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Tutorial Class: TUT05, Tuesday 2-4pm

Question 1
Describe all structural features that affect the mechanical properties of polymers. [**5%**]

1. **The intrinsic chemistry of the polymer.** This is essentially based on what the repeat unit or monomer for the polymer looks like — the size(s) of the functional group(s) present, the number of bonds between the carbon backbone atoms (whether the resulting polymer is saturated or unsaturated), whether the polymer is a homopolymer or copolymer, the functionality of the monomer, the types of bonding which are present within the monomer etc.

2. **The size of the polymer.** This has an effect on the amount of intermolecular bonding present between polymer chains, which in turn affects the strength, ductility, and other mechanical properties of the polymer. Note that during the polymerisation process a multitude of chain sizes may occur, and thus the size of the polymer is usually represented as an "average": either the number average $\overline{M}_n$ or the weight average $\overline{M}_w$.

3. **The overall shape of the polymer.** As single chain bonds are able to rotate and bend whilst still maintaining their desired angle of $109.5°$, a single chain molecule may contain many bends, twists and kinks along its body. This results in extensive intertwining and entanglement of neighbouring chain molecules, which in turn affects the intermolecular forces and thus the mechanical properties of the polymer. The phenomenon of isomerism (where atoms are in the same order but arranged differently in their spatial arrangement) also plays a part in determining the polymer's mechanical properties.

4. **The structure of the polymer.** There are four molecular structures associated with polymers: (1) linear polymers, where repeat units are joined end to end in long single chains, (2) branched polymers, where some side-branch chains are connected to the main chain, (3) crosslinked polymers, where adjacent linear chains are chemically joined to one another through covalent bonds, and (4) network polymers, which are three-dimensional networks of multifunctional monomers. Each of these structures have certain characteristics which affect the resulting polymer's mechanical properties; for example, branched polymers have a decreased packing efficiency which lowers the overall polymer density. This in turn leads to a weaker polymer which is easier to degrade and break down.

5. **The molecular configuration, including isomerism and symmetry.** The regularity and symmetry of the side group arrangements can significantly influence the mechanical properties of the resulting polymer. Molecular configuration includes qualities such as head-to-head vs head-to-tail structure, stereoisomerism and geometric isomerism.

6. **Crystallinity.** Due to the increased degree of intermolecular bonding in crystalline regions, the mechanical properties of polymeric materials are influenced by the degree of crystallinity of the polymer. Increased crystallinity leads to a higher overall strength and increased resistance to heat softening.

Question 2

A constant load is applied instantaneously to materials at time t_s and then released at time t_f. Please describe briefly and draw schematically the strain–time responses for totally elastic, viscous, and viscoelastic behaviours. **[10%]**

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1. **Elastic behaviour:** Elastic deformation is instantaneous (i.e. independent of time), and so the strain in the material will increase instantaneously when a load is applied at t_s. The strain remains constant for the duration for which the load is applied. When the load is removed, the strain drops to zero.

2. **Completely viscous behaviour:** In response to an applied stress, deformation is dependent on time. The strain is proportional to time and hence increases linearly with time. It then remains constant until the load is removed. This deformation is not reversible or completely recovered after the stress is released.

3. **Viscoelastic behaviour:** An intermediate between elastic behaviour and viscous behaviour. There is an increase in strain when the load is applied, increasing in a non-linear way to a maximum.
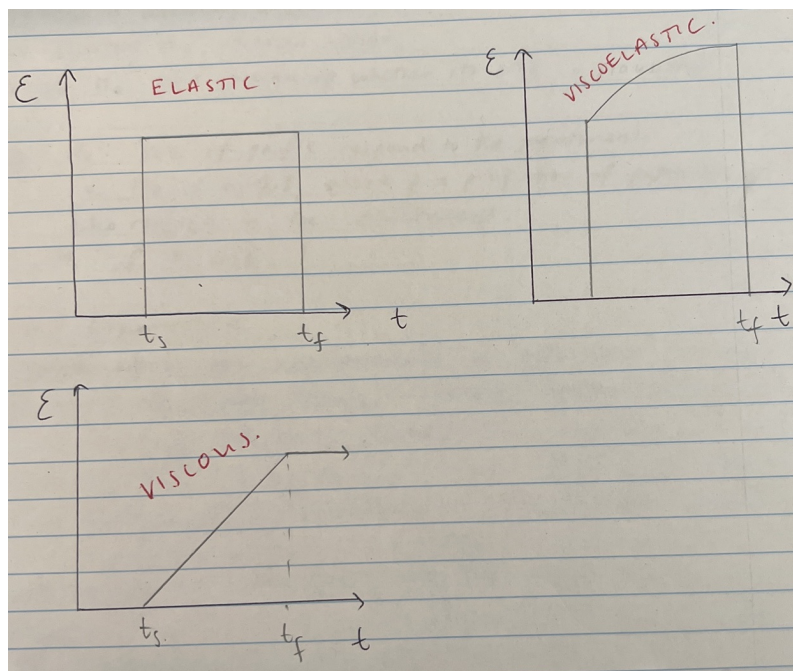

Figure 1: The three strain-time responses.

Question 3

Define the following terms: monomer, polymer, elastomer, side group, degree of polymerisation. Draw the **monomer** of polyethylene and calculate its molecular weight. **[10%]**

- **Monomer:** A stable molecule which can react together with other monomer molecules to synthesise a polymer chain. Not to be confused with repeat unit which is the part of the polymer whose repetition would produce the complete polymer chain. Monomers may be either natural (e.g. glucose) or synthetic (e.g. ethylene).

- **Polymer:** A compound of high molecular weight, the structure of which is composed of chains of small repeat units. Polymers may be either natural (e.g. proteins) or synthetic (e.g. polyethylene), depending on their monomers.

- **Elastomer:** A polymeric material that may experience large and reversible elastic deformations.

- **Side group:** A group of atoms attached to the backbone chain of a polymer. For example, the side group in polystyrene is the benzene (C_6H_6) ring.

- **Degree of polymerisation:** The average number of repeat units in a chain. Related to the number average $\overline{M_n}$ by equation 1 where m is the repeat unit's molecular weight.

$$\text{DP} = \frac{\overline{M_n}}{m} \tag{1}$$

The monomer of polyethylene is ethene, perhaps more commonly known as ethylene. It is drawn in Figure 2. It's molecular weight is the sum of 2 carbon atoms and 4 hydrogen atoms, i.e. $M = 2 \times 12.01 + 4 \times 1.008 = 28.05 \, \text{g mol}^{-1}$.
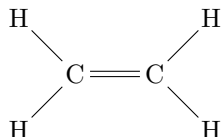

Figure 2: The monomer of polyethylene: ethene (IUPAC) or ethylene (common name).

Question 4

Describe factors that can affect degree of crystallinity of polymers. [**10%**]

- **The rate of cooling of the polymer during solidification.** In order to form a crystalline structure, the polymer chains (which are originally distributed randomly throughout the molten polymer solution) must assume some ordered configuration. For this to occur, sufficient time must be allowed for the chains to move and align themselves.

- **The molecular chemistry of the polymer.** Crystallisation is not favoured in those polymers with complex repeat units, while crystallisation is almost impossible to prevent for simple polymers (even with rapid cooling rates). The bulkier the side group, the lower the levels of crystallinity in the polymer cell.

- **The molecular weight.** As the molecular weight of a polymer increases, the length of the individual chains become longer. Hence, it is more difficult for all regions along the chains to align in order to produce a crystalline region.

- **The chain configuration of the polymer.** Linear polymers display high crystallinity, branched polymers display moderate crystallinity, and crosslinked and network polymers are almost always totally amorphous. Furthermore, isotactic and syndiotactic polymers are more likely to form crystalline regions than their atactic counterparts.

Question 5

For the following two polymers, is it possible to determine whether one polymer has a higher melting temperature than the other? If yes, note which has the higher melting temperature and then cite reason(s). If no, explain why. [**10%**]

1. Isotactic polystyrene that has a density of $1.12 \, \text{g/cm}^3$ and a weight-average molecular weight of $150\,000 \, \text{g mol}^{-1}$.

2. Syndiotactic polystyrene that has a density of $1.10 \, \text{g/cm}^3$ and a weight-average molecular weight of $125\,000 \, \text{g mol}^{-1}$.

Yes; the isotactic polystyrene will have a higher melting temperature. This is because the melting temperature of a polymer is a function of the strength of the intermolecular bonds between the polymer chains.

1. Polymers exhibit secondary bonding (hydrogen bonding and the van der Waals force) whose strength is inversely related to the intermolecular distance between molecules. Hence, a material with molecules which are closer together will exhibit stronger intermolecular forces and thus have a higher melting temperature.

2. The "amount" of the intermolecular force between molecules is a function of the surface area of the molecules; a greater surface area between atoms allows for secondary bonding to occur more freely. Hence, molecules with longer chains will exhibit greater amounts of intermolecular forces, thus resulting in higher melting temperatures.

The isotactic polystrene has a greater density than the syndiotactic polystyrene ($1.12\,\mathrm{g/cm^3}$ vs $1.10\,\mathrm{g/cm^3}$ respectively) which effectively means the polymer strands are packed closer together. Also, the weight-average molecular weight of the isotactic polystyrene is higher, meaning that the strands in this polystyrene are on average longer than those in the syndiotactic polystyrene. Hence, by points 1 and 2, the isotactic polystyrene will have a higher melting temperature.

Question 6

List factors that affect the mechanical properties of composite materials. [**10%**]

- The interfacial structure between the matrix and the dispersed phase.

- Production techniques/chemical treatments.

- Mechanical properties of the matrix and the dispersed phase.

- Volume fraction, distribution, orientation, size and shape of the dispersed phase.

Question 7

Table 1 lists four hypothetical aligned fiber-reinforced composites (labelled A through D), along with their characteristics. On the basis of these data, rank the four composites from highest to lowest strength in the longitudinal direction, and then justify your ranking. [**15%**]

Table 1: 4 hypothetical aligned fiber-reinforced composites along with their characteristics.

Composite	Fiber Type	Vol. Fraction Fibers	Fiber Strength (MPa)	Avg. Fiber Length (mm)	Critical Length (mm)
A	glass	0.20	3.5×10^3	8	0.70
B	glass	0.35	3.5×10^3	12	0.75
C	carbon	0.40	5.5×10^3	8	0.40
D	carbon	0.30	5.5×10^3	8	0.50

The strength of these fiber-reinforced composites depends largely on the fiber type and the volume fraction of the fibers. As carbon fibers are stronger than glass fibers, we instantly know that C and D are stronger than A and B. Furthermore, as a greater volume fraction of fibers increases the strength of the material, C is stronger than D, and B is stronger than A.

Hence the order of strength of these composites from strongest to weakest is $C > D > B > A$.

> **Question 8**
> Briefly describe (a) addition polymerisation and condensation polymerisation, and (b) 3 forming techniques for plastics learnt in Materials 1. **[10%]**

Q8.1 Addition polymerisation

Additional polymerisation is the process whereby individual monomer units are added one-at-a-time in order to form a polymer chain. There are three main steps: initiation, propagation and termination.

1. **Initiation:** A initiator molecule undergoes an addition reaction with an unsaturated monomer. The initiator molecule must be 'active'; that is, it must have a free radical which can 'attack' the double bond of the monomer and allow the initiator to bond to the molecule. This is represented in Figure 3.
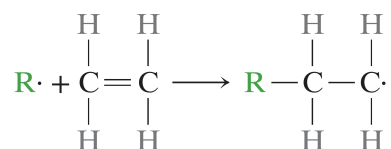
Figure 3: Initiation step of the addition polymerisation process.

2. **Propagation:** The addition reaction continues with sequential unsaturated monomer units joining the polymer chain through the reaction of free radicals with the double bond, as seen in Figure 4.
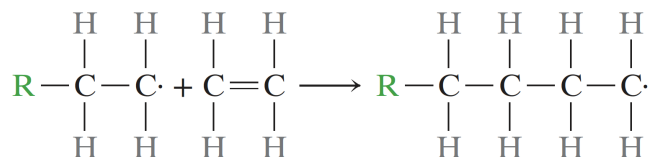
Figure 4: Propagation of the addition polymerisation process.

3. **Termination:** The propagation process can terminate in two ways: (i) the active ends of two propagating chains may link together to form one molecule in a *combination* reaction (see Figure 5), or (ii) two chains may react in a *disproportionation* reaction to again form two chains which are chemically inert (see Figure 6).
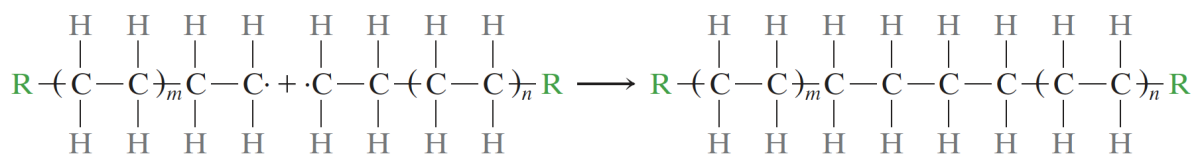
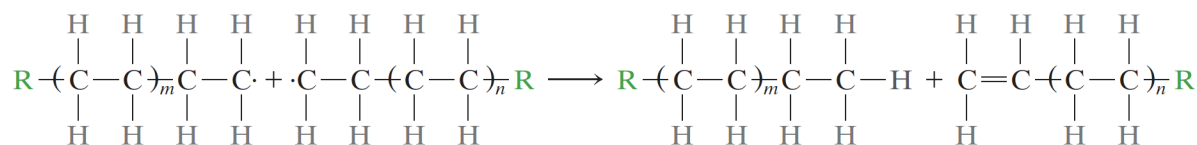Figure 5: A combination reaction of two active polymer chains.

Figure 6: A disproportionation reaction resulting in two 'dead' chains.

Q8.2 Condensation polymerisation

Condensation polymerisation is the process where a polymer is synthesised through the repetition of *condensation reactions*. These involve two molecules, each with their own particular functional groups, undergoing a chemical reaction characterised by the loss of a small molecule such as water (thus being named *condensation* reactions). For example, consider the reaction between dimethyl terephthalate and ethylene glycol to produce polyethylene terephthalate illustrated in Figure 7. The mechanism of this reaction is such that
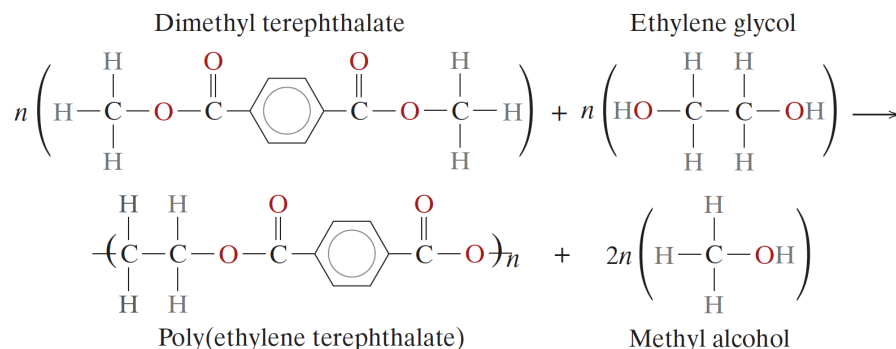

Figure 7: Producing PET through a condensation reaction.

- Each CH_3 group at the terminal of the dimethyl terephthalate molecule reacts with an alcohol ($-OH$) group at the end of the ethylene glycol molecule. This produces 2 methyl alcohol molecules (note the $2n$ stoichiometry in the reaction above).

- The remaining terephthalate molecule reacts with the remaining ethane molecule to produce the main body of the polymer, polyethylene terephthalate.
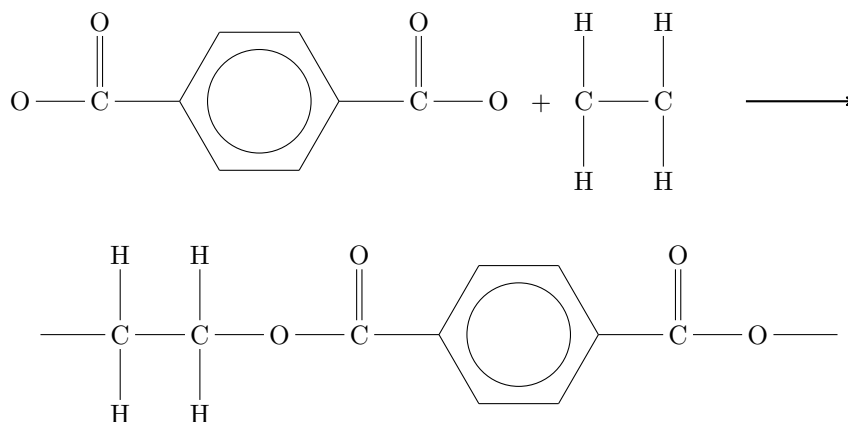
Q8.3 Forming techniques for plastics

Molding is the most common method for forming plastic polymers. It essentially involves liquefying the polymer and then shaping it through one of the many molding techniques available such as compression, transfer, blow, injection, and extrusion. Three of these are described below.

1. **Compression and transfer moulding:** The idea of compression moulding is similar to slip-casting for ceramics; essentially, the liquid polymer (which has been mixed with any additives if necessary) is placed in a female mould which is completely stationary. Then, the male mould, which is placed on a moveable hydraulic, is able to close itself around the female mould. Heat and pressure are applied which causes the material to

conform to the mould shape. Transform moulding is simply a variation of compression moulding and involves the solid polymeric material first being melted in a separate chamber. Afterwards, the molten material is injected into the mould chamber. This process allows for a more even pressure distribution over all the final surfaces of the material.

2. **Injection moulding:** In this process, the material starts out as solid pellets which are fed into the moulding machine by a plunger. This ram pushes the pellets into a heating chamber, where the polymeric material is melted to form a viscous liquid. Once again through the use of the ram, the liquid is squeezed through a nozzle into the mould cavity and pressure maintained until the plastic has solidified. The mould is then open and the process is complete. Injection moulding is the most widely used and fastest technique used for fabricating thermoplastic materials.

3. **Blow moulding:** Blow molding is a manufacturing process that is used to create hollow plastic parts by inflating a heated plastic tube until it fills a mould and forms the desired shape. First, a *parison* is extruded. While still in a semimolten state, the parison is placed in a two-piece mould having the desired container configuration. The hollow piece is formed by blowing air or steam under pressure into the parison, forcing the tube walls to conform to the contours of the mould. See Figure 8 for a schematic of the blow moulding method.
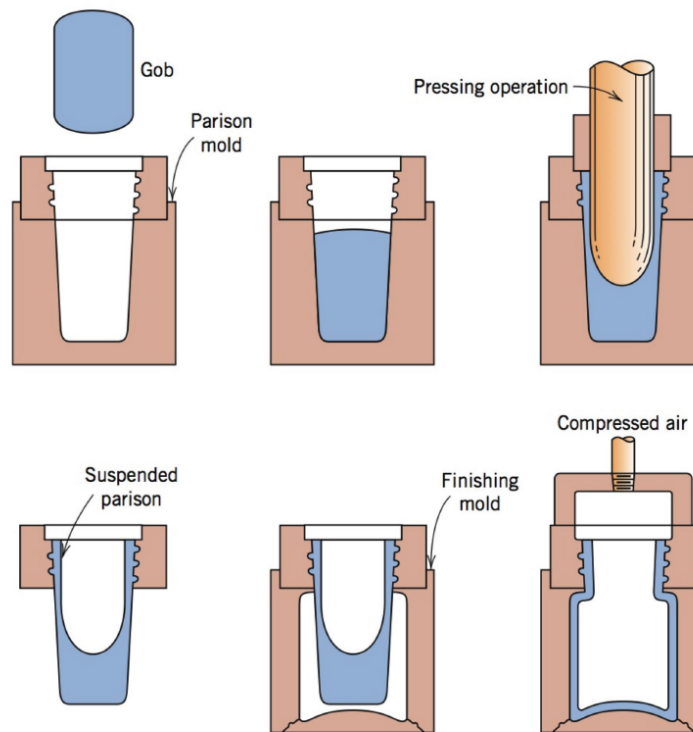

Figure 8: Blow moulding schematic.

> **Question 9**
>
> For continuous and aligned fibre composites, prove that the Young's modulus of the composites along the longitudinal and transverse directions can be described using the equations:
>
> $$E_{cl} = E_m V_m + E_f V_f \qquad \text{and} \qquad (2)$$
>
> $$E_{ct} = \frac{E_m E_f}{V_m E_f + V_f E_m} \qquad (3)$$
>
> respectively. [**15%**]

Q9.1 Along the longitudinal direction

The load on the composite equals to the sum of the loads on the fibres and the load on the matrix:

$$F_C = F_F + F_M \qquad (4)$$

As $\sigma = F/A \implies F = \sigma \times A$,

$$\sigma_C \times A_C = \sigma_F \times A_F + \sigma_M \times A_M \qquad (5)$$

Dividing through by A_C,

$$\sigma_C = \sigma_F \cdot \frac{A_F}{A_C} + \sigma_M \cdot \frac{A_M}{A_C} \qquad (6)$$

As the area fractions are equal to the volume fractions (by assumption),

$$\sigma_C = \sigma_F V_F + \sigma_M V_M \qquad (7)$$

Further by assumption, $\varepsilon_C = \varepsilon_M = \varepsilon_F$. Dividing through by this strain,

$$\frac{\sigma_C}{\varepsilon_C} = \frac{\sigma_F}{\varepsilon_F} V_F + \frac{\sigma_M}{\varepsilon_M} V_M \qquad (8)$$

$$\implies E_{cl} = E_F V_F + E_M V_M \qquad (9)$$

Q9.2 Along the transverse direction

For this condition, it is assumed that $\sigma_C = \sigma_M = \sigma_F$. Therefore

$$\varepsilon_C = \varepsilon_M V_M + \varepsilon_F V_f \qquad (10)$$

$$\frac{\sigma_C}{E_{ct}} = \frac{\sigma_M}{E_M} V_M + \frac{\sigma_F}{E_F} V_F \qquad (11)$$

$$\frac{1}{E_{ct}} = \frac{V_M}{E_M} + \frac{V_F}{E_F} \qquad (12)$$

$$= \frac{E_F V_M + E_M V_F}{E_M E_F} \qquad (13)$$

$$\implies E_{ct} = \frac{E_M E_F}{E_F V_M + E_M V_F} \qquad (14)$$

> **Question 10**
>
> List three main classification of engineering Fibre-reinforced composites. Name one example of both the dispersed phase material and matrix phase material for each classification. [**5%**]

Q10.1 Continuous aligned

- Kevlar composite

- Dispersed phase - Kevlar (Aramid fibres)

- Matrix phase - epoxy resin

Q10.2 Discontinuous aligned

- Carbon fibre

- Dispersed phase - carbon fibre

- Matrix phase - epoxy (or polyester)

Q10.3 Discontinuous random

- Gordon-Aerolite

- Dispersed phase - high grade flax fibre

- Matrix phase - phenolic resin