

G. S. Mandal's

**Maharashtra Institute of Technology, Aurangabad**

(An Autonomous Institute)

END SEMESTER EXAMINATION

**Second Year B.Tech (Plastic and Polymer Engineering) – Feb/Mar-2023**

Course Code: PPE202

Course Name: Introduction to Polymer Engineering

Duration: 2 Hrs

Max. Marks: 50

Date:

Q. 1	Solve/Answer the following questions	
	Answer/Solution	Stepwise Marking Scheme
a)	A polymer is a substance or material consisting of very large molecules called macromolecules, composed of many repeating subunits. Due to their broad spectrum of properties, they play essential and ubiquitous roles in everyday life. For example, polyethylene, polypropylene, proteins, etc.	• 2 marks for the generic definition
b)	Any polymeric material such as neoprene, isoprene, butyl rubber, SBR, etc. as rubber. Any polymeric material such as nylon, polyester, cellulose, etc as fibre.	• One mark for naming any material from the lot
c)	A copolymer is a polymer formed when two (or more) different types of monomers are linked in the same polymer chain, as opposed to a homopolymer where only one monomer is used.	• 2 marks for the generic definition. Incomplete but indicative can be given 1 mark.
d)	When a polymer is crystalline, its molecular chains are organized and oriented in a fixed direction. Most crystalline polymers have amorphous regions, which means crystalline polymers are never completely crystalline. Hence, they are referred to as semi crystalline	• Two marks for the correct reason.
e)	Glass transition temperature (T <sub>g</sub> ) is the temperature of transition from glassy state to rubbery state or we can say below which polymer	• Two marks for

	<p>behave as a glassy material and above which it behaves as a rubbery material. Glassy state is hard and brittle while rubbery state is soft and flexible.</p>	<p>generic definition of the term as asked. Incomplete but indicative can be given one mark.</p>
f)	<p>The right monomer for polyethylene is</p> <p>i. <math>\text{CH}_2 = \text{CH}_2</math></p> <p>The problems with other two chemical formulas are given as follows:</p> <p>i. <math>(\text{CH}_2 = \text{CH}_2)_n</math></p> <p>This represents the polymer itself which is polyethylene and hence is incorrect.</p> <p><math>\text{CF}_2 = \text{CN}_2</math></p> <p>This represents an incorrect monomer with the presence of F and N atoms in the structure.</p>	<ul style="list-style-type: none"> <li>• One mark for identifying the right answer</li> <li>• One mark for mentioning why each of the other two is wrong.</li> </ul>
g)	<p>Macromolecule, any very large molecule, usually with a diameter ranging from about 100 to 10,000 angstroms (<math>10^{-5}</math> to <math>10^{-3}</math> mm). Macromolecules are composed of much larger numbers of atoms than ordinary molecules.</p> <p>Example of macromolecule includes polymers, carbohydrates, proteins etc.</p>	<ul style="list-style-type: none"> <li>• One mark for each definition as given here/generic in nature.</li> <li>• One mark for the example.</li> </ul>
h)	<p>Commodity plastics or commodity polymers are plastics produced in high volumes for applications where exceptional material properties are not needed (such as packaging, food containers, and household products). For eg. LLDPE, HDPE, PP, etc.</p>	<ul style="list-style-type: none"> <li>• One mark for each material characteristics and one for example.</li> </ul>
Q.2	<p>Optical properties are related to both the degree of crystallinity and the actual polymer structure. The effect of polymer structure on refractive index, clarity/transparency, reflectance and absorbance can be explained as follows (<i>Any two can be considered as complete answer</i>):</p> <p>i. Refractive Index: The velocity of light passing through a polymer is affected by the polarity of the bonds in the molecule. The</p>	<ul style="list-style-type: none"> <li>• Two marks for meaning of optical properties.</li> <li>• Three marks for description of effect of</li> </ul>

	<p>polarizability <math>P</math> of a polymer is related to the number of molecules present per unit volume, and the polarizability of each molecule is related to the number and mobility of the electrons present in the molecule. The RI values usually increase as the number of polarizing groups present in the molecule increases. If a material is structurally isotropic, as in the case of an unstressed amorphous polymer, then it is optically isotropic, and a single <math>n</math> value (and other related optical properties) can be assigned.</p> <p>ii. Clarity: Clarity is noted when the light passes through a homogeneous sample, such as a crystalline, ordered polymer or a completely pure amorphous phase. Interference occurs when the light beam passes through a heterogeneous sample in which the polarizability of the individual units varies slightly, such as a polymer containing both crystalline and amorphous regions.</p> <p>iii. Absorption and Reflectance: Heterogeneity of <math>n</math> values is related to a number of factors, including end groups, differences in density between amorphous and crystalline regions, anisotropic behavior of crystalline portions, incorporation of additives, and the presence of voids. The reflection <math>R'</math> is related to the magnitude of the difference between the <math>n</math> value of the polymer, <math>n_1'</math> and that of air, <math>n_2'</math>. Charring of polymers, such as PS, is accompanied by a darkening of the residue through the formation of highly aromatic intermediate networks. Black polymers, such as polyacetylene, absorb all visible light, but opaque polymers scatter the incident light.</p>	<p>structure on each optical property</p>				
<p><b>3 a)</b></p>	<p>A polymer's molecular weight is the sum of the atomic weights of individual atoms that comprise a molecule. It indicates the average length of the bulk resin's polymer chains. All polymer molecules of a particular grade do not have exactly same molecular weight. There is a range or distribution of molecular weights. Polydispersity index (PDI) is used as a measure of broadness of molecular weight distribution. The larger the PDI, the broader the molecular weight. The fractions can be calculated using the table given below:</p> <table border="1" data-bbox="300 1960 1209 2076"> <thead> <tr> <th data-bbox="300 1960 451 2076">Polymer entity</th> <th data-bbox="451 1960 699 2076">No. of unit in each entity (<math>n</math>)</th> <th data-bbox="699 1960 965 2076">Weight of each entity (grams) <math>M</math></th> <th data-bbox="965 1960 1209 2076">Total weight of each entity (<math>W</math>)</th> </tr> </thead> </table>	Polymer entity	No. of unit in each entity ( $n$ )	Weight of each entity (grams) $M$	Total weight of each entity ( $W$ )	<ul style="list-style-type: none"> <li>• Molecular weight definition: 1 mark</li> <li>• PDI definition: 1 mark</li> <li>• Formulae: 0.5 mark for formula of <math>M_w</math>, <math>M_n</math> and PDI each</li> <li>• Calculations: 1.5 mark each for</li> </ul>
Polymer entity	No. of unit in each entity ( $n$ )	Weight of each entity (grams) $M$	Total weight of each entity ( $W$ )			

			= nM)
Poly 1	33	343	11319
Poly 2	43	2223	95589
Poly 3	22	4563	100386
Poly 4	432	5543	2394576
Poly 5	56	462	25872
Poly 6	340	9	3060
	926		2630802

calculations  
leading to right  
answer of Mw,  
Mn and PDI

Number average molecular weight ( $M_n$ ) =

$$\frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + n_4 M_4 + \dots}{\sum n_i} = \frac{\sum n_i M_i}{\sum n_i} = M_n$$

$$M_n = \frac{33}{926} * 343 + \frac{43}{926} * 2223 + \frac{22}{926} * 4563 + \frac{432}{926} * 5543 + \frac{56}{926} * 462 + \frac{340}{926} * 9$$

$$M_n = 12.22 + 103.23 + 108.41 + 2585.94 + 27.94 + 3.30$$

$$M_n = 2841.04$$

Weight average molecular weight ( $M_w$ ) =

$$\frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + n_4 M_4^2 + \dots}{\sum n_i M_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i} = M_w$$

$$M_w = \frac{11319}{2630802} * 343 + \frac{95589}{2630802} * 2223 + \frac{100386}{2630802} * 4563 + \frac{2394576}{2630802} * 5543 + \frac{25872}{2630802} * 462 + \frac{3060}{2630802} * 9$$

$$M_w = 1.48 + 80.77 + 174.11 + 5045.28 + 4.54 + 0.01$$

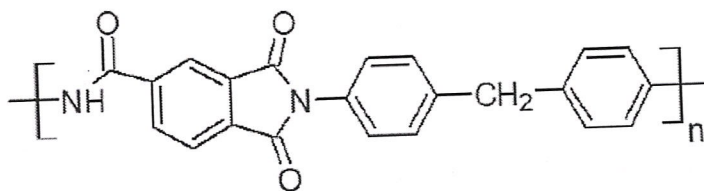
$$M_w = 5306.20$$

$$\text{Polydispersity index} = \frac{M_w}{M_n}$$

$$\text{PDI} = \frac{5306.2}{2841.04} = 1.87$$

$$\text{PDI} = 1.87$$

<p><b>3 b)</b></p>	<p>The co-relationship of electrical properties such as dielectric constant, power factor, dissipation factor on polymer structure can be explained as discussed below:</p> <ul style="list-style-type: none"> <li>Dielectric constant: Certain group structures and elements within the polymer chains exhibit a high polarizability, such as aromatic rings, sulphur, iodine and bromine atoms. Their presence is therefore likely to increase the dielectric constant of the corresponding parent material. In the context of aromatic rings, the <math>\pi</math> bonding electrons around such rings are loosely bound compared to direct sigma bonds, and consequently get polarized straightforwardly. With regards to large atoms such as bromine and iodine, the surrounding electron cloud is similarly also loosely bound to the nucleus, due to its relatively large size and large separation distance of the outermost electrons. An opposite example would be the fluorine atom, which has instead much more tightly-packed electrons due to its small atomic radius, and therefore low polarizability. The dielectric constant (permittivity) is related to the polarizability of the polymer, is low for nonpolar molecules such as highdensity polyethylene (HDPE), which cannot store much energy, but is relatively high for polar polymers. The dielectric constant increases as the temperature increases but reaches a plateau at relatively high temperatures.</li> </ul> <p>Electrical Conductivity: Insulation property of polar polymers destroy in humidity because water has high dielectric constant, which raise the overall dielectric constant of polymer-water mixture. So, resistivity decreases and electrical conductivity increases. -In case of nonpolar polymer vice-a- versa is true. Polymers may also be converted from nonconductors to conductors of electricity by the addition of conductive fillers. Graphite-filled polymers are semiconductors, and polymers filled with aluminum flakes or aluminum filaments are relatively good conductors of electricity.</p>	<ul style="list-style-type: none"> <li>Four marks for each property explanation in context to polymer structures where three marks are for explanation and one mark for example.</li> </ul>
<p><b>4</b></p>	<p>The degree of polymerization, or DOP, is the number of monomeric units in a macromolecule or polymer or oligomer molecule.</p> <p>The structure of the polymer given is:</p>	<ul style="list-style-type: none"> <li>Definition of DOP: 1 mark</li> <li>Finding total number of</li> </ul>



Identification of Formula for polymer PAI:  $C_{22}H_{14}O_3N_2$

Molar Mass of repeating unit for PAI =  $(22 \times 12) + (14 \times 1) + (16 \times 3)$

$(2 \times 14) = 354$

Molecular Weight Given = 224562

$$\text{Degree of Polymerization} = \frac{\text{Molecular weight of polymer}}{\text{Molar/Atomic mass of repeating unit}}$$

DOP =  $224562/354 = 634.35$  or **634 monomeric units**

Two structure related properties for the above polymer are:

1. Presence of aromatic structures may lead to an increase in the HDT and thermal stability of the polymer.
2. Polyamide-imides can resist plasticization because of the strong intermolecular interactions arising from the polyimide functions as well as the ability of the polymer chains to hydrogen bond with one another as a result of the amide bond.

elements: 2 marks

• Solving Molar Mass calculation: 1 mark

• Formula and Final DOP value: 2 marks

• Two structure property relationships: 2 marks

5 a)

Based on internal molecular and chain structures, polymers can be classified into amorphous, semi crystalline, and crystalline polymers.

*Explanation about chain segments, molecular motion and segmental motion (vibrations) needs to be included.*

- Amorphous polymers are a type of polymer that has a seemingly random and coiled molecular structure and does not immediately melt when heated. Without a sharp melt point, these materials gradually soften. Depending on their specific molecular composition, they will experience a change, becoming either more glassy and less rubber-like or more rubber-like and less glassy. Amorphous polymers are easier to process. Additionally, amorphous polymers offer better dimensional stability and are isotropic in flow, melting more evenly to provide less shrinkage. For eg, PC, ABS, PMMA, etc.
- Semi-crystalline polymers are a type of compound with a highly ordered molecular structure. With a sharp melting point, semi-crystalline polymers remain solid until it absorbs a specific

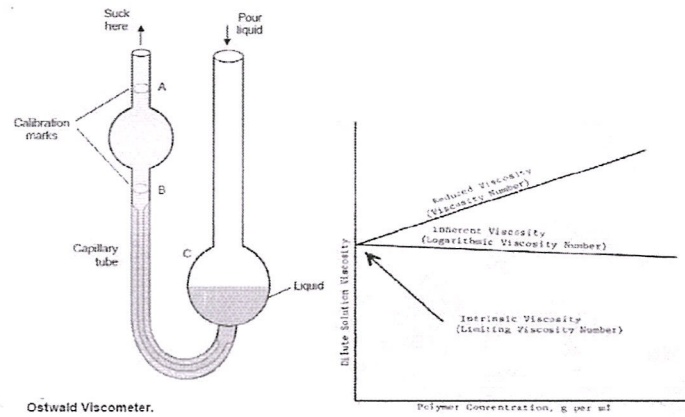
- One mark for classification
- One mark for introducing the concept.
- Three marks for each explanation with example

	<p>amount of heat. Then the polymer experiences a change becoming a low viscosity liquid. The tightly packed molecular chains create a much more defined melting point, whereas amorphous polymers have more variance. Semi-crystalline polymers are anisotropic in flow, the opposite of amorphous, meaning they will experience non-uniform shrinkage. These polymers will shrink less in the direction of the flow compared to the direction traverse. For eg. Nylons, PBT, PP, etc.</p> <ul style="list-style-type: none"> <li>• Crystalline Polymers: These offer a ordered or regular arrangement of molecules in its macromolecular structure. Highly crystalline polymers are rigid, high melting, and less affected by solvent penetration. Crystallinity makes a polymer strong, but also lowers their impact resistance. As an example, samples of polyethylene prepared under high pressure (5000 atm) have high crystallinities (95 - 99%), but are extremely brittle. Small molecules and ions form a three-dimensional lattice with an extended regular structure that makes large crystals possible. For eg. LCP</li> </ul>	
5 b)	<p>Polymerization, or polymer synthesis, is a chemical reaction in which monomers are joined together by covalent bonding to form polymer structures. The length of the polymer chain is characterized by the number of repeating units in the chain, which is referred to as degree of polymerization (DP).The polymers can be classified based on synthesis as addition and condensation polymers.</p> <ul style="list-style-type: none"> <li>• An additional polymer is a polymer that is formed by simply linking monomers. This is done without the co-generation of other by-products. It is important to note that additional polymers can be formed through chain polymerization. This done when the polymer is formed by sequentially adding different monomer units to an active site of the chain reaction. For e.g., ethylene to polyethylene and styrene to polystyrene.</li> <li>• Condensation polymers, on the other hand, are formed by linking monomers. The difference exists in the fact that this process generates various other products; these products include water. These polymers are formed by carrying out condensation</li> </ul>	<ul style="list-style-type: none"> <li>• One mark for classification</li> <li>• One mark for giving info about synthesis.</li> <li>• Three marks for each explanation with example</li> </ul>

	<p>reactions. In this reaction, the molecules are joined together by losing small molecules as by-products. The most commonly lose molecules in this reaction are water and methanol. For e.g., Polyester formed by the reaction of a dibasic acid and a diol.</p>	
6	<p>The determination of dilute solution viscosity is determined using an Ostwald's viscometer. The procedure for determination is as follows:</p> <ol style="list-style-type: none"> <li>1. The test sample is made by the dissolution of a specified amount of polymer in the appropriate solvent.</li> <li>2. This solution and the glass viscometer are put in a constant-temperature bath maintained at the standard testing temperature.</li> <li>3. A suitable amount of solution is fed into the viscometer using a transfer pipe.</li> <li>4. Once temperature equilibrium is attained, the liquid level in the viscometer is brought above the upper graduation mark by gently blowing air into the arm opposite the capillary.</li> <li>5. The timer is started exactly when the meniscus passes the upper graduation mark, and stopped exactly when the meniscus passes the lower graduation mark.</li> <li>6. Three readings are taken by repeating the test for solution and pure solvent individually.</li> <li>7. The time for the liquid to pass through the graduation marks is called efflux time.</li> <li>8. Once the test is done, we have the readings of average time taken (in seconds) for the time taken for the solution and pure solvent to pass in between upper and lower graduation marks. These readings will help us in calculating viscosity and even Viscosity average molecular weight by using Mark Howink's equation</li> </ol> $\text{Relative viscosity} = \eta_{rel} = t/t_0$ $\eta_{sp} = \eta_{rel} - 1$ $\eta_{red} = \eta_{sp}/c$ $\eta_{inh} = \frac{\ln \eta_{rel}}{c}$	<ul style="list-style-type: none"> <li>• One mark for the figure</li> <li>• Two marks for the formula</li> <li>• One marks for Mark Howink's equation.</li> <li>• Four marks for the procedure</li> </ul>



- After achieving the inherent viscosity, the limiting viscosity number or intrinsic viscosity can be easily calculated using a curve plot.



$$[\eta] = K(M_v)^a$$

where  $[\eta]$  = Intrinsic Viscosity,  $k$  = Mark-Houwink constant,  $a$  = Mark-Houwink constant relating to structure (0 to 0.1 – sphere, 0.35 to 0.80 – random coil, 1.5 to 2 – rigid rod), and  $M_v$  = viscosity average molecular weight

  
 Course Coordinator

