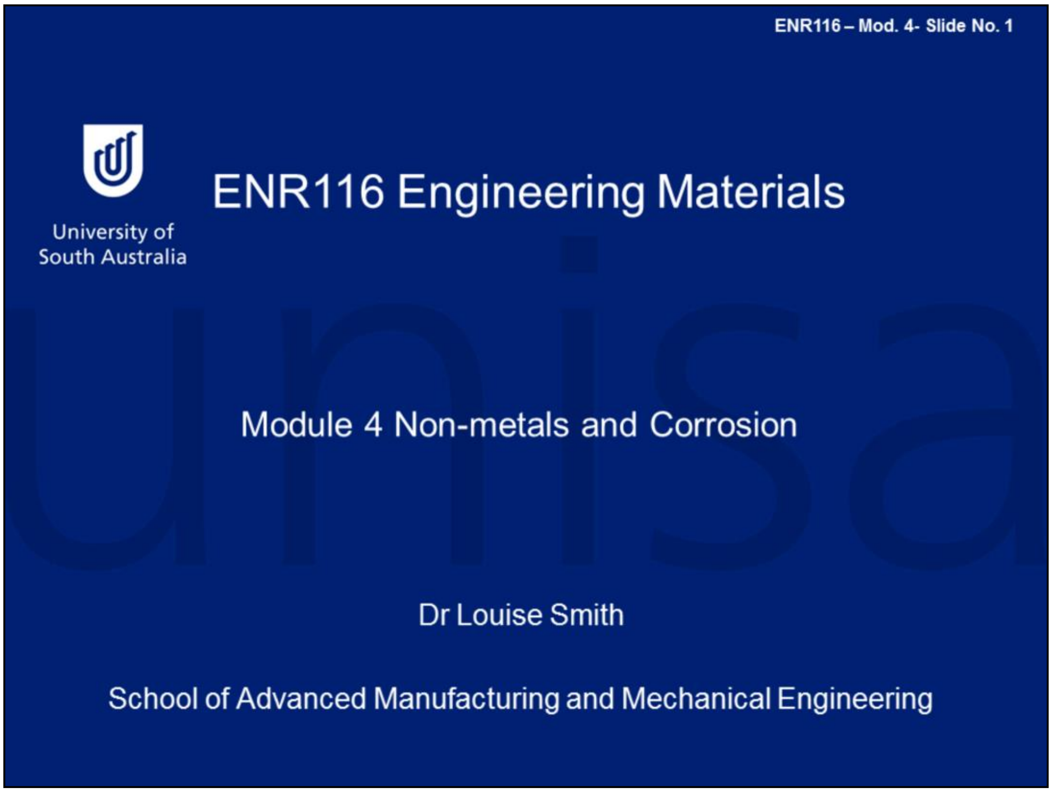

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ENR116 Engineering Materials

Module 4 Non-metals and Corrosion

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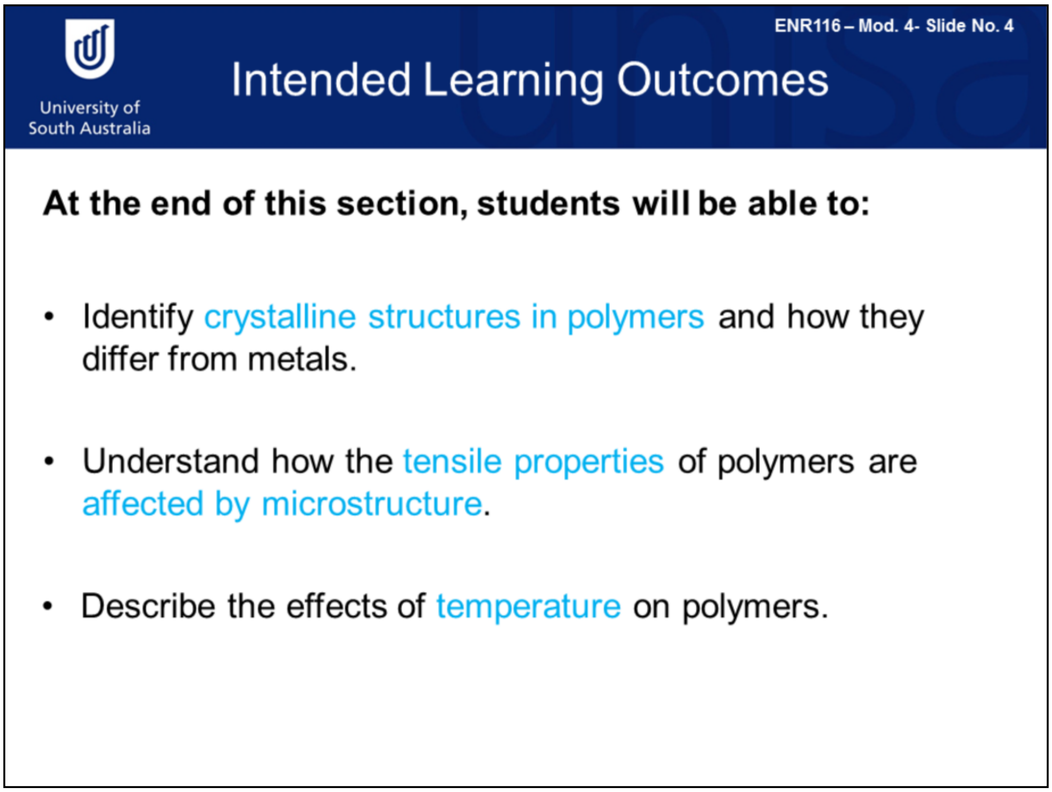
Polymer structure and properties



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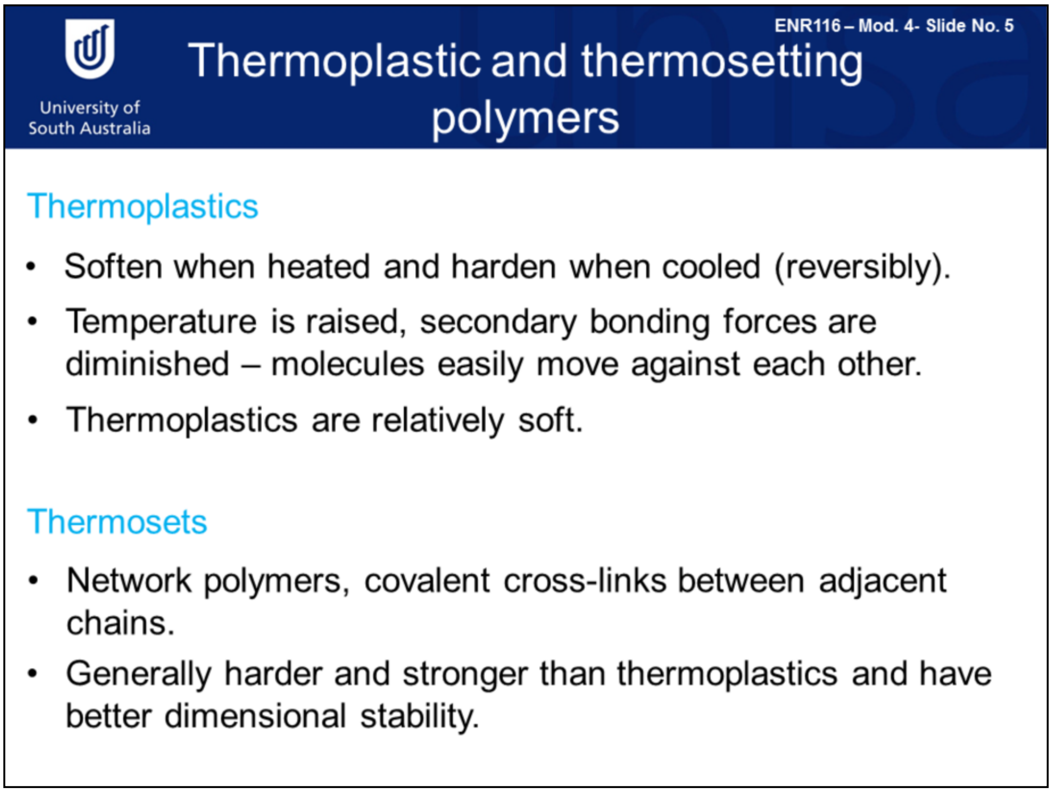
Intended Learning Outcomes

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

- Identify crystalline structures in polymers and how they differ from metals.
- Understand how the tensile properties of polymers are affected by microstructure.
- Describe the effects of temperature on polymers.

•The intended learning outcomes from this presentation are for students to be able to recognise and describe the crystalline structures present in some polymers.

•To understand how the tensile properties of polymers are affected by the polymer microstructure and how this is also affects by temperature.



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Thermoplastic and thermosetting polymers

Thermoplastics

- Soften when heated and harden when cooled (reversibly).
- Temperature is raised, secondary bonding forces are diminished – molecules easily move against each other.
- Thermoplastics are relatively soft.

Thermosets

- Network polymers, covalent cross-links between adjacent chains.
- Generally harder and stronger than thermoplastics and have better dimensional stability.

We're going to start by considering some of the properties of particular classes of polymer, including copolymers, and thermoplastics and thermosetting polymers. We came across both of the last two types of polymer in the previous summary lecture summary. Thermoplastic polymers are linear or branched chain polymers, and thermosets are cross-linked or network polymers. The two types of material behave very differently at elevated temperature.

Thermoplastics soften when heated and eventually they may liquefy. They will harden when cooled.

This process of heating/cooling is reversible. As the temperature is raised the secondary bonds, between polymer chains which are (generally) weak van der Waals forces are readily overcome and these long chain molecules move easily, by sliding against each other.

Thermo-plastics are relatively soft.

In contrast, thermosetting polymers are cross-linked or networked polymers. Typically somewhere between ten to fifty percent of the chain units in a thermopsetting materials are cross linked. Thermosets are harder and stronger than thermoplastics and show better dimensional stability. When they are heated they do not liquefy; and in the presence of oxygen they burn. An example of a thermosetting polymer is a phenol formaldehyde resin, such as bakelite.

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Copolymers

Copolymers: Two or more monomers polymerized together.

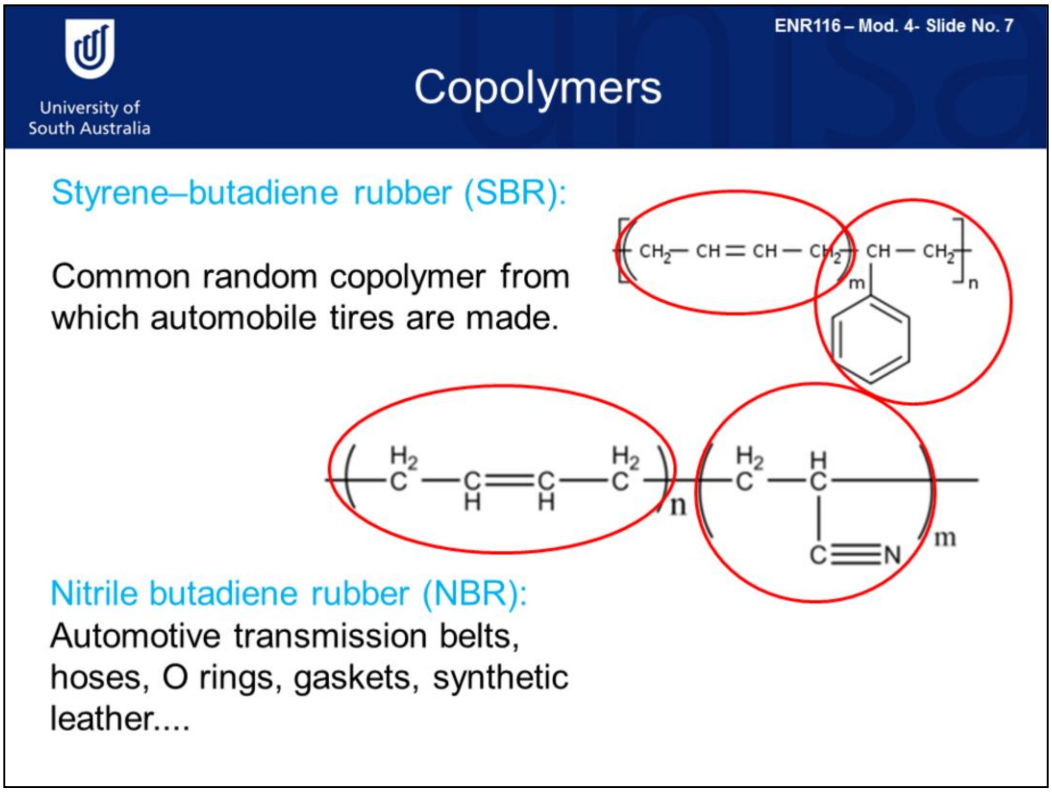
Adapted from Fig. 14.9, *Callister & Rethwisch 8e.*

Lets now take a lot of some of the properties of co-polymers. This model copolymer comprises of 2 different monomer units, A and B.

Following polymerisation the units A and B may be randomly distributed along the polymer chain or, alternatively, they may alternate in a regular manner along the chain.

A distinct variant is where we find large blocks of A alternating with large blocks of B. These are termed Block Copolymers. As we will discuss a little later, these blocks can display distinctly different properties from each other.

The final variant is where we have a backbone of A, which forms the polymer chain. To this backbone we find B grafted as side chains. Again, later we will consider the influence of such side chains on the overall physical properties of a copolymer.



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Copolymers

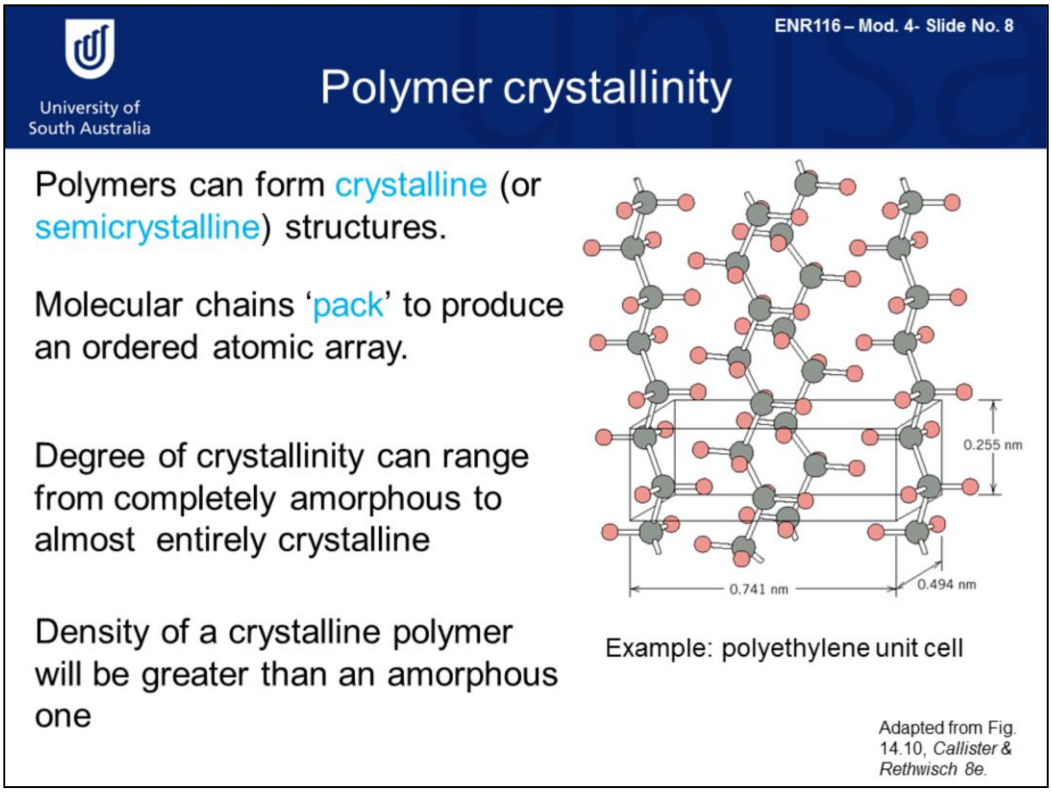
Styrene–butadiene rubber (SBR):

Common random copolymer from which automobile tires are made.

Nitrile butadiene rubber (NBR):
Automotive transmission belts, hoses, O rings, gaskets, synthetic leather....

Some examples of common copolymers. Styrene butadiene rubber, SBR, is a random copolymer of styrene and butadiene units. This is the butadiene component, and this is the styrene. SBR is widely used in the manufacture of car tires.

Nitrile rubber is found automotive transmission belts, hoses, o-rings, gaskets and synthetic leather. It’s a copolymer of acrylonitrile and butadiene.



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Polymer crystallinity

Polymers can form crystalline (or semicrystalline) structures.

Molecular chains ‘pack’ to produce an ordered atomic array.

Degree of crystallinity can range from completely amorphous to almost entirely crystalline

Density of a crystalline polymer will be greater than an amorphous one

Example: polyethylene unit cell

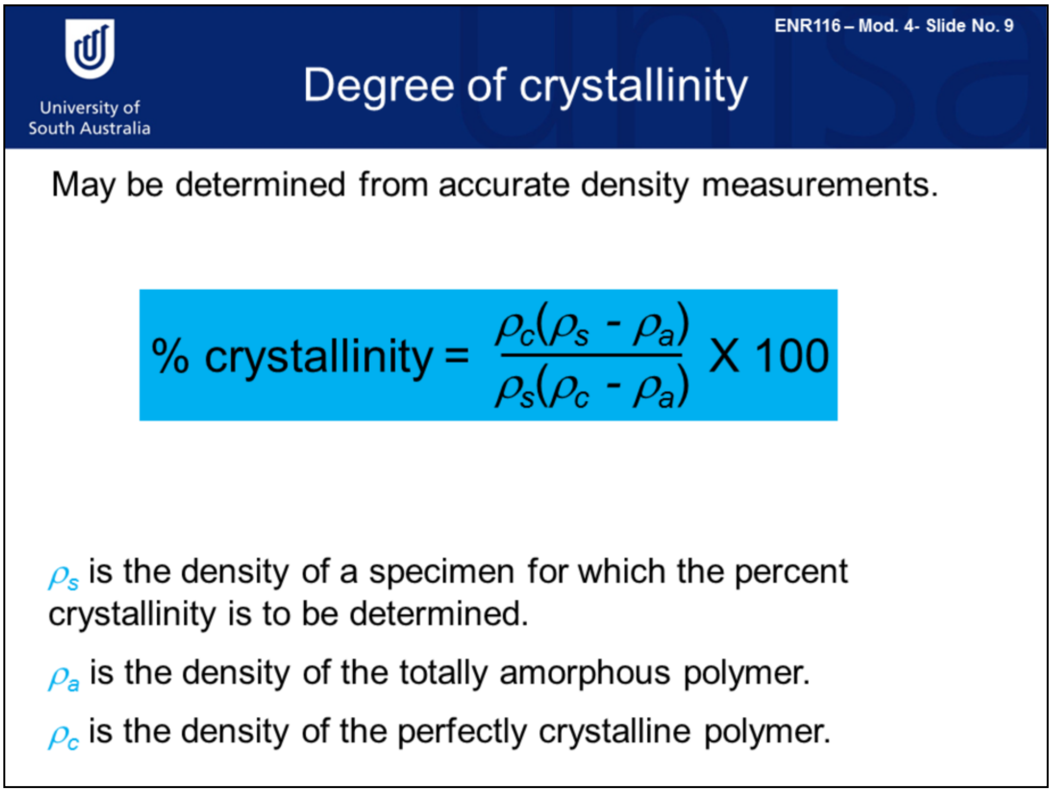
Adapted from Fig. 14.10, *Callister & Rethwisch 8e*.

One of the surprising properties of polymers is that they can undergo crystallisation to form crystalline, or semi crystalline structures.

Polymer crystallinity arises from the packing of the molecular chains to form ordered arrays. Given the large size of the molecules involved, the unit cells for structures are generally very complex, and you can see that in the illustration shown here. These are polyethylene chains with the repeat unit C2H4, packed in an ordered fashion to give a polyethylene unit cell. This cell has an orthorhombic geometry.

Now again because of the large size of the polymer chains, polymer molecules are actually tend to be only partially crystalline, with amorphous regions separating the ordered parts of the structure. This two phase style system is in contrast to the metal and ceramic structures we’ve look at previously, which were all either completely crystalline or entirely non crystalline.

As a last point, note that the density of a crystalline polymer will be substantially greater than that of its amorphous counterpart, by virtue of the close packing within the crystalline structure. We can use this fact to calculate the degree of crystallinity within a given polymer structure, as we will see on the next slide.



Degree of crystallinity

May be determined from accurate density measurements.

$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \text{ X } 100$$

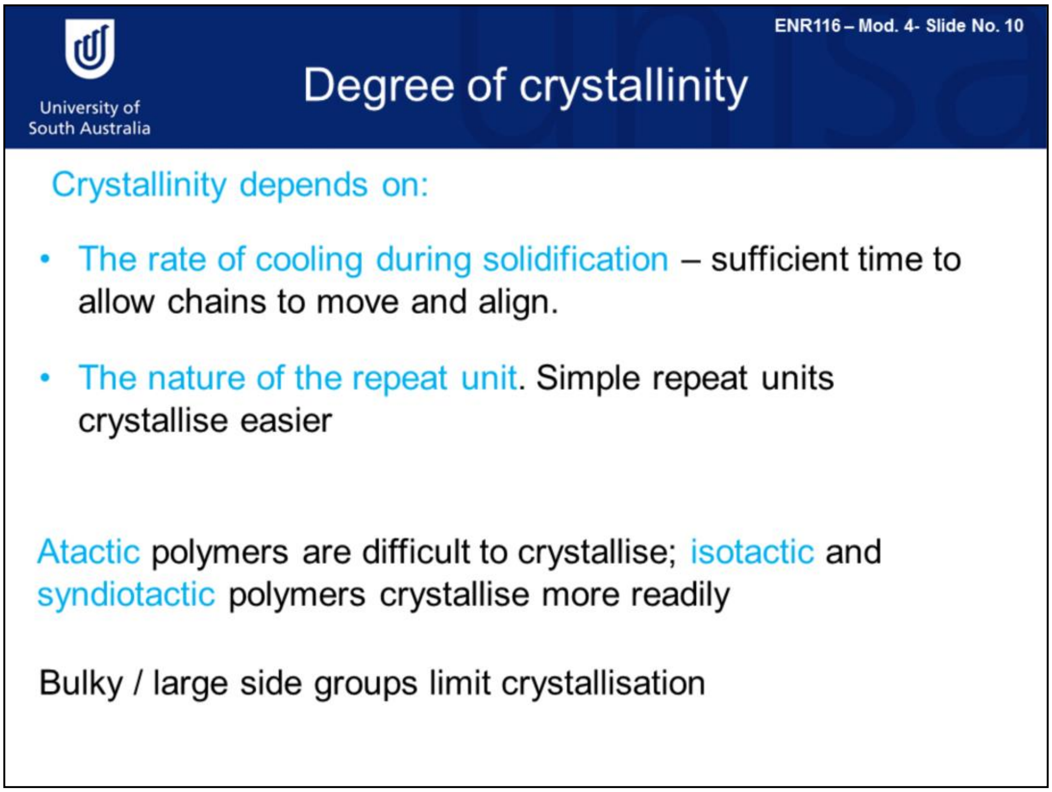
ρ_s is the density of a specimen for which the percent crystallinity is to be determined.

ρ_a is the density of the totally amorphous polymer.

ρ_c is the density of the perfectly crystalline polymer.

So, if we have already have values for the densities of a total amorphous polymer and its 100% crystalline counterpart, we only need to measure the density of a third, semi crystalline specimen in order to be able to calculate its percentage crystallinity.

Percentage crystallinity is given by the crystalline density, multiplied by difference between the mixed sample density and the amorphous density; divided by the semi crystalline sample density, multiplied by the difference between the crystalline and amorphous densities. Multiplying by 100 then converts the fraction into a percentage.



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Degree of crystallinity

Crystallinity depends on:

- The rate of cooling during solidification – sufficient time to allow chains to move and align.
- The nature of the repeat unit. Simple repeat units crystallise easier

Atactic polymers are difficult to crystallise; isotactic and syndiotactic polymers crystallise more readily

Bulky / large side groups limit crystallisation

What are the factors that influence the crystallisation and degree of crystallinity of a polymer?

Well, one of the most influential parameters is the rate of cooling of the material during the solidification stage. Sufficient time must be allowed during cooling for the polymer chains to move and to align.

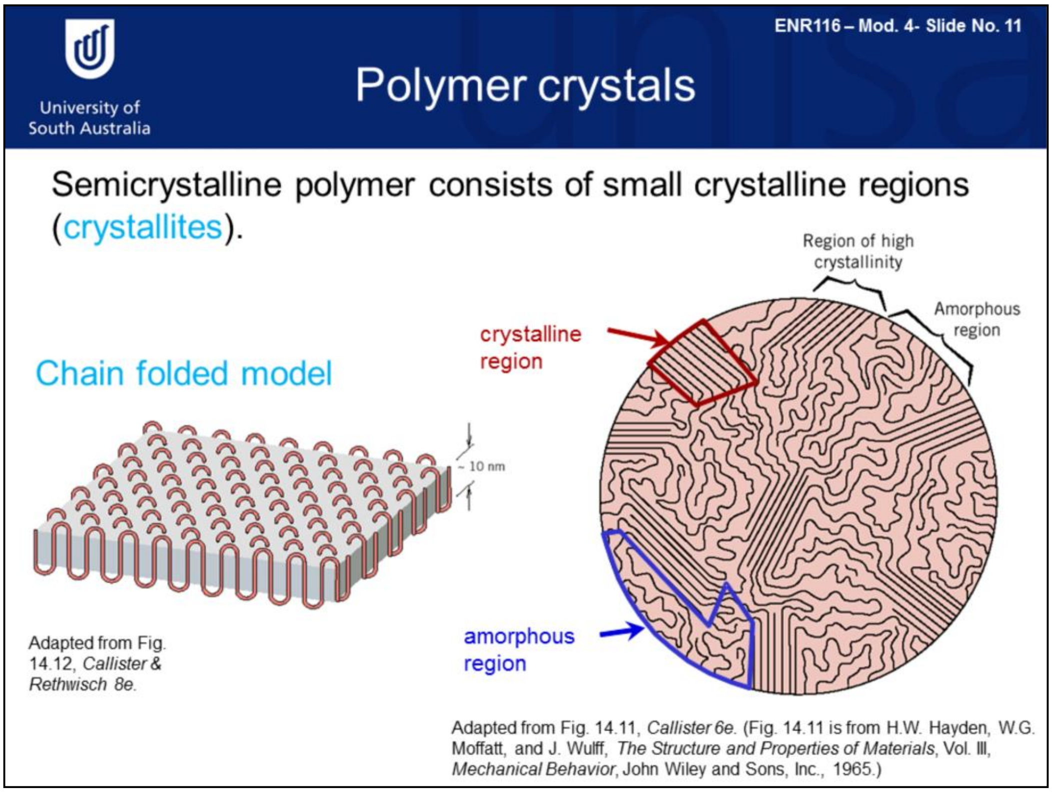
Rapid cooling, forces the polymer through the liquid-solid transition too quickly, without allowing sufficient time for crystallisation to occur.

Another important factor is the simplicity of the repeat unit. In general, simple repeat units crystallise more readily. For (most) linear polymers, crystallisation is easily accomplished because there are so few restrictions to the chains moving and aligning.

Atactic polymers, that is polymers where there is no regularity in the position of a side group heteroatom or side group (along the polymer chain), are difficult to crystallise. However, isotactic and syndiotactic polymers generally crystallise much more readily because of the regularity and geometry of side groups.

We already known that bulky side groups impede rotation in polymers. These groups also have a tendency to reduce the degree of crystallinity in a polymer.

There is a complication with alternating or block copolymers that crystallisation may only occur in one part of the polymer. In block copolymers, where the blocks are large, there is the possibility that one block may crystallise, whereas the other remain amorphous. The block that will crystallise is most likely to be that with more regular, simpler arrangement of repeat units.



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Polymer crystals

Semicrystalline polymer consists of small crystalline regions (crystallites).

Chain folded model

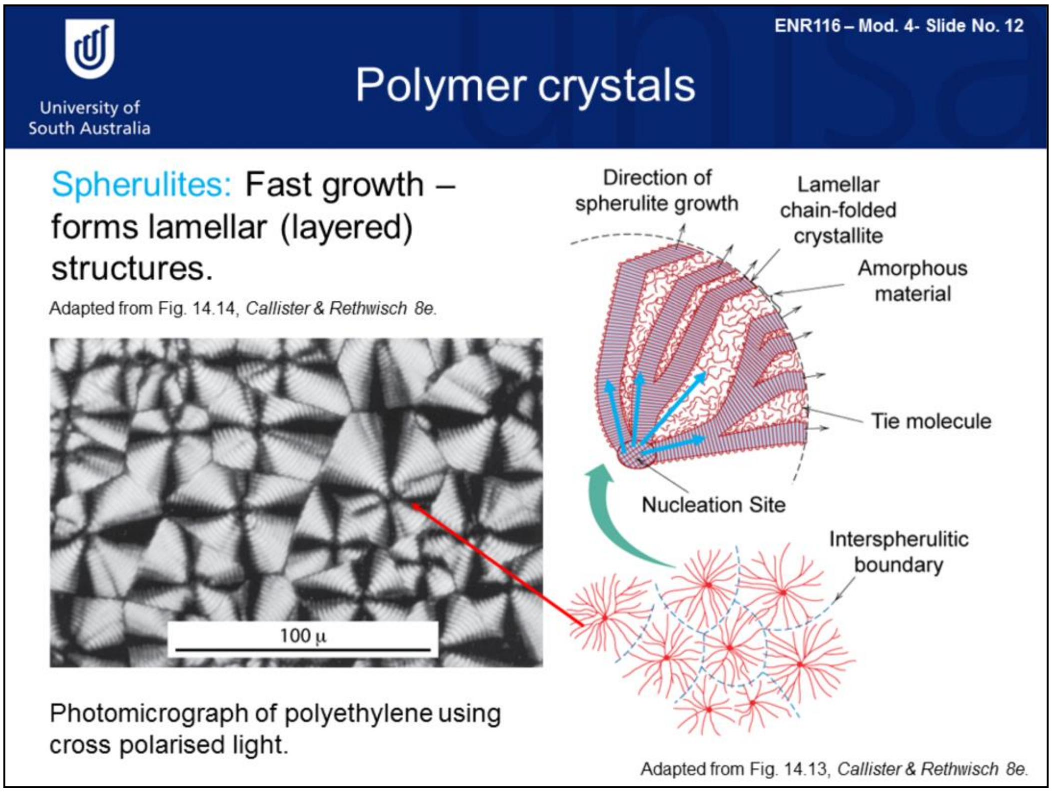
Adapted from Fig. 14.12, *Callister & Rethwisch 8e.*

Adapted from Fig. 14.11, *Callister 6e.* (Fig. 14.11 is from H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

So, we now know that polymers rarely crystallise perfectly, but rather tend to exist as semi-crystalline materials that consist of small regions of crystallinity embedded in a matrix of amorphous material.

However, we can investigate the crystal structure of polymers by carefully growing single crystals under very controlled conditions. From such studies, we known that crystalline polyethylene has a structure like this, with long chains folded back and forth on themselves. This is called the chain folded model.

When small regions of crystalline polymer form in the amorphous matrix, they are known as crystallites. In the illustration here, you can see a spherulite; a spherical structure formed from a polymer melt under conditions of controlled cooling. These are basically the polymer analogue of grains in a polycrystalline metal. The spherulite contains both crystallites, here, in the form of plates or lamellae of folded chains, surrounded by amorphous regions such as this one.



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Polymer crystals

Spherulites: Fast growth – forms lamellar (layered) structures.

Adapted from Fig. 14.14, *Callister & Rethwisch 8e.*

Photomicrograph of polyethylene using cross polarised light.

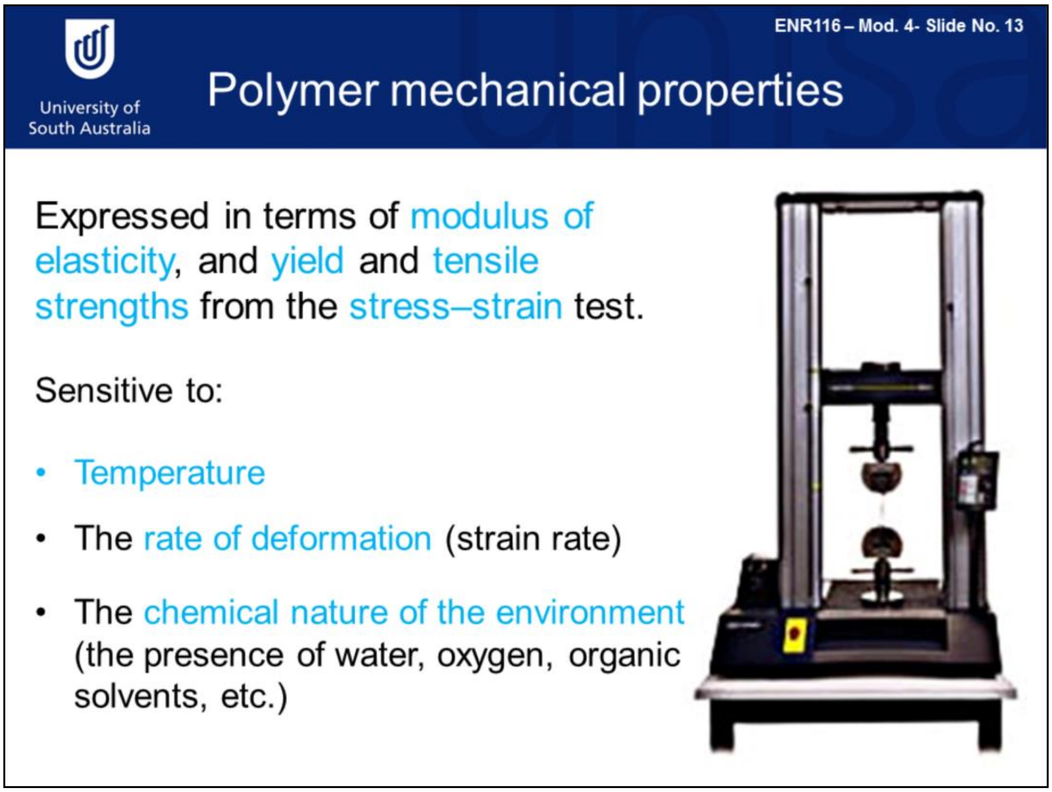
Adapted from Fig. 14.13, *Callister & Rethwisch 8e.*

So, spherulites are spherical shapes comprising both crystalline and amorphous regions can be considered as the polymer version of a grain.

Spherulites are formed from a nucleus, typically a speck or impurity within the melt, and steadily grow. You can see the different regions radiating out from the nucleus in the illustration here.

We can control the rate of growth of the spherulite by controlling the temperature. You may recall from previous lectures covering the growth of a new phase that an important factor is the degree of supercooling from the usual melting temperature of the system. The larger the degree of supercooling, the more we lower the temperature beyond the usual melting point, the faster rate of spherulite growth. But - if the supercooling is too great, the molten polymer will be locked in an amorphous state, so it has to be carefully controlled.

If you know look at this picture, you’re seeing an optical image of polyethylene obtained using cross polarised light. The crystal regions (lamellae) display birefringence, that is, they have the property of rotating the plane of polarised light and consequently appear bright, whilst the amorphous regions are dark. The individual spherulites and their boundaries are therefore clearly visible.



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Polymer mechanical properties

Expressed in terms of modulus of elasticity, and yield and tensile strengths from the stress–strain test.

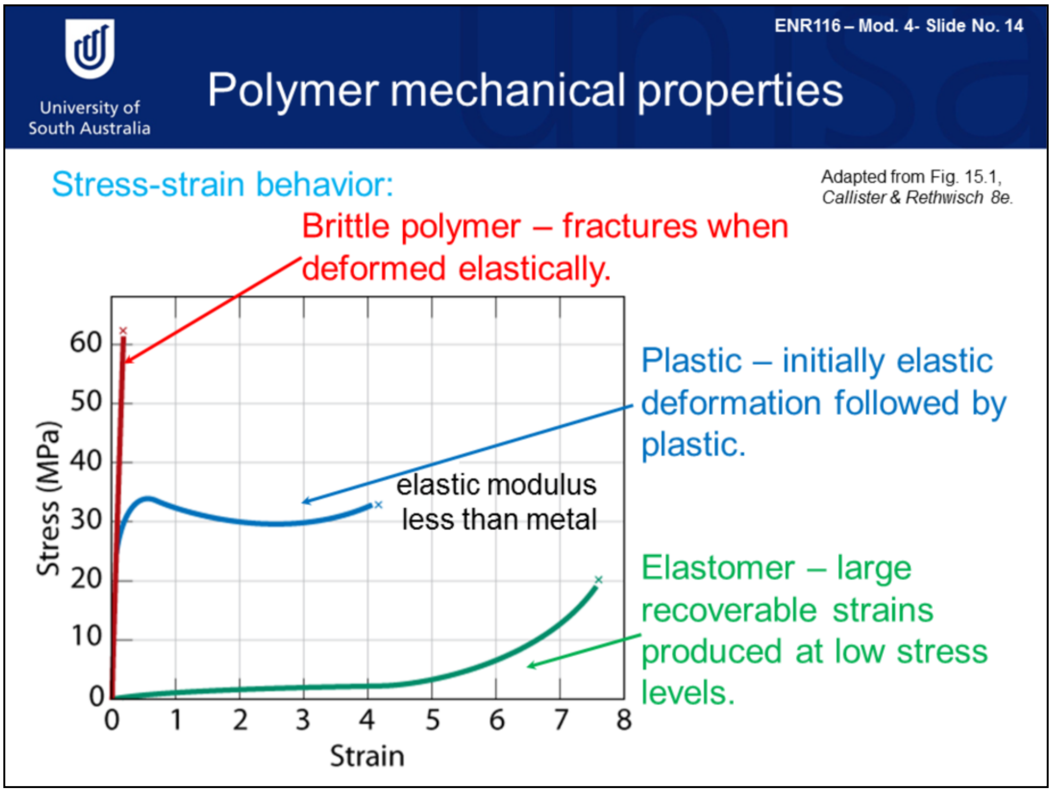
Sensitive to:

- Temperature
- The rate of deformation (strain rate)
- The chemical nature of the environment (the presence of water, oxygen, organic solvents, etc.)

We've talked now about the semi crystalline nature of polymers, and their structure. We are now going to move on and for the rest of this lecture summary will focus on how these features affect the mechanical properties of polymers.

In many respects, polymers are not that different from metals, and we use the same parameters to describe the mechanical properties of both. Typically we'll characterise a polymers' performance in terms of its modulus of elasticity, its yield point and tensile strength. These are all determined experimentally via stress strain testing.

Perhaps where polymers really differ from metals is that they are particularly sensitive to changes in temperature. The strain rate of the experiment and the chemical stability of the polymer in the testing environment can also have a a significant influence on the mechanical properties measured.



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Polymer mechanical properties

Stress-strain behavior:

Adapted from Fig. 15.1, *Callister & Rethwisch 8e.*

Brittle polymer – fractures when deformed elastically.

Plastic – initially elastic deformation followed by plastic.

elastic modulus less than metal

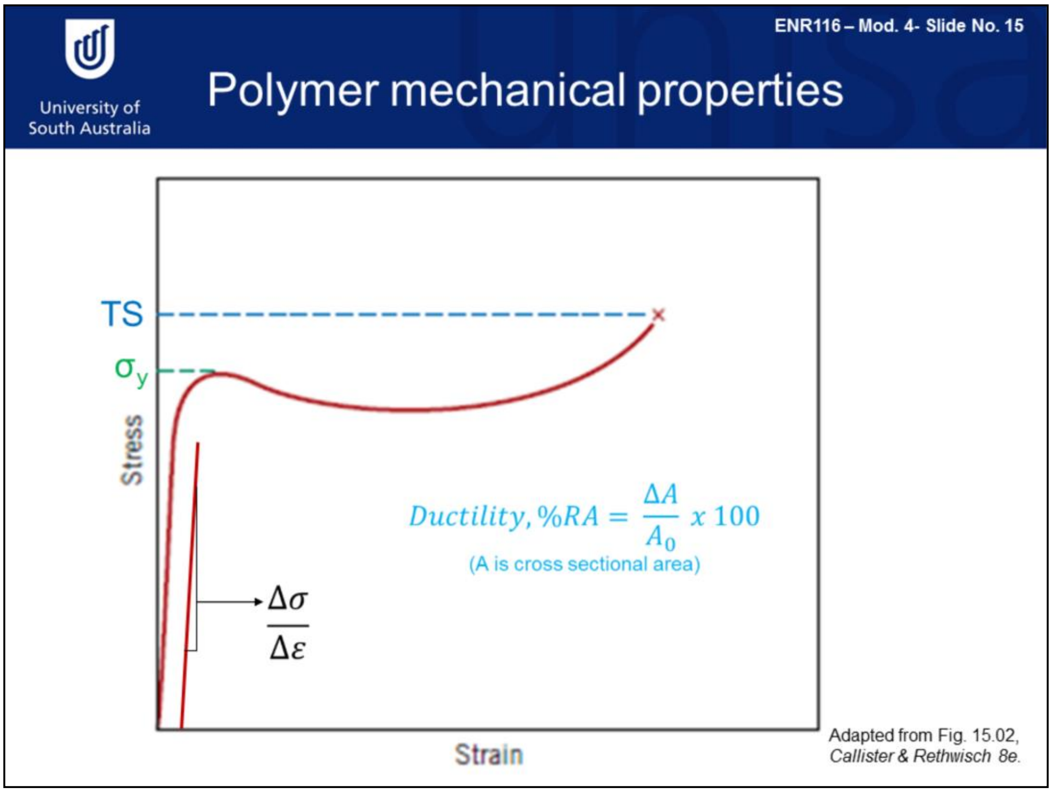
Elastomer – large recoverable strains produced at low stress levels.

Here’s a now familiar type of graph, of stress vs strain. The data shown are for 3 general types of polymer behaviour.

The red line represents brittle polymers. Here we see elastic deformation, up to the point at which fracture occurs. There is no plastic deformation.

For plastic materials, as with many metals, there is an initially elastic deformation which is followed by a yielding point and then a region of plastic deformation, up to the point at which the polymer fails.

Finally for elastic materials, we see extraordinary elastic behaviour even at very low stress levels.



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Polymer mechanical properties

$$Ductility, \%RA = \frac{\Delta A}{A_0} \times 100$$

(A is cross sectional area)

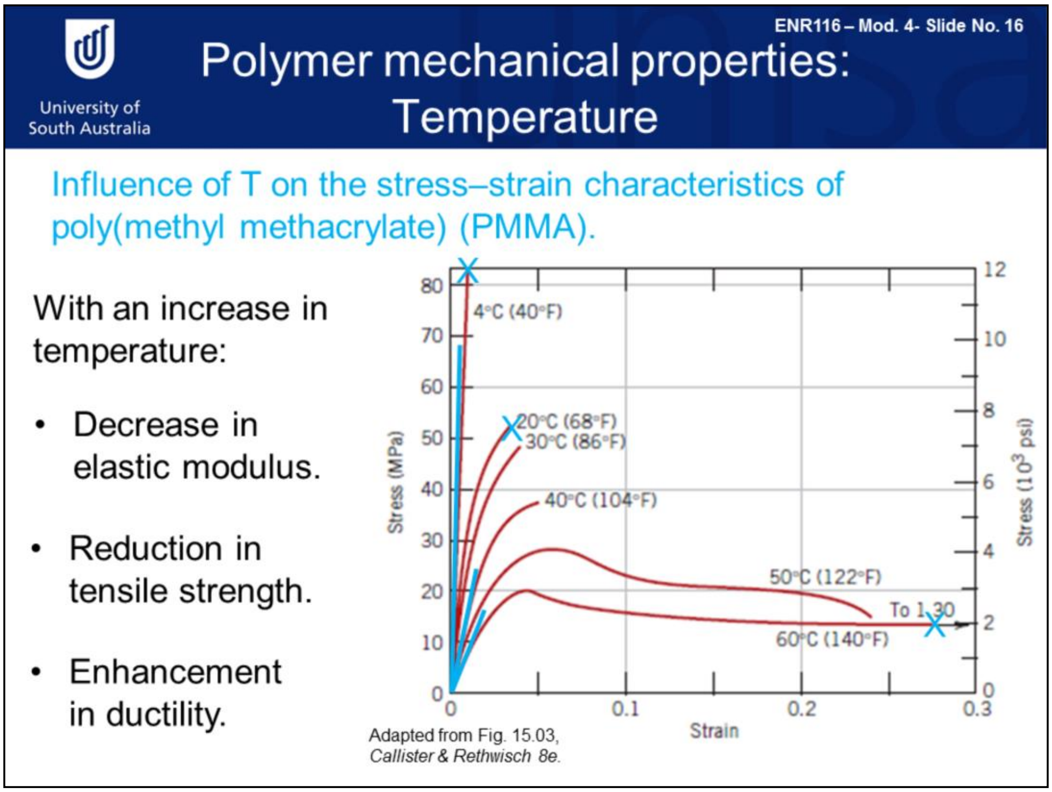
Adapted from Fig. 15.02, *Callister & Rethwisch 8e.*

The modulus of elasticity of a polymer is determined in a similar fashion to that of a metal, that is, it's the slope of the linear portion of the stress strain curve. The modulus of elasticity of polymers ranges typically from about 7 megapascals to 4 gigapascals. Compare this to metals, where the modulus of elasticity is typically in the range of 50-400 gigapascals.

An important point on the stress strain curve is the yield point. For plastic polymers, this is taken as this maximum point, here, and occurs just after the elastic to plastic transition.

The tensile strength corresponds to the stress at which fracture occurs. The tensile strength may be greater than or less the yield strength.

As a final point, the ductility of a polymer is determined in exactly the same way as for metals. However, elongation in polymeric materials can be as much as 1000%, which is considerably greater than that for the vast majority of metals.



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Polymer mechanical properties: Temperature

Influence of T on the stress–strain characteristics of poly(methyl methacrylate) (PMMA).

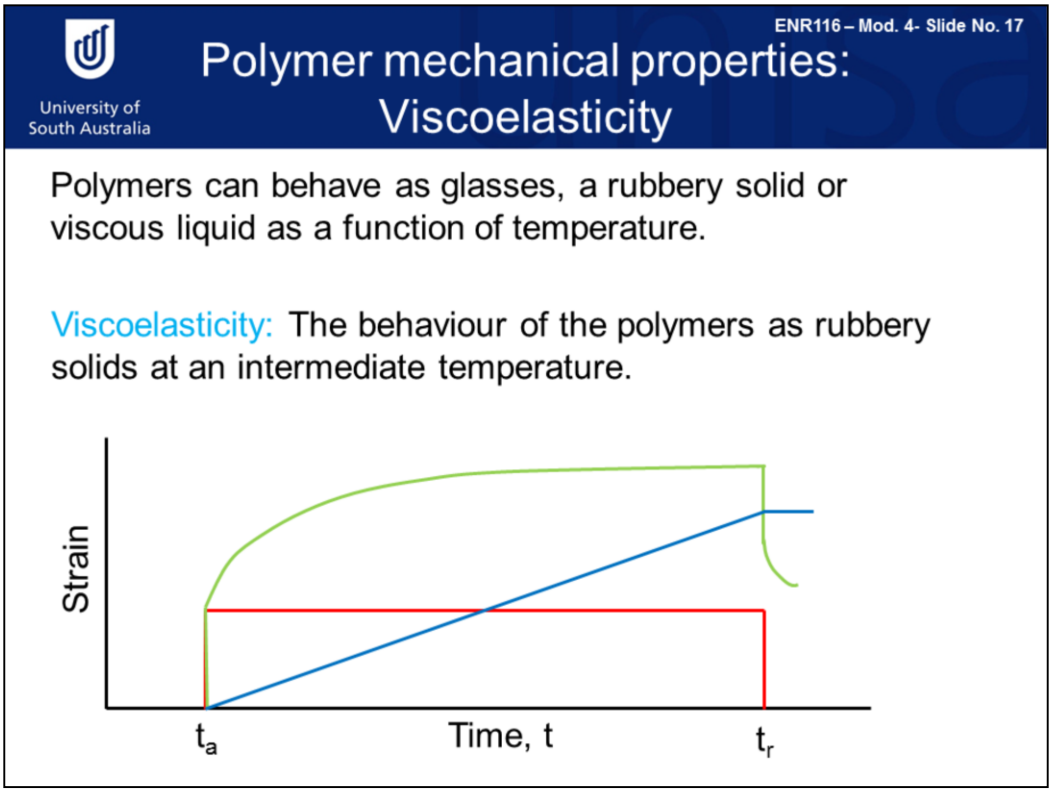
With an increase in temperature:

- Decrease in elastic modulus.
- Reduction in tensile strength.
- Enhancement in ductility.

Adapted from Fig. 15.03, *Callister & Rethwisch 8e.*

We’ve already mentioned that polymers are particularly sensitive to changes in temperature. In this slide we’ve going to explore the example of temperature upon the mechanical properties of a polymer, using PMMA as an example.

In the figure here, we see that in the range of 4-60 degrees Celsius, increasing the temperature has 3 effects: first of all, there is a decrease in the elastic modulus; secondly, there is a reduction in the tensile strength and thirdly, there is an enhancement in the ductility of the polymer. In fact, at 4 degrees the material is completely brittle.



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Polymer mechanical properties: Viscoelasticity

Polymers can behave as glasses, a rubbery solid or viscous liquid as a function of temperature.

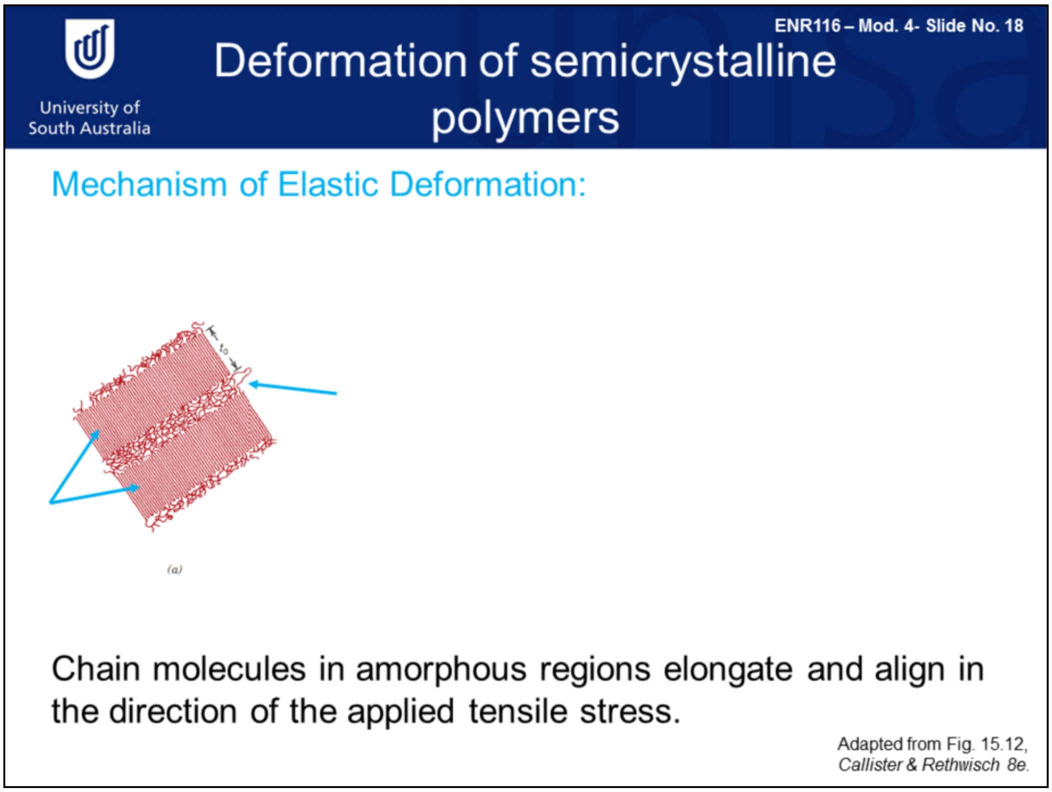
Viscoelasticity: The behaviour of the polymers as rubbery solids at an intermediate temperature.

An important concept in polymer science is that of viscoelasticity. An amorphous polymer can behave like a glass at low temperature, a rubbery solid at intermediate temperatures and as a viscous liquid at relatively high temperatures. Viscoelasticity is the term used to describe the behaviour seen in polymers during this intermediate phase - as rubbery solids, polymers exhibit behaviour that is a combination of the two extremes of purely elastic and purely viscous materials. This is viscoelasticity.

Viscoelasticity is characterised by an instantaneous elastic strain, viscous time-dependent strain behaviour. This is a difficult concept to visualise, but have a look at the plot of strain vs. time on screen now. For a purely elastic system, we apply a load at time, ta, and the material instantly deforms. When we remove the load at time tr, the material recovers immediately.

When a material is totally viscous, the strain is time dependant, and therefore does not occur as soon as the load is applied. It doesn’t completely recover after the load is removed either.

If the material is viscoelastic, we see a combination of these behaviour. Typically, when the load is applied the material will respond elastically, and deforms instantly. However, the strain then switches to a time dependant behaviour and, when the load is finally removed at time tr, it only partially recovers. The recovery continues after tr.



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Deformation of semicrystalline polymers

Mechanism of Elastic Deformation:

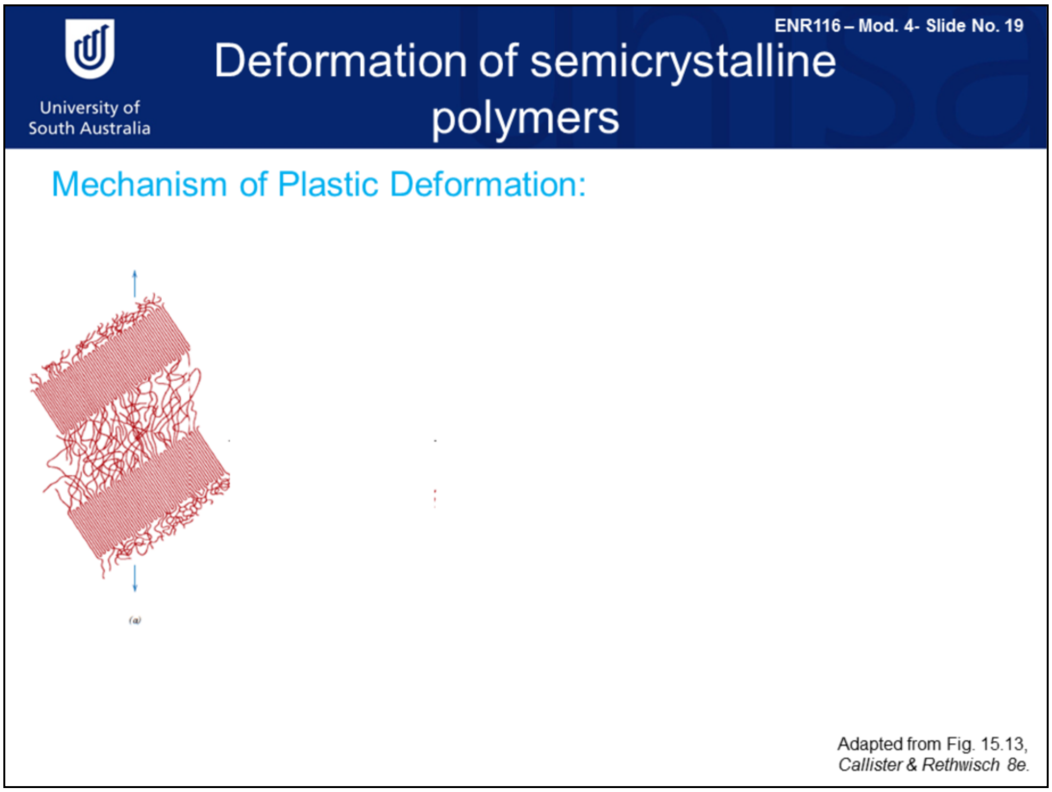
Chain molecules in amorphous regions elongate and align in the direction of the applied tensile stress.

Adapted from Fig. 15.12, *Callister & Rethwisch 8e.*

Lets have a look at the mechanism by which semi crystalline polymers deform. We know already that many polymers are composed of spherulites, the polymer version of grains, but what we don’t know is how these structures respond on a molecular level when a load is applied to the bulk.

At relatively low stress, the deformation will be elastic. We can consider the process of elastic deformation as occurring in two distinct stages. In the first instance, we start with two crystalline regions, separated by an amorphous portion. As the load is applied, the coiled and kinked chains within the amorphous region, stretching and start to align. This is stage one.

As the stress increases, the chains in the amorphous region continue to stretch and align, but this is now also accompanied by stretching in the crystalline regions. This is seen as a small but still reversible, elastic, increase in the lamella thickness. This is stage two.



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Deformation of semicrystalline polymers

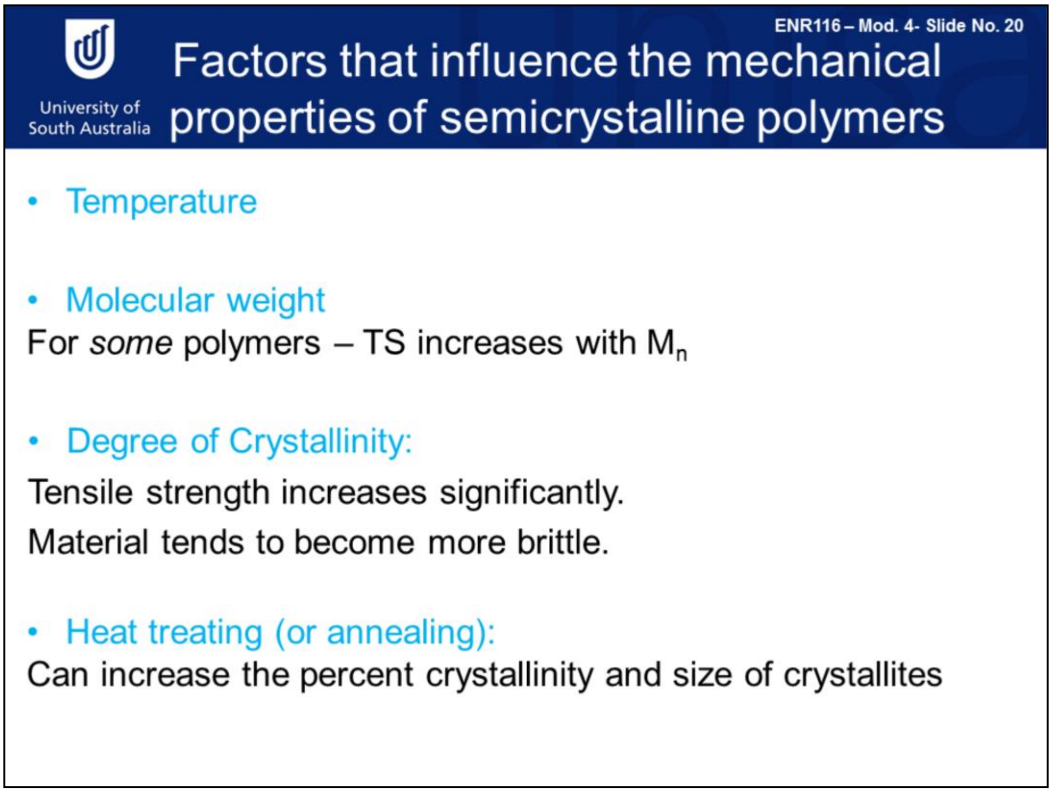
Mechanism of Plastic Deformation:

Adapted from Fig. 15.13, *Callister & Rethwisch 8e.*

As the applied stress continues to increase, the deformation transitions from elastic to plastic with permanent deformation of the lamella structures.

Plastic deformation occurs across three stages. We start with the elastically deformed structure, and then increase the applied load. The chains start to side past each other, such that the lamella begin to align with the applied stress. This is stage 3.

Eventually the stress becomes too great for the lamella to remain intact, and they begin to fragment into individual crystalline block segments. Finally, in stage 5 these segments and the tie chains align with each other in the direction of the tensile stress.



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Factors that influence the mechanical properties of semicrystalline polymers

- Temperature
- Molecular weight

For *some* polymers – TS increases with M_n

- Degree of Crystallinity:

Tensile strength increases significantly.

Material tends to become more brittle.

- Heat treating (or annealing):

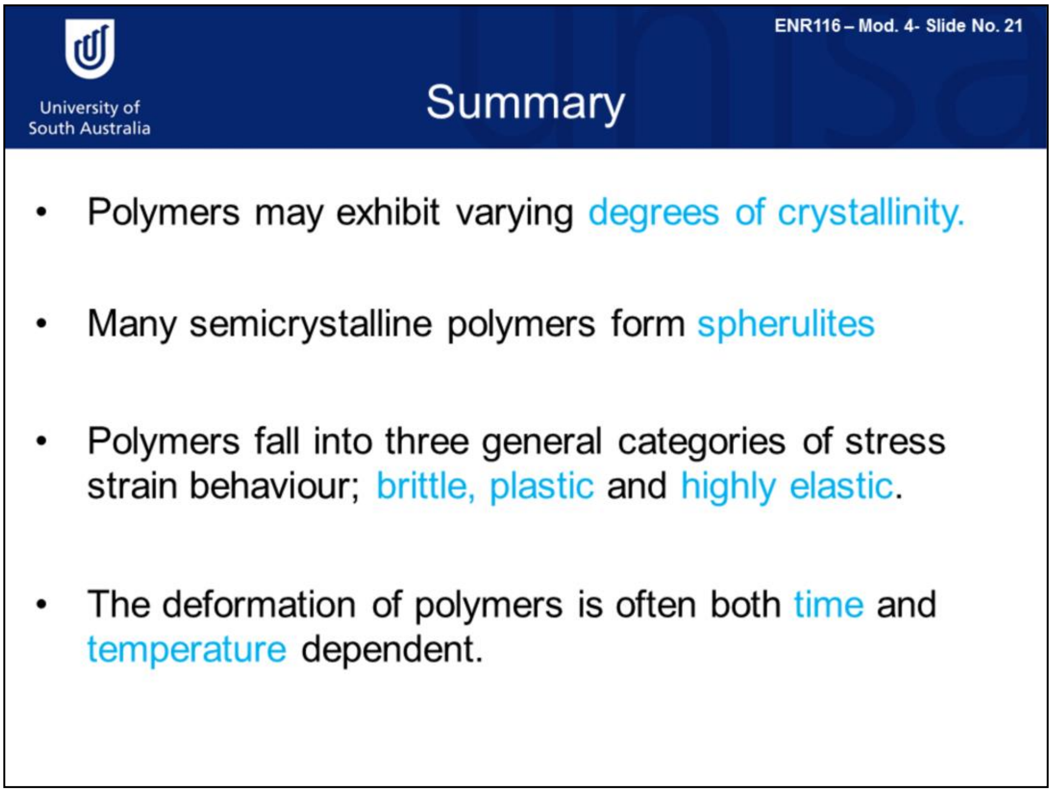
Can increase the percent crystallinity and size of crystallites

We'll finish by reviewing some of the factors that influence the mechanical properties of a semi crystalline polymer. We've already noted the significant impact that a change in temperature can have on a polymer, so we'll include it in the list, but won't discuss it further here.

The tensile strength of some polymers species will increase as the molecular weight of the sample increases. This is thought to be because of an increase in the number of entanglements as the chains get longer.

As the degree of crystallinity increases the strength of the polymer increases. Within the crystalline regions, the chains are aligned and therefore experience greater secondary bonding interactions than their amorphous counterparts, and this in turn improves the strength of the materials. However, an increase in strength is at a cost of a decrease in ductility.

Finally, heat treatments can also improve the strength of the semicrystalline polymer. The elevated temperature drives a reorientation of the polymer chains which results in greater alignment and consequently larger, more structured crystallites.



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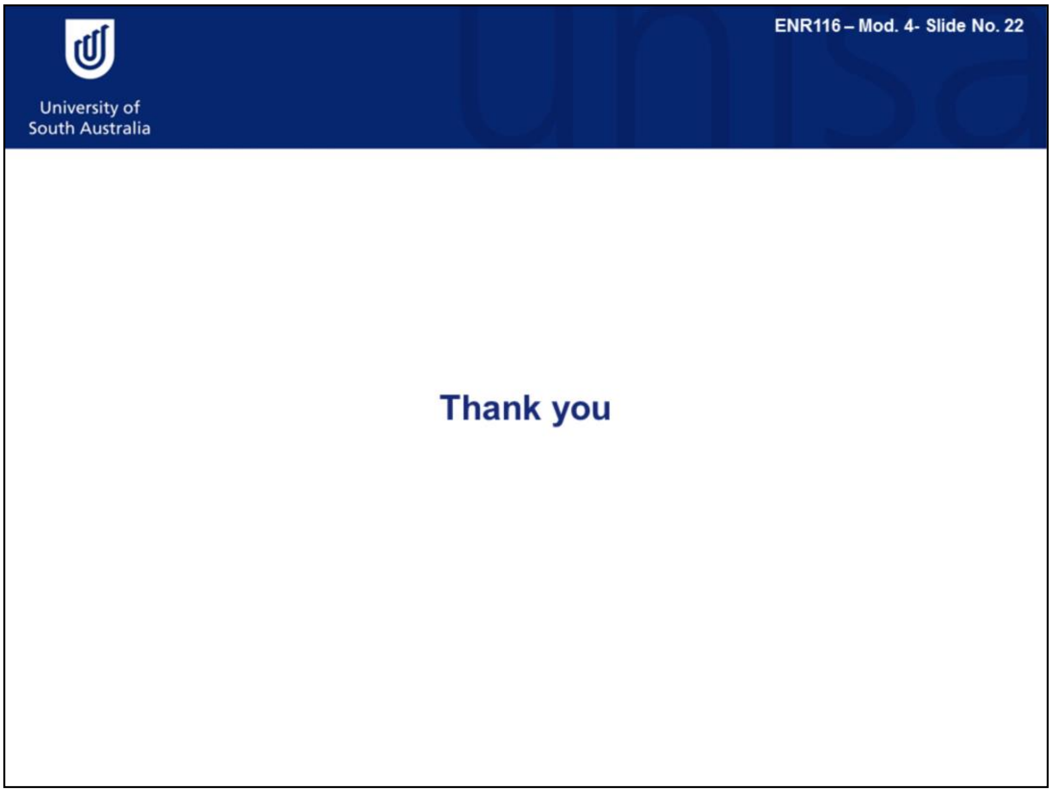
Summary

- Polymers may exhibit varying degrees of crystallinity.
- Many semicrystalline polymers form spherulites
- Polymers fall into three general categories of stress strain behaviour; brittle, plastic and highly elastic.
- The deformation of polymers is often both time and temperature dependent.

•So in summary, in the first part of this summary we focussed on polymer crystallinity, and introduced the idea that polymers may exhibit varying degrees of crystallinity, with crystalline regions interdispersed within amorphous regions.

•Many semicrystalline polymers form spherulites

•Polymers fall into three general categories of stress strain behaviour; brittle, plastic and highly elastic.



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Thank you

If you have any questions or desire further clarification please post a question or comment on the Engineering Materials Discussion Forum.