



Indian Institute of Technology Kharagpur
End-Autumn Semester 2023 – 2024

Date of Examination: Session: Duration 3 hrs Full Marks 130
Subject Number: CH61017 Subject: Rheology of Complex Fluids

Department: Chemical Engineering

Specific Instructions: Assume and write any assumption and data that you feel are missing.

Q1. a) Table-1 shows the data of normalized autocorrelation function ($g_2(\tau) = 1 + b * \exp(-t/\tau)$) obtained from Dynamic Light Scattering measurements for a polymer-grafted nanoparticle (PGNP) dissolved in solvent-A and solvent-B. Use the data to obtain the estimate of hydrodynamic size of PGNP for both cases. Other information: $\lambda=642$ nm, viscosity of both solvent are roughly equal to water-viscosity (10^{-3} Pa.s). Stokes-Einstein equation: $D = \frac{k_b T}{6\pi\mu R_h}$, where $k_b = 1.380649 \times 10^{-23}$ Joule/K. All DLS measurements done at $T=298K$ (Hint: rearrange expression of $g_2(\tau)$ in linearized form). (15)

(No step-marking)

b) “Good solvent” the polymer chain prefers more stretched configuration whereas in “bad solvent” the polymer chain shrinks within itself. Based on this definition, explain your estimates of hydrodynamic size and the type of solvent for A and B. (Use the graph paper given on the second last page for plotting if required) (6)

Table-1

	Solvent-A	Solvent-B
$\tau(s)$	$g_2(\tau) - 1$	$g_2(\tau) - 1$
0.000335	0.930165	0.99948
0.000872	0.711163	0.857335
0.00136	0.557156	0.745734
0.001849	0.436501	0.64866
0.002304	0.347584	0.569492
0.002711	0.283617	0.507009
0.003362	0.204838	0.420978
0.00398	0.150367	0.352811
0.004501	0.115903	0.304045
0.004972	0.091545	0.265699
0.005395	0.074093	0.23545
0.006795	0.036807	0.15786
0.00795	0.020658	0.113483
0.008389	0.016584	0.100097

Q2. Relaxation modulus decay data for a polymer melt at four different temperatures is given below:

Temperature	323K		298K		233K		214K	
	t (s)	G(t) (Pa)						
0.01879	134231.2	0.00321	217720.5	0.005	368306.8	0.00161	3.72E+06	
1.37084	31456.95	0.10992	152281.8	0.30161	252247.1	0.11708	537766	
14.14764	5491.943	3.31549	77698.2	1.28703	217720.5	0.26586	435782	
32.12546	1691.648	36.44542	32808.11	6.63616	172759.8	5	305781	

- a) Demonstrate time-temperature superposition by creating a master curve. Use the shift factor data given in Table-2. (Create the master curve on log-log scale graph given on the last page of question paper). (15)

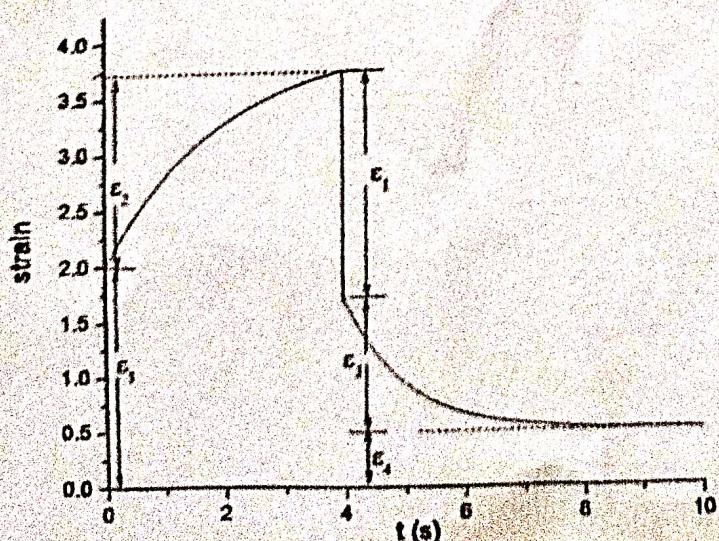
Table-2

T (Kelvin)	Horizontal Shift factors
214	1
233	93
298	13953.5
323	302325.6

- b) Create the relaxation modulus decay plot (up to 10^5 s) at 233K using the master curve. Hence, explain the advantage of time-temperature superposition. (15+5)
- c) Explain the physics behind such time-temperature superposition. (5)

(log-log graph is given in next page)

Q3. Figure below shows strain evolution during a creep-recovery test.



- a) Mark the following in the above diagram: Instantaneous elastic strain, viscoelastic strain, instantaneous elastic strain-recovery, viscoelastic strain recovery, permanent strain. (5)

- b) Suggest a model to capture the above shown strain evolution during creep-recovery test. (10)
c) Obtain the strain as a function of time during creep (over time 0 to t_1) and during recovery ($t > t_1$). (15)

Short Answer type questions (answer briefly and precisely in few lines)

- 4) Describe the experimental profile to obtain dynamic and static yield stress. (5)
5) In case of Electrorheological Fluids, explain the effect of electric field strength on yield stress. (5)
6) Concentrated aqueous solution of few long polymers show rod-climbing effect. Which rheological property is responsible for such phenomenon? Explain the physics of this phenomenon? (7)
7) A polymer solution is undergoing cross linking reaction to form a gel. Define gel physically (in terms of microstructure)?

As a rheologist you have chosen to measure the gel point as the cross over time of storage and loss modulus measure as a function of time at a given frequency. Such gel-point is called apparent gel-point. Explain why the word "apparent" is used ? Plot qualitatively the apparent gel-point as function of frequency. Suggest a more accurate rheological test to measure true gel-point and justify it?

(3+3+4+7)

- 8) Plot qualitatively the relaxation modulus decay to compare concentrated aqueous dispersion of bare silica particle, Polymer grafted silica nanoparticle with low grafting density, , Polymer grafted silica nanoparticle with very high grafting density (all dispersion have identical concentration in vol/vol%). Explain your plot. (5)