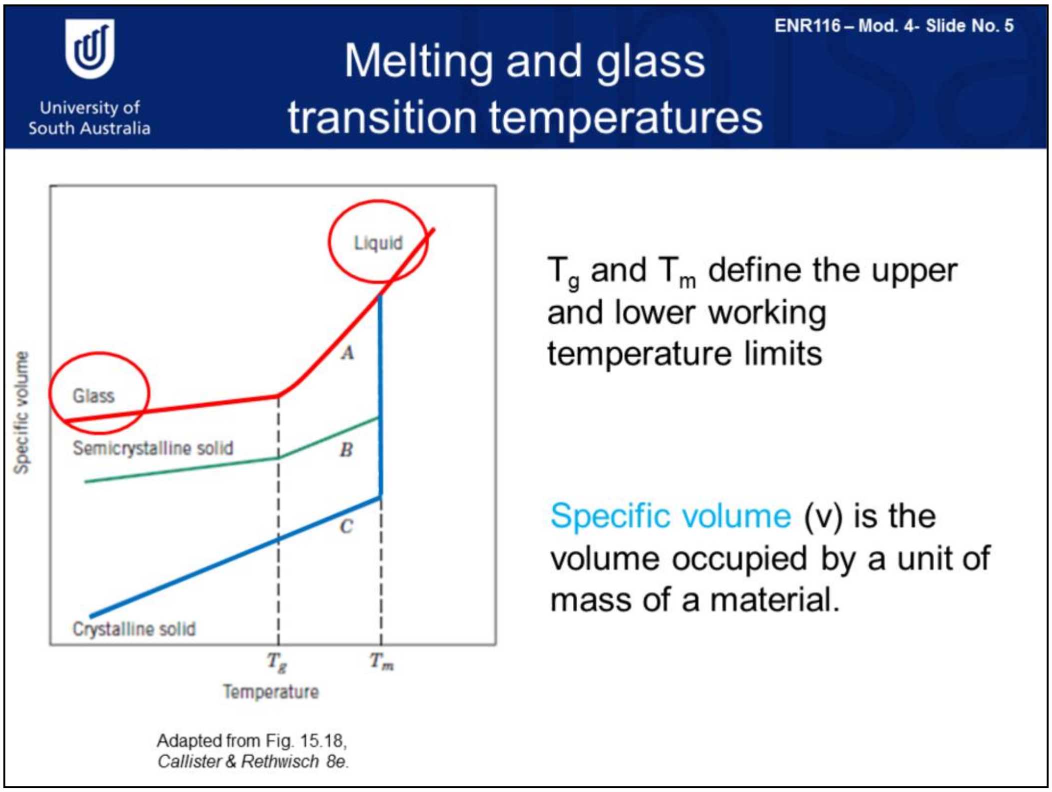
Intended Learning Outcomes

At the end of this section, students will be able to:

- Describe typical polymer applications in relation to polymer classes.
- Describe some of the commonly used polymer processing techniques.

By the end of this lecture summary, you should be able to describe typical polymer applications in relation to the different polymer classes, and also, some of the commonly used polymer processing techniques.



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Melting and glass transition temperatures

Adapted from Fig. 15.18, *Callister & Rethwisch 8e.*

T_g and T_m define the upper and lower working temperature limits

Specific volume (v) is the volume occupied by a unit of mass of a material.

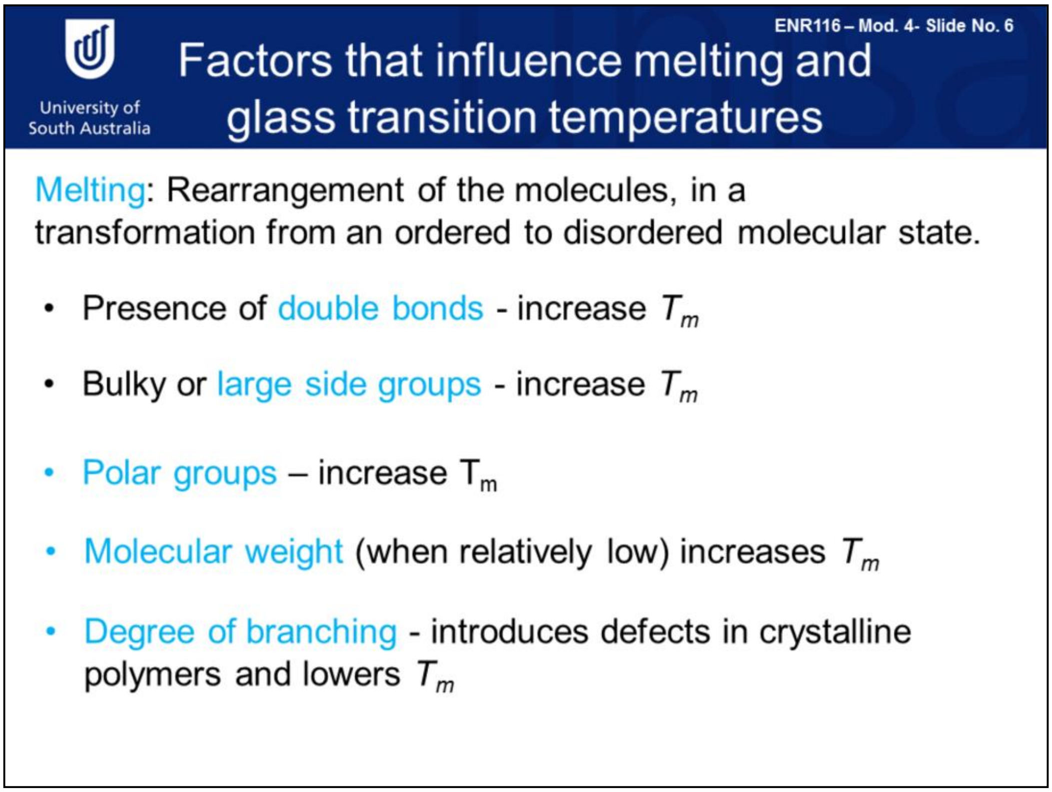
There are three important processes that important when it comes to the design and processing of polymer materials. These are crystallisation, melting and the glass transition. We covered polymer crystallinity in the previous lecture summary. Melting is a familiar phenomenon, and covers the transition from an ordered solid material to a liquid, within which the structure is highly random. The transition occurs at the melting temperature, Tm.

The glass transition temperature describes the temperature at which, upon cooling, a non crystalline polymer transforms from a super cooled liquid to a rigid glass. So, above the glass transition temperature, an amorphous polymer will generally exist as a viscous liquid. However, below the glass transition the material will be solid, hard and brittle yet still lack long-range molecular order. We call this kind of solid an amorphous solid, or a glass.

Together the melting temperature and the glass transition temperature dictate the upper and lower working limits of the polymer, and therefore the kind of applications they can be used in.

On your screen you can see a plot of specific volume – 1 over density – vs temperature for three different kinds of polymer. These plots are used to determine the glass transition and melting temperatures for a system. The blue data, here is for a totally crystalline system. .The specific volume – increases in a linear fashion up to the melting temperature, then sharply rises. Compare this to the amorphous system, in red, where the specific volume increases in one continuous curve, with just distinct change in gradient at the glass transition point, Tg. The semicrystalline solid, the green line, is intermediate to the two extremes.

If you find the concept of specific volume, or 1 over density difficult, it may help to think of it as the volume occupied by a unit mass of a material.



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Factors that influence melting and glass transition temperatures

Melting: Rearrangement of the molecules, in a transformation from an ordered to disordered molecular state.

- Presence of double bonds - increase T_m
- Bulky or large side groups - increase T_m
- Polar groups – increase T_m
- Molecular weight (when relatively low) increases T_m
- Degree of branching - introduces defects in crystalline polymers and lowers T_m

Both the solid to liquid transition, and the transition from liquid to glass rely on the motion and rearrangement of molecules. Therefore, the values of both temperatures depend strongly on the nature of the polymer chains, and their ability to move freely.

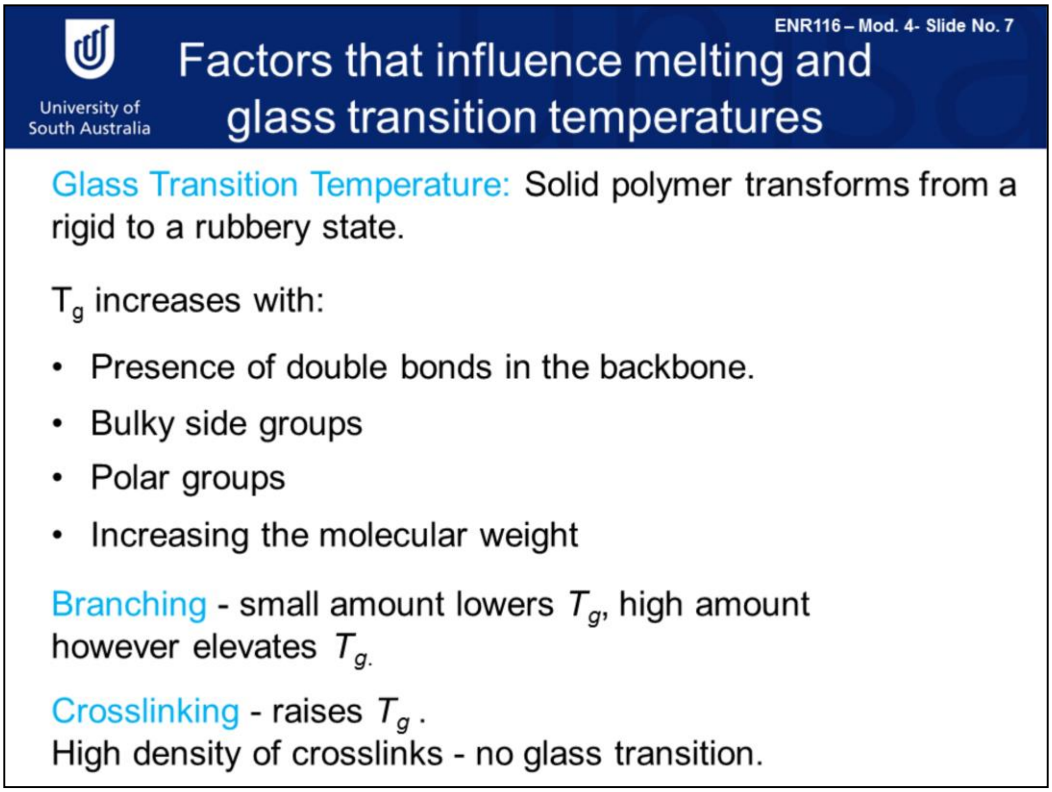
In the case of melting, the molecules rearrange from a highly ordered, organised array to a disordered state.

The presence of double bonds restricts rotation around the bonds in the chain, and therefore increases the melting temperature. Likewise, large, bulky side groups such as aromatic rings will also hinder rotation, and consequently increase Tm.

A lesser, but still significant influence comes from the presence of polar functional groups such as OH or halogen groups. These increase the strength of the intermolecular bonds between the chains, and therefore drive up the melting temperature.

The melting temperature is also a function of molecular weight. At relatively low molecular weights, an increase in mass will push up the melting temperature.

Finally, the introduction of side branches into a polymer introduces defects into crystalline materials and subsequently lowers T_m.



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Factors that influence melting and glass transition temperatures

Glass Transition Temperature: Solid polymer transforms from a rigid to a rubbery state.

T_g increases with:

- Presence of double bonds in the backbone.
- Bulky side groups
- Polar groups
- Increasing the molecular weight

Branching - small amount lowers T_g, high amount however elevates T_g.

Crosslinking - raises T_g .
High density of crosslinks - no glass transition.

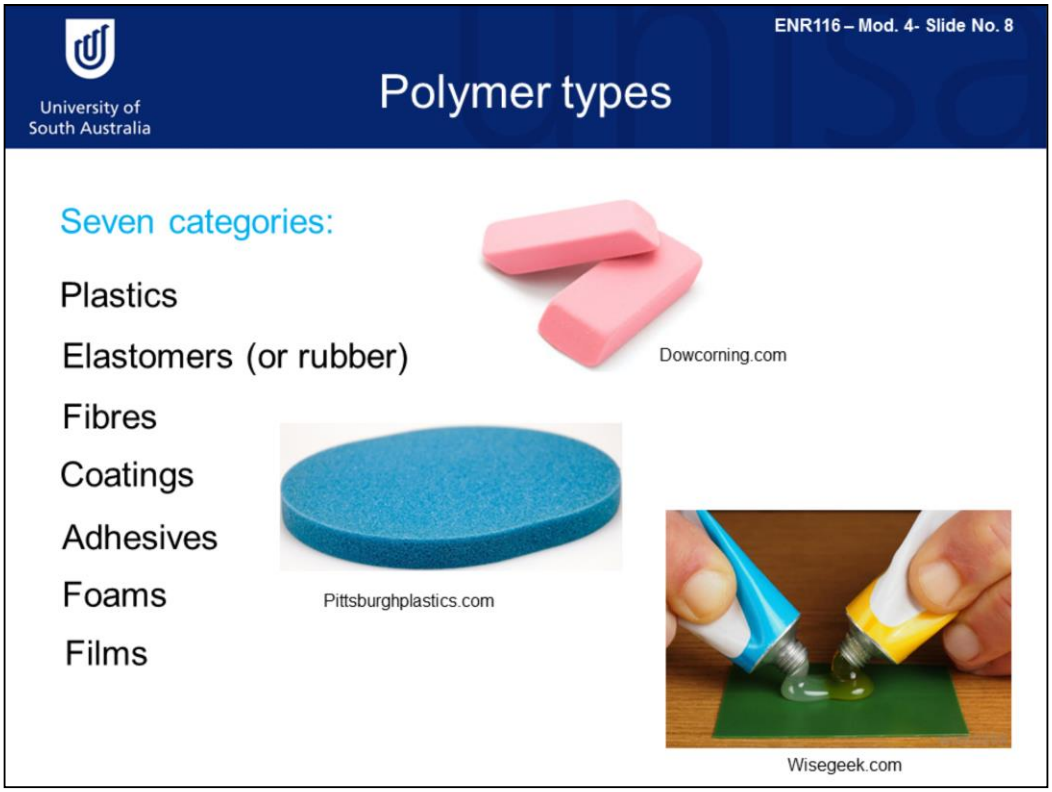
Lets now consider the factors that influence the glass transition temperature. When we heat through the glass transition, an amorphous – glassy – solid transforms into a rubbery state, and subsequently a viscous liquid. As with the case of melting, this transformation relies on free movement and rotation of the polymer chains – if we introduce factors that restrict motion of the chains, we will increase the temperature at which the transition occurs.

The list of features that increase the glass transition temperature is much the same as that for increasing the melting temperature:

Introducing double bonds into the backbone, or large or bulky side groups pushes up the Tg; as does the presence of polar groups.

Increasing the molecular weight will also tend to increase the glass transition temperature.

The influence of branching on the glass transition is slightly complicated. A low degree of branching will lower Tg, however, as the density of branching increases, mobility of the chains is hindered and Tg will start to increases. Crosslinking the chains will always raise the glass transition temperature and in fact, a very high degree of crosslinking may prevent the transition from occurring at all.



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Polymer types

Seven categories:

Plastics

Elastomers (or rubber)

Fibres

Coatings

Adhesives

Foams

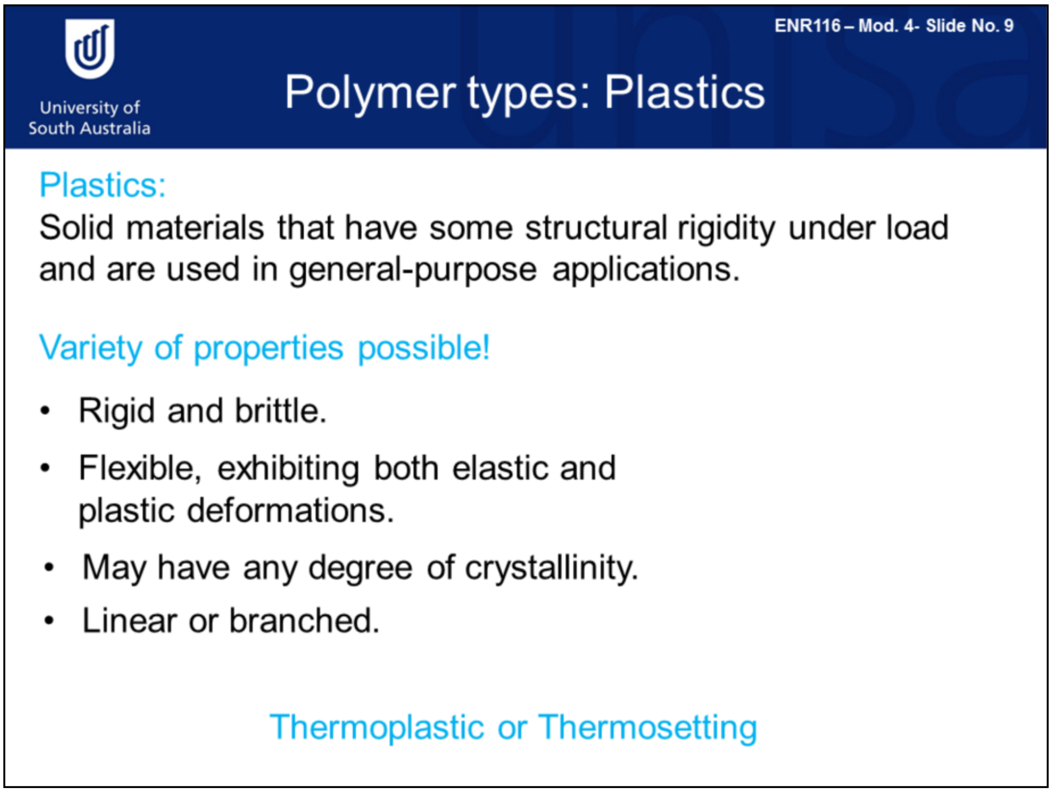
Films

Dowcorning.com

Pittsburghplastics.com

Wisegeek.com

Polymers can be classified in a number of different ways. For this course, we’re going to group polymers based on their end use, with is in good agreement with the method used in your course textbook. Under this scheme we have seven categories of polymer: plastics, elastomers (or rubbers), fibres, coatings, adhesives, foams and films. Depending on its specific properties, a polymer may fall into more than one of these application categories.



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Polymer types: Plastics

Plastics:
Solid materials that have some structural rigidity under load and are used in general-purpose applications.

Variety of properties possible!

- Rigid and brittle.
- Flexible, exhibiting both elastic and plastic deformations.
- May have any degree of crystallinity.
- Linear or branched.

Thermoplastic or Thermosetting

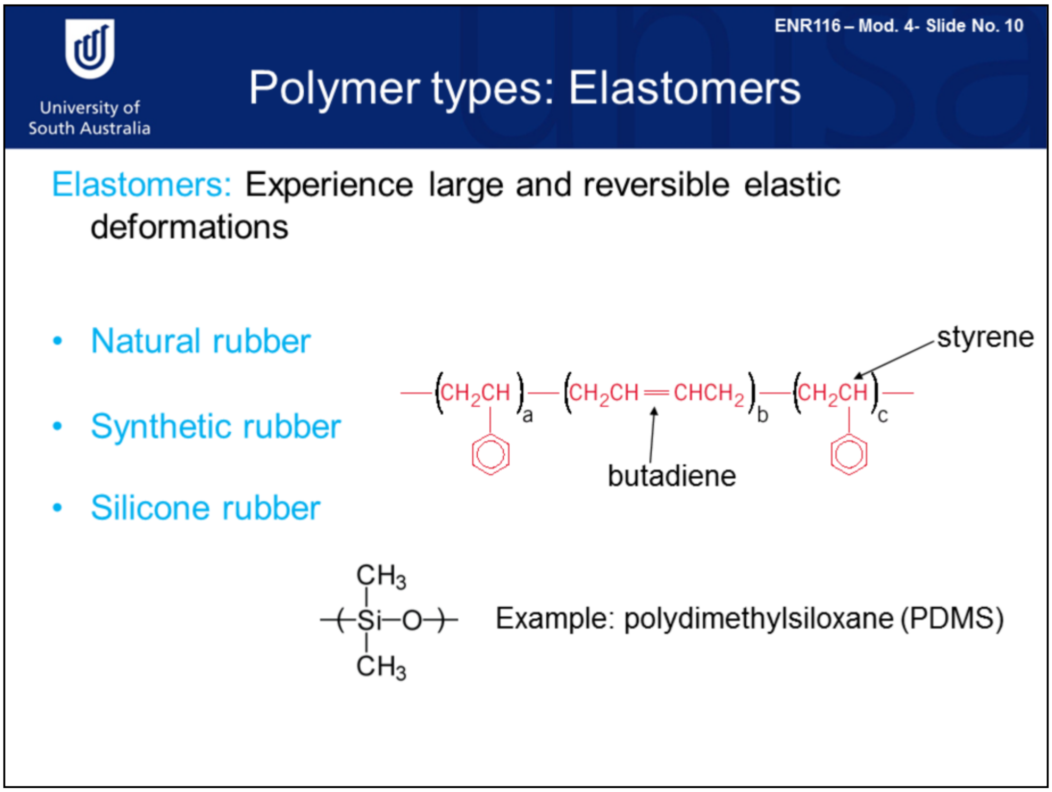
We'll start with plastics. Plastics form the largest group of polymers, and are probably the most well known. Formally, we define a plastic as being a solid, organic polymer of high molecular weight, that has some structural rigidity under load and is used in a general purpose application.

This rather broad definition means that plastics can have any of a variety of properties. Some are rigid and brittle, whilst others are very flexible and capable of experiencing considerable plastic deformation prior to fracture.

Plastics can have any degree of crystallinity, and may be linear, branched, cross linked or networked.

Plastic materials are usually sub classified as one of two types, thermosetting or thermoplastic. We have come across both of these terms in a previous summary, but to recap, thermoplastics will melt upon heating, and harden again upon cooling. They tend to be linear or branched polymers. In contrast, thermosetting plastics will not soften or melt when heated. This is a consequence of their highly crosslinked and networked structure.

Finally, ‘plastics’ is one of those names that is often used incorrectly. Its probably safe to say that all plastics are polymers, but not all polymers are plastics! When dealing with engineering materials, the distinction is important.



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Polymer types: Elastomers

Elastomers: Experience large and reversible elastic deformations

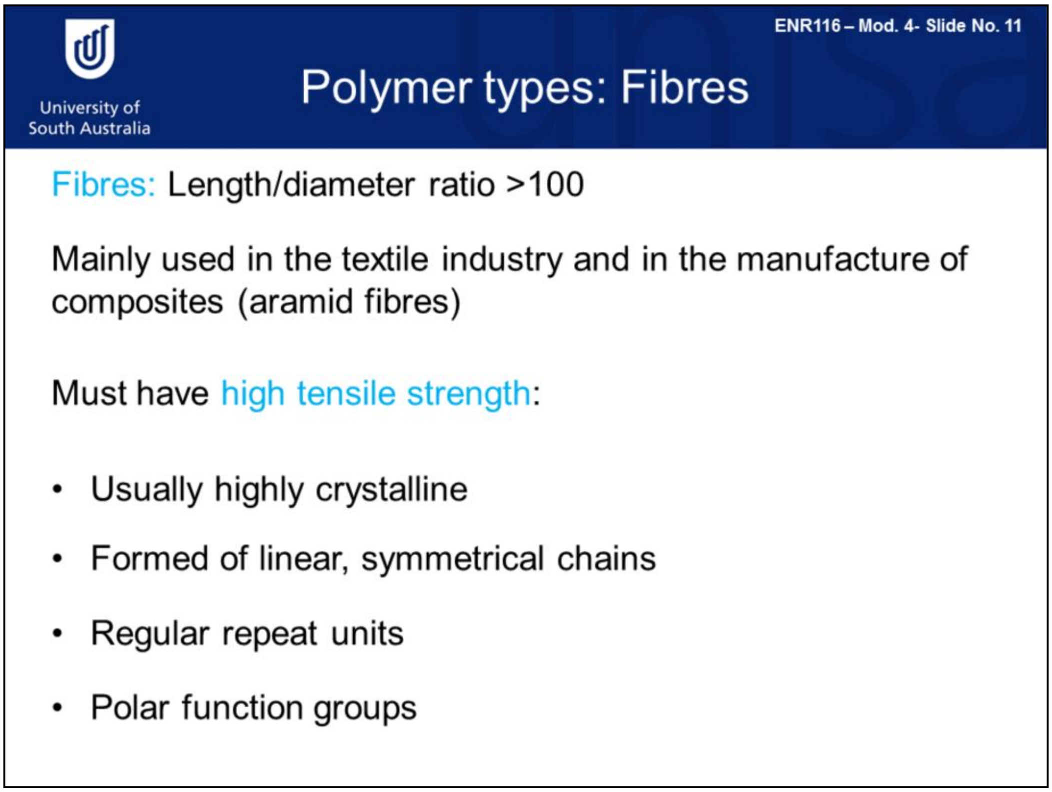
- Natural rubber
- Synthetic rubber
- Silicone rubber

Example: polydimethylsiloxane (PDMS)

The next group of polymers is the elastomers. Elastomers have the ability to experience very large strains but still spring back elastically to recover their original form. This property comes about as a result of crosslinking within the polymer structure, which provide a force to pull the chains back into their un-deformed shape.

Natural rubber, from the para latex tree, is still widely used. The most important synthetic rubber is SBR, styrene butadiene rubber, which has the structure shown here.

Silicon rubbers have a backbone consisting of alternating silicon and oxygen atoms, with side bonded groups. In the example here, Polydimethylsiloxane, these side groups are both methyl groups. As elastomers, all of these examples contain crosslinks.



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Polymer types: Fibres

Fibres: Length/diameter ratio >100

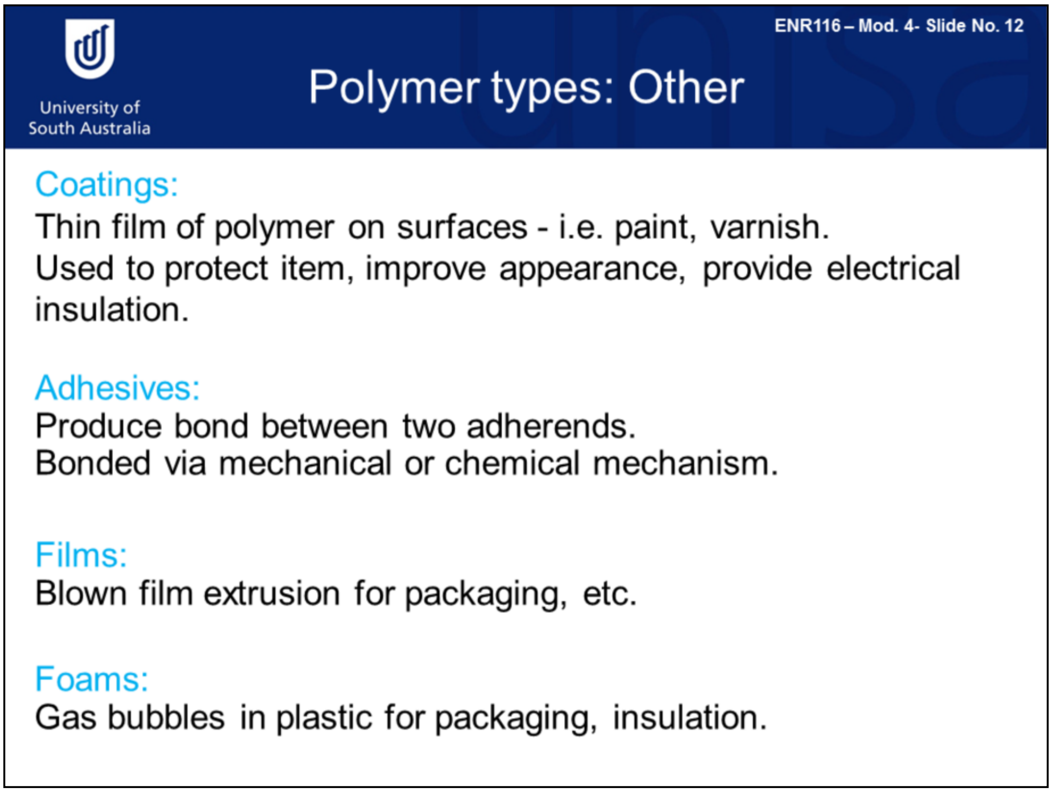
Mainly used in the textile industry and in the manufacture of composites (aramid fibres)

Must have high tensile strength:

- Usually highly crystalline
- Formed of linear, symmetrical chains
- Regular repeat units
- Polar function groups

Fibre polymers are capable of being drawn into long filaments with a length to diameter ratio of at least 100 to 1. Fibre polymers are mostly used in the textile industry, where they are knit or woven into fabric. Nylon and polyester are familiar examples of textiles based on polymer fibres. Aramid fibres are a type of polymer fibre used in the manufacture of composite materials.

You can imagine that as a component of a cloth or fabric, polymer fibres will be subject to a variety of tensile, bending, shearing or twisting forces. Consequently, they need to have considerable tensile strength. We've seen previously that tensile strength increases with the degree of crystallinity of the polymer, and therefore fibre polymers tend to be highly crystalline; comprising linear, symmetrical chains with regular repeat units and polar functional groups.



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Polymer types: Other

Coatings:
Thin film of polymer on surfaces - i.e. paint, varnish.
Used to protect item, improve appearance, provide electrical insulation.

Adhesives:
Produce bond between two adherends.
Bonded via mechanical or chemical mechanism.

Films:
Blown film extrusion for packaging, etc.

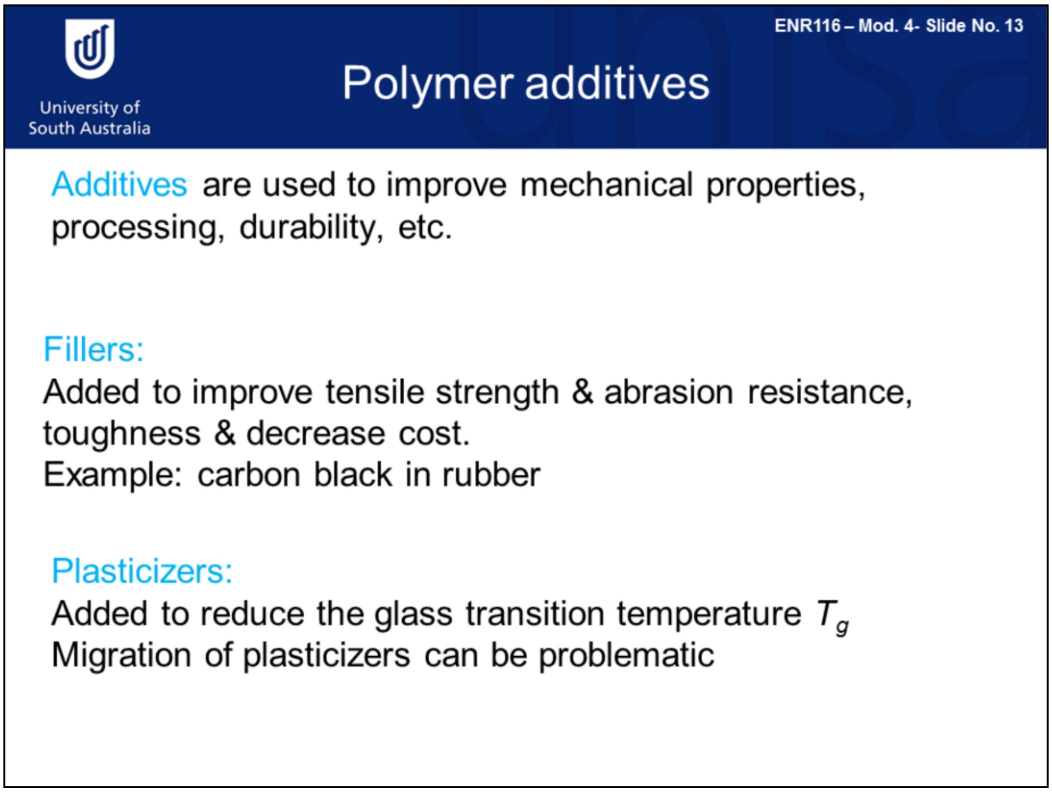
Foams:
Gas bubbles in plastic for packaging, insulation.

We'll now summarise the last few types of polymer. Polymer coatings are thin films applied to a surface, usually to protect the bulk material underneath, or to improve it's appearance or provide electrical insulation.

An adhesive is a substance used to bond together the surfaces of two solid materials, which are known as the adherents. There are two main types of bonding mechanism, chemical and mechanical. In mechanic bonding, the adhesive actually penetrates into the material, whereas in chemical bonding, intermolecular bonds are formed between the adhesive and the material. These bonds can be primary or secondary.

Polymeric materials can also form films. Very thin polymer films are used extensively as packaging materials, particularly in the food industry. These polymers may have low density, a high degree of flexibility, low gas permeability and be resistant to chemicals.

Our last group contains polymer foams. Foams are plastic materials with a high percentage volume of pores, and therefore trapped gas bubbles. Polyurethane, rubber and polystyrene can all form foams. Polymer foams are commonly used as cushioning material, and in packaging and thermal insulation.



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Polymer additives

Additives are used to improve mechanical properties, processing, durability, etc.

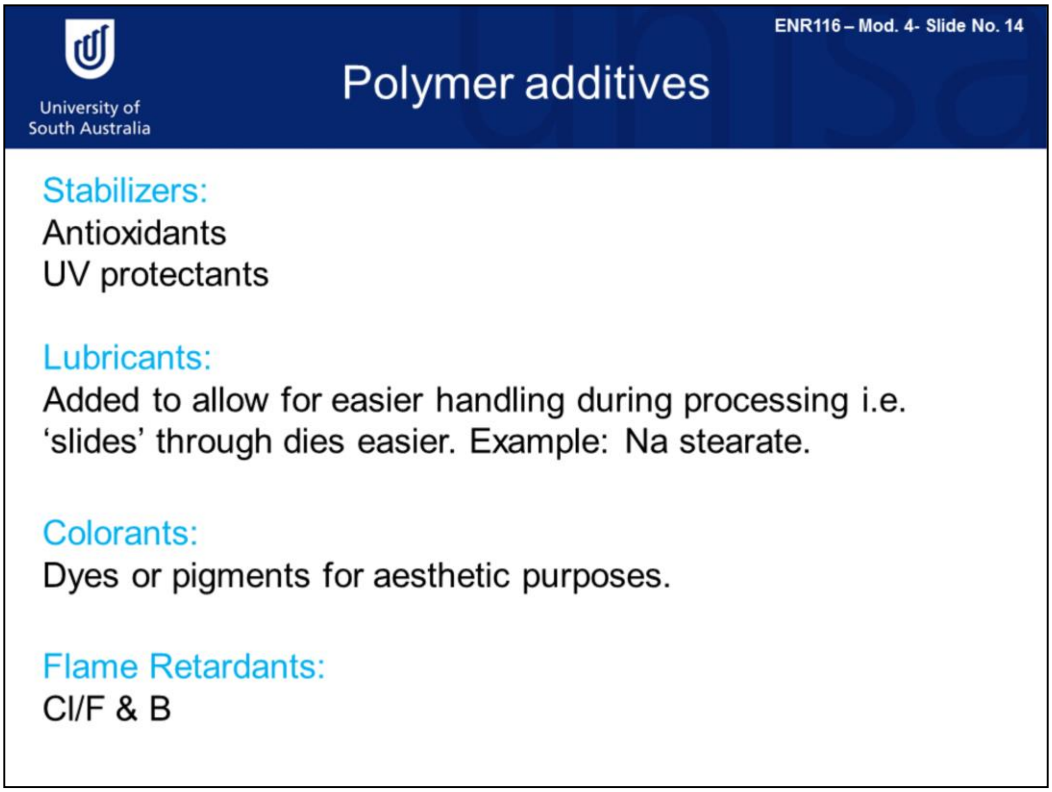
Fillers:
Added to improve tensile strength & abrasion resistance, toughness & decrease cost.
Example: carbon black in rubber

Plasticizers:
Added to reduce the glass transition temperature T_g
Migration of plasticizers can be problematic

We talked a lot now about the application of polymers, but it's important to realise that actually, polymers are almost never used as a pure material. Additives are foreign substances that are deliberately added to the bulk polymer in order to improve its mechanical properties, ease of processing or durability. We'll now briefly address a few specific types of additive.

Fillers are a type of additive that act to improve the tensile strength, abrasion resistance and toughness of a material. They can also be added to reduce the cost of the final product. An example of a filler is carbon black, which is commonly added to rubber in order to ??.

Plasticizers are another form of additive. Plasticizers act to lower the glass transition temperature, improving the ductility and flexibility of the polymer. Plasticiziers are typically small molecules that occupy positions inbetween the large polymer chains. They effectively act as a lubricant, helping the chains to move and slide past other. However, plasticizer addition is not without its problems - because the molecules are small they can migrate with relative ease through the material, towards the surface. This is a particular concern in materials used for food packaging.



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Polymer additives

Stabilizers:
Antioxidants
UV protectants

Lubricants:
Added to allow for easier handling during processing i.e. ‘slides’ through dies easier. Example: Na stearate.

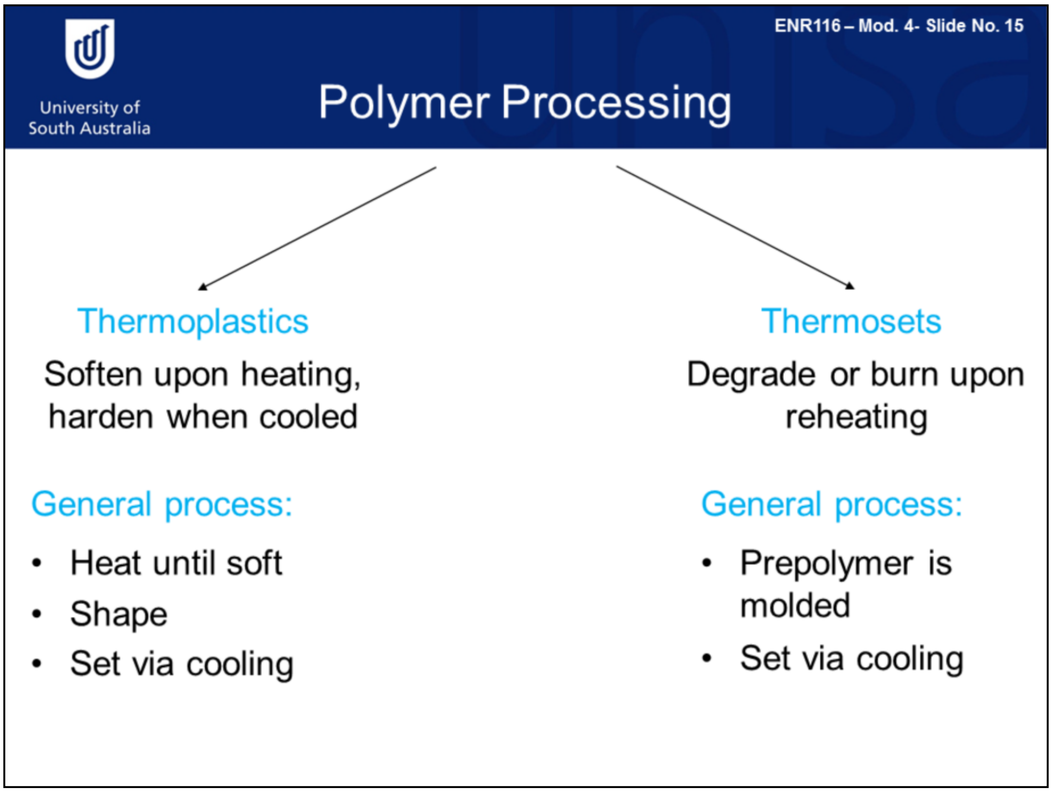
Colorants:
Dyes or pigments for aesthetic purposes.

Flame Retardants:
Cl/F & B

Other additives added to polymers include stabilizers. Stabilizers prevent or at least reduce oxidation, and therefore degradation of the product. UV stabilizers act to reduce deterioration of the product as a result of exposure to light.

Lubricants allow for easier polymer processing, and colorants impart a particular colour to polymer, either for aesthetic purposes or to make it opaque.

Finally, one of the major concerns with organic compounds such as polymer compounds are their flammability. Flame retardant additives such ??? as are used to reduce this risk.



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Polymer Processing

Thermoplastics

Soften upon heating, harden when cooled

General process:

- Heat until soft
- Shape
- Set via cooling

Thermosets

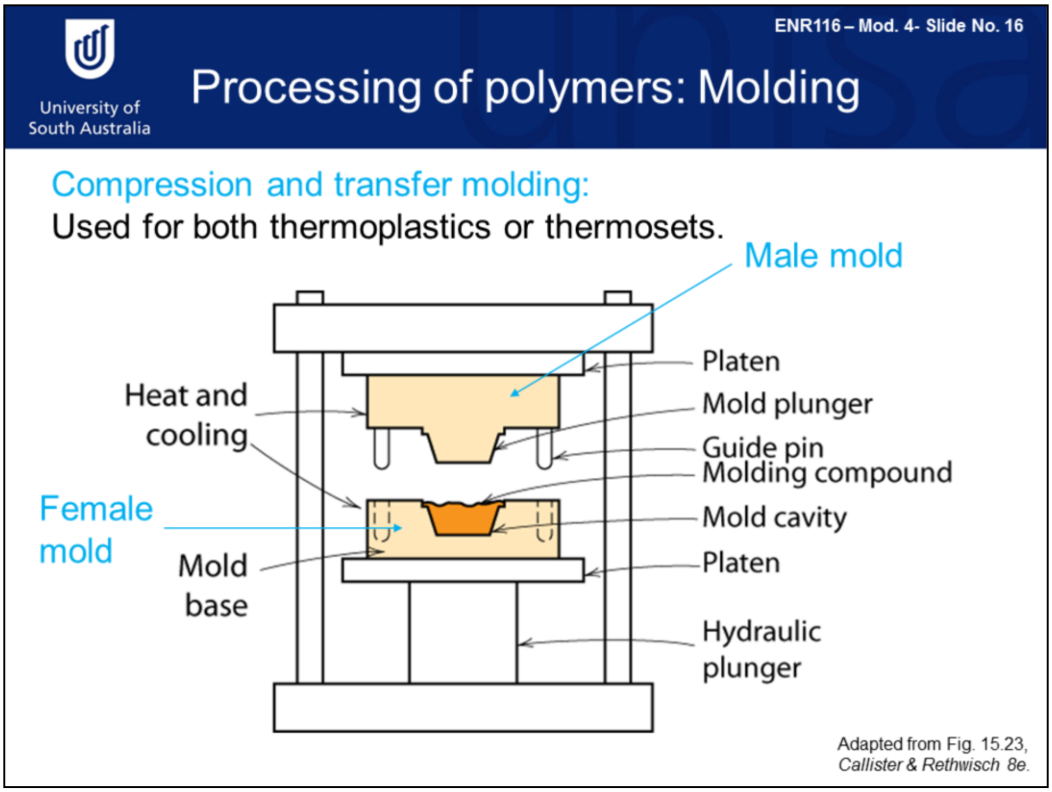
Degrade or burn upon reheating

General process:

- Prepolymer is molded
- Set via cooling

For the last part of this lecture summary, we're going to focus on describing some of the techniques used to form polymeric materials.

There are a number of different polymer fabrication techniques available, but the type used really only depends on one thing; whether the polymer is a thermoplastic or thermoset. You'll recall that thermoplastics can be reversibly cooled and reheated. Recyclable plastics tend to be thermoplastics. To form these, the polymer is generally heated until soft, then shaped as required. They will harden and set upon cooling. Thermosets crosslink when heated, so that when they are reheated they either degrade or burn, rather than melt. To process these, the prepolymer is moulded and then allowed to set and cure.



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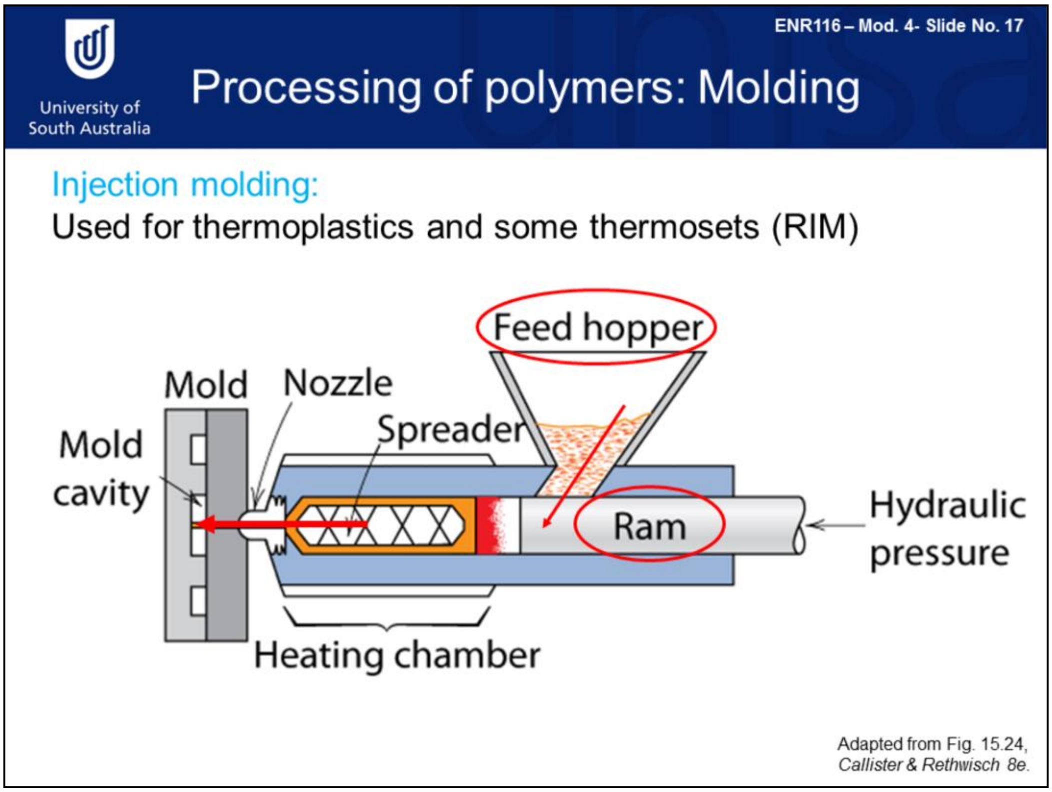
Processing of polymers: Molding

Compression and transfer molding:

Used for both thermoplastics or thermosets.

Adapted from Fig. 15.23, *Callister & Rethwisch 8e.*

We'll now look at some specific types of polymer forming techniques. The first of these is molding, and this is a technique that can be used with either thermoplastics or thermosets. Compression and transfer molding use male and female molds. The softened, or molten polymer is placed between the molds, both of which are heated. One of them will then move to close the mold. Further heat and or pressure are then applied, which cause the polymer to flow and completely take the shape of the mold.



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Processing of polymers: Molding

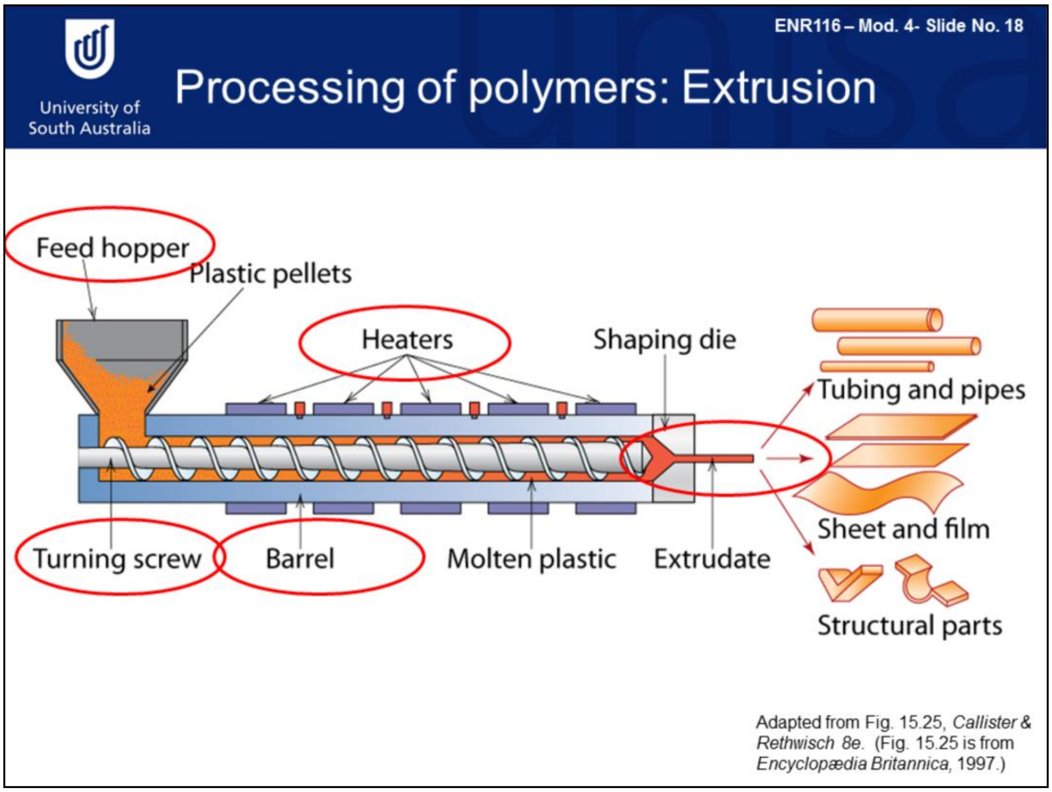
Injection molding:

Used for thermoplastics and some thermosets (RIM)

Adapted from Fig. 15.24, *Callister & Rethwisch 8e.*

Injection molding can be used with thermoplastics and some thermosets. Polymer pellets are placed into a feed hopper, and fed into the heated barrel of the injection molding machine. A spreader, or screw, mixes the pellets within the barrel. The ram then forces out set amounts of the polymer under pressure into the die. The pressure is maintained on the polymer in the die until it is solidified. This may be only be a matter of seconds. Once set, it is ejected from the mold.

Reaction injection molding is the term used when this process is used to produce a thermoset. In this case, curing takes place after the polymer has been injected into the mold. This typically has a longer cycle time than for thermoplastics.



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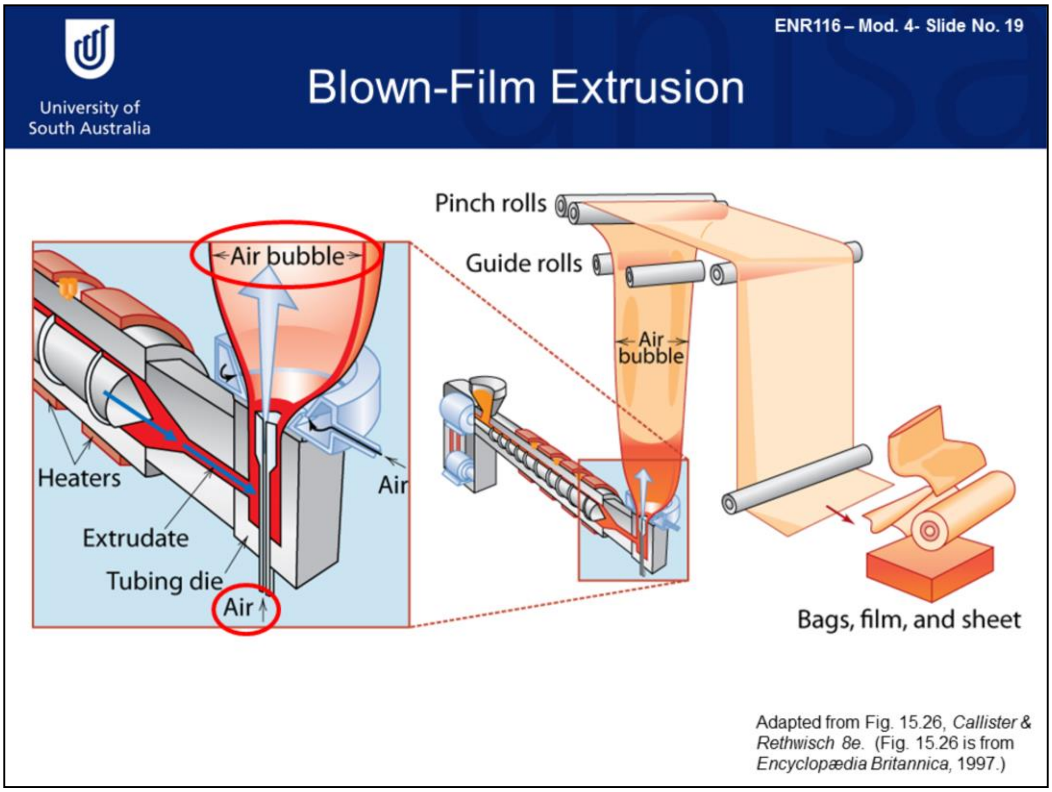
Processing of polymers: Extrusion

Adapted from Fig. 15.25, *Callister & Rethwisch 8e*. (Fig. 15.25 is from *Encyclopædia Britannica*, 1997.)

Numerous polymer components are produced by extrusion. Tubing and pipes, sheets, film and structural components are all formed by this method.

Once again, the polymer pellets are placed into a feed hopper which gradually adds polymer to the heater barrel of the extruder. The turning screw within the barrel thoroughly mixes the polymer and melts it, by forcing it into close proximity with the heaters. The screw also forces the polymer out of the end of the extruder, which compresses the polymer stream out and into a mold. The formed polymer is then cooled with air blowers, water spray, or a water bath.



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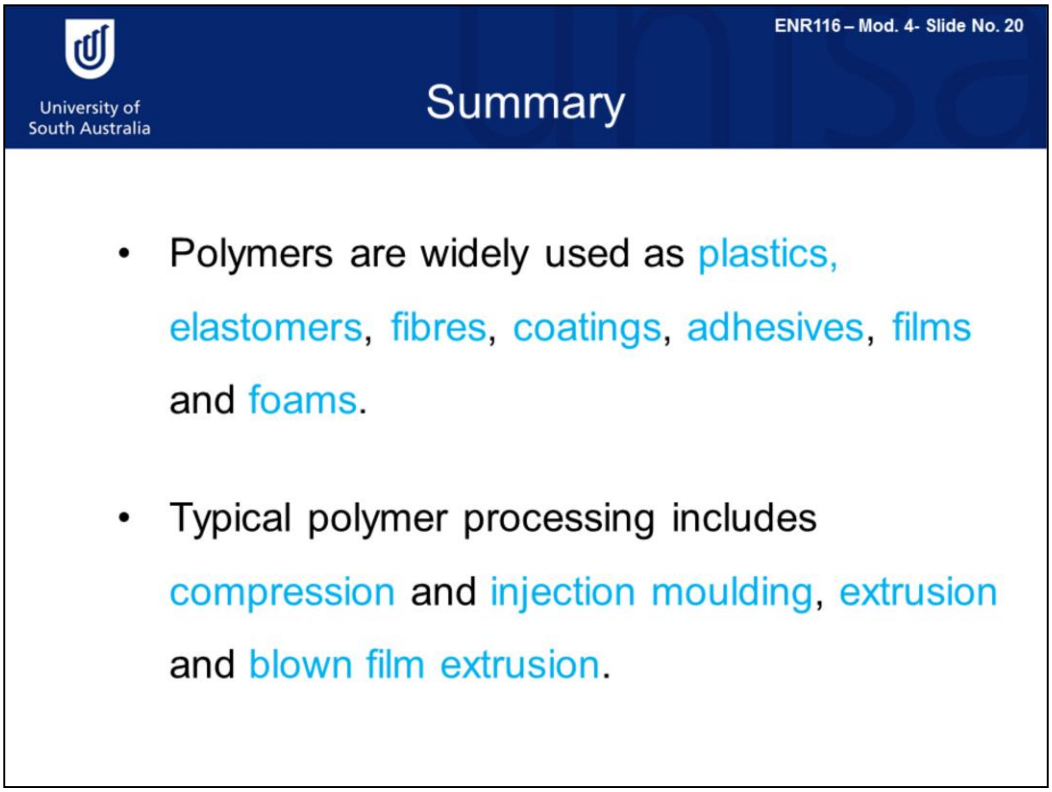
Blown-Film Extrusion

Adapted from Fig. 15.26, *Callister & Rethwisch 8e*. (Fig. 15.26 is from *Encyclopædia Britannica*, 1997.)

Blown film extrusion starts in the same way as for normal extrusion, however, as the polymer melt is forced out of the barrel, it hits a special die. This die is in two parts: In the first stage, the molten polymer is extruded into a narrow tube, and then air is blown up through the centre of the tube.

This forces the walls out, making them take the shape of the second mold. Bubble wrap, thin films, bags and sheets are all made using this technique. It does however rely on precise control of the temperature and the viscosity of the polymers used.



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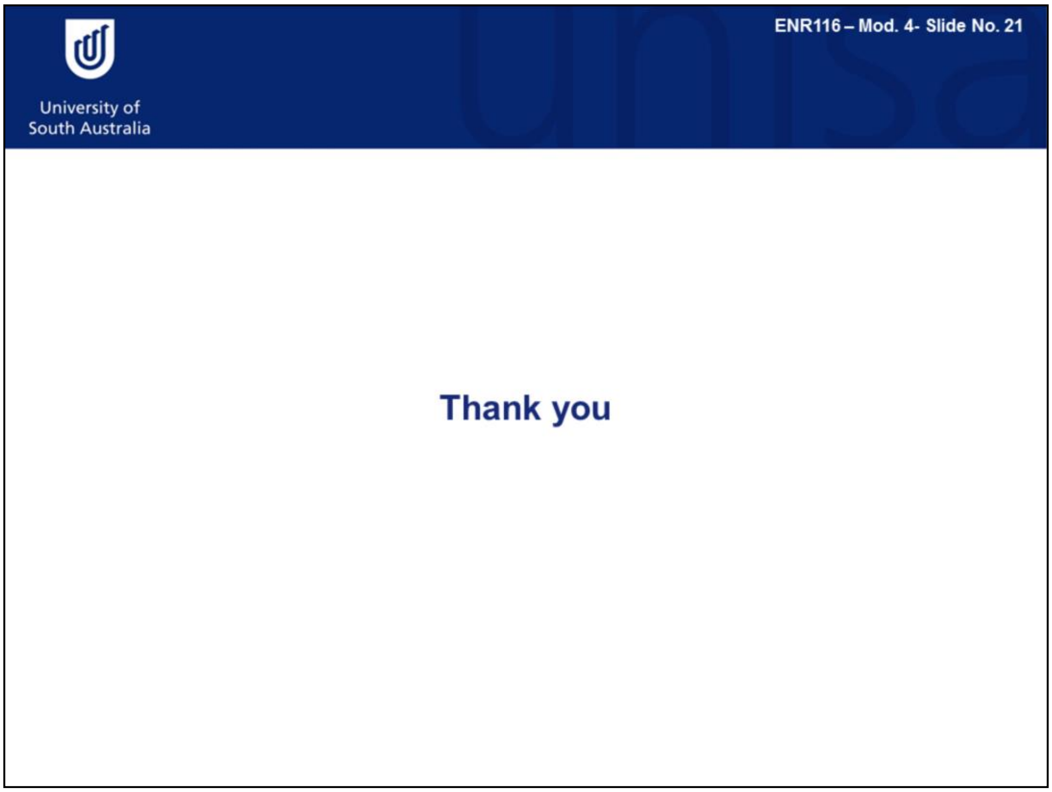
Summary

- Polymers are widely used as plastics, elastomers, fibres, coatings, adhesives, films and foams.
- Typical polymer processing includes compression and injection moulding, extrusion and blown film extrusion.

We’ve covered a lot of material in this lecture. We’ve seen that not all polymers are plastics, they may be elastomers, fibres, coatings adhesives, films and foams. Four commonly used methods for processing polymers are compression molding, injection molding, extrusion and blown film extrusion.



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