High strength high modulus Fibres

Module 2: FAQ

Q1. Define aramids.

Ans: A manufactured fibre in which the fibre-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide (-CO-NH-) linkages are attached directly between two aromatic rings.

Q2. How are the aramids produced?

Ans: These are generally prepared by **low temperature solution polycondensation** of various aromatic amines and diacids or diacid chlorides. The polymerization medium is an inert solvent for at least one of the reactant and solvent or swelling agent for the polymer (preferably a solvent to allow the completion of polymerization).

Q3. What are liquid crystals?

The liquid crystal state is a distinct phase between the crystalline (solid) and isotropic (liquid) states, here the molecules have an order (like solids) as they points along a common axis, called the director and they flow like liquids.

Q4. Is Aramid a thermotropic liquid crystal ?

Ans: No, It is lyotropic

Q5. What are the critical parameters during this polymerization of aramids process?

- Stochiometry
- Solvent composition
- Temperature
- Reactant concentration
- Mixing

Q6. With the help of chemical reactions briefly explain one suitable technique for synthesis of polymer for Kevlar fibre?



Q7. Meta aramids have superior : temperature resistant or mechanical properties compared to para aramids

Ans: Temperature resistance

Q8. Name one solvent for Kevlar

Ans: Concentrated sulphuric acid

Q9. Explain how the spinning of liquid crystal polymers is different from conventional fibres?

Ans: In case of liquid crystal polymers one can spin higher concentrations as beyond the critical concentration with increase in concentration the viscosity of the solution decreases unlike the other non-liquid polymer solution where the reverse happens (viscosity increases) resulting in problematic or no spinning

Q10. Explain why a particular concentration and temperature is used in aramid spinning.

Ans: This is because it shows liquid crystal behaviour under such conditions.

Q11. "Aramid fibres have very high specific strength". Justify this statement on the basis of microstructure of the fibre.

Ans: Bonding of rigid phenylene rings in para position helps in acquiring a high degree of alignment of long straight polymer chains parallel to fibre axis. The occurrence of amide groups at regular intervals along the linear chain facilitate extensive hydrogen bonding and this leads to a high degree of crystallinity and thus high specific strength.

Q12. Explain the role of annealing or heat treatment in the production of aramid and thermotropic polyesters?

Ans: Heat treatment of aramid and thermotropic polyesters increases their tenacity and modulus as drawing is not required because the fibres are already highly oriented. It is probable that the heat treatments promote molecular chain displacement, thus allowing the formation of regular chain bonding between highly oriented regions of crystalline order leading to increase in crystallinity, structure perfection, and orientation.

Q13. Melt spun aramids have superior properties

Ans: (False) because aramids are not melt spun as they have a very high melting point ~ $500 \,^{\circ}$ C and degrade before they melt.

Q14. Name two solvents suitable for polymerization

Ans: The suitable solvents are

- HMPA/NMP (2:1 vol. /vol.)
- 1:1.4 ratio of DMAc: HMPA

Q15. What structural characteristics are necessary to improve the compressive properties of fibres produced from rigid rod polymers?

Ans: Rigid rod like polymers with the possibility of forming strong intermolecular hydrogen bonds are desirable.

Q16. Why do fibres obtained from rigid rod polymers like PBO have very poor compressive strength?

Ans: Because they don't have any group which can help in inter molecular hydrogen bonding in the lateral direction.

Q17. Explain briefly the synthesis scheme (including the monomer selection) for a polymer with high compressive strength.

Ans: Monomers were selected on the basis if they can result in a polymer with hydroxyl groups at appropriate position to contribute to the hydrogen bond network envisioned for improved lateral strength so polymerization of 2,3,5,6-tetra aminopyridine with 2,5-dihydroxyterephthalic acid (DHTA) was done. The reactions are given below:

2,3,5,6- Tetraaminopyridine (TAP)

2,5- Dihydroxyterephthalic acid



Q18. Write down the main categories of rigid rod polymers

Ans:

- Polybenzazole
- Polybenzimidazole
- Polypyridobisimidazole

Q19. Why M5 has higher compressive strength compared to PBO?

Ans: The rod like polymer molecules feature internal hydrogen bonds between -O-H groups and imidazole N atoms, and a network in both directions perpendicular to the rod like chains between imidazole N-H atoms and the O-H groups. This leads to a high shear modulus and shear strength and thus to good compressive properties of the M5 fibre

Q20. What is TD complex?

Ans: TAP:DHTA 1:1 complex

Q21. How PIPD structure is different from PBO and PBT



One can readily observe that the structure of PIPD or M5 is similar to PBO and PBT except for the following differences

- 1. The central aromatic ring in M5 is pyridinyl rather than benzyl
- 2. Presence of hydroxyl groups at 2-and 5-positions of diacid and
- 3. The X group in benzazole ring structure is NH.

Q22. What are thermotropic liquid crystals

Ans: Wholly aromatic polyesters that form liquid crystalline phase over a certain temperature range in the melt are called thermotropic liquid crystalline polymers (TLCP).

Q23. How are thermotropic liqid crystals different from conventional thermoplastics?

Ans: Flexible polymers such as PET generally maintain their viscosity in low shear region, but in case of thermotropic liquid crystal polymers the viscosity falls linearly as shear rate increases (even in low shear rate region).

Q24. Explain the effect of heat treatment on the thermotropic aromatic polyester fibres.

Ans: On heat treatment below the melting temperature (250-300 $^{\circ}$ C) for several hours, tenacity of 23-28 g/denier tenacity is achieved, however the modulus increases only slight, the crystallinity increases to 20% and molecular weight increases by three times.

Q25. The tenacity of the thermotropic polyester fibres increases substantially on heat treatment. Why? Explain in one line.

Ans: Because of the increase in crystallinity and moleculer weight

Q26. What are the different approaches for lowering the melting point.

Ans:

a) By introducing different lengths of comonomers / or aliphatic flexible groups to disturb the ordered structure along the fibre direction

- b) kinks can be designed into chemical structures
- c) a disturbance can be made in the lateral packing by introducing large range of pendant groups

Q27. What is vectran?

Ans: It is a commercially available TLCP fibre



Q28. How is it polymerized?

Ans: It is obtained by acetylation polymerization of p-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA)



Q29. How are these spun?

Ans: The polymers with intrinsic viscosity in the range of 1.5-3 dL/g can be spun easily from their liquid crystalline state, in a temperature range of 280 °C to 360 °C. The spinning process for these thermotropic copolyesters is similar to the conventional PET melt spinning process.

In case of thermotropic liquid crystal polymers the viscosity falls linearly as shear rate increases (even in low shear rate region). These fibres attenuate rapidly and solidify within 10 cm from the orifice without exhibiting any 'die swell'.

Q30. The textile grade acrylic polymer is not suitable as precursor for carbon fibre." Why?

Ans: Because defect free highly oriented fibres with high tenacity and modulus are required as the precursor fibre which textile grade acrylic fibre doesn't have.

Because fibre with higher surface area was required (which textile grade acrylic polymer don't have as they can't be drawn to 12-16 times) as stabilization process in carbon fibre making is diffusion controlled and rate of diffusion is in fact the rate determining step of cyclization reaction.

Q31. What structural characteristics in the carbon fibre make it suitable as a high performance fibre (of outstanding mechanical properties) ?

Ans: Carbon fibres consist of polyaromatic carbons and exist as turbostatic carbon. Carbon fibres have a sheath core type macroscopic structure, with greater perfection and of packing and orientation of graphite layers and larger crystallites in the sheath.

Q32. What is the role of comonomer in acrylic precursor suitable for carbon fibre?

Ans: These monomer lowers the stabilization temperature. Incorporation of neutral acrylate monomers slows down the cyclization reaction and reduces the heat release rate.

Q33. How would you check the level of thermo-oxidative stabilization of stabilized acrylic precursor fibres?

Ans: As this is an exothermic reaction, the manner in which heat dissipation takes place decides the further performance of the fibre

Q34. Briefly describe the important steps (with process conditions) for producing carbon fibre from acrylic precursor.

Ans: The manufacturing of carbon fibres based on acrylic fibres involves three successive stages of heat treatment:



Q35. Explain the production of carbon fibres from both cellulosic and pitch precursors.

Ans: Cellulosic Based Carbon Fibre



Q36. Write the Structure of turbostatic carbon

Ans:



Q37. Write the Structure of oxidized PAN fibre

Ans:



Q38. Why is the stabilization necessary prior to carbonization?

Ans: It converts the PAN precursor into thermally stable structure capable of withstanding high temperature processing in subsequent steps

Q39. Write the sequence of reactions occurring during stabilization

Ans: The three main phenomenon occurring during stabilization process are:

- Mass transfer
- Heat transfer
- Shrinkage

Q40. During stabilization process role of heating rate is very critical, why?

Ans: Because it is an exothermic process and slow rate is required to properly complete the cyclization reaction as high rate will lead to incomplete cyclization with improper stabilization thus leads to weak carbon fibres.

Q41. Why carbonization of pan based stabilized fibres carried out in two steps

Ans: Beacause for initial temperature of 600 $^{\circ}$ C low heating rate (less than 5 $^{\circ}$ C/min) is required as it is a crucial step and involves intermolecular crosslinking of stabilized fibre, elimination of water or other gases and the low rate keeps the mass transfer slow as a faster mass transfer at higher heating rates may cause surface irregularities in the form of pores and above 600 till 1300 $^{\circ}$ C higher heating rates can be used because of the reduced possibility of damage due to exothermic reaction.

Q42. The cellulosic fibre most suitable for carbon fibre is:

Ans: Viscose rayon

Q43. What kind of products are formed on treatment of cellulose at 400 C

Ans: Formation of carboneous intermediates and four carbon residues

Q44. Structure of four component carbon residue

Ans:



Q45. What are the main steps for conversion of pitch to carbon fibre

Ans:



Q46. Describe the polymer characteristics required for gel spinning.

Ans: A polymer solution, where just sufficient entanglements exist between polymer chains, the spinning stresses are able to transfer to all the chains without any hindrance.

Q47. Explain the fundamental concept used for producing ultra high molecular weight PE fibres.

Ans: The gel spinning concept was used where the polymer is extruded at conditions where it forms gel structure which allows the individual molecular chains to connect optimally with each other, and on coagulation, form a network structure which is able to undergo very high draw ratios to give fibre with high tensile strength and modulus. In case of polyethylene the ultra-drawing can be applied as the crystallization during drawing does not prevent drawability due to weak interactions between polymer chains.

Q48. What are the structural requirements of an ideal super strong fibre?

Ans:

- Suitable polymer solution, where just sufficient entanglements exist between polymer chains, the spinning stresses are able to transfer to all the chains without any hindrance
- the highest values of theoretical tenacity and modules among flexible polymers
- simple planar zigzag chain structure without any bulky side group
- lack of high inter-molecular interactions
- high crystallinity
- possibility of producing ultra high molecular weight polymer

Q49. Explain how the gel spinning technique is used to create an ideal structure in PE fibres?

Ans: Using gel spinning technique when the polymer is extruded it forms gel structure which allows the individual molecular chains to connect optimally with each other, and on coagulation, form a network structure which is able to undergo very high draw ratios to give fibre with high tensile strength and modulus.

Q50. State whether the following statements are TRUE or FALSE. Give justification for your answer and <u>IF FALSE</u>, also write the correct statement.

- a. For the preparation of carbon fibres from PAN precursor, the carbonization and graphitization are carried out in nitrogen atmosphere. (True)
- b. In carbon fibres the perfect orientation of graphite crystals is not desirable.(True)
- c. As-spun thermotropic aromatic polyester fibres are not drawable but the properties of the fibres can be enhanced by heat treatment.(True)
- d. In the lyotropic liquid crystalline polymers the concentration at which the liquid crystalline behavior is observed depends primarily upon the molecular weight of the polymers. False, it depends on both molecular weight and temperature of the solution
- e. The diameter of the electrospun nanofibres can be decreased only by increasing the applied field.

(False) Can also be decreased by using lower molecular weight polymer or the lower concentration, or by increasing the temperature and suitably altering the humidity.