030530   Quiz 9 Properties

1) Explain the following observations:

a) A filled balloon is placed in an oven at 50°C from room temperature. The balloon's diameter is measured before being placed in the oven and while it is in the oven and the diameter remains unchanged.

b) A rubber band is wrapped tightly around a thin glass tube. The tube and rubber band are left on a car dashboard in Cincinnati in August. The tube shatters.

c) Two rubbers are made with hydroxyl terminated PDMS of 1000 g/mole and 10,000 g/mole. The 1000 g/mole rubber is much stiffer than the 10,000 g/mole.

d) A tensile measurement on a rubber sample leads to a non-linear stress-strain curve with a plateau in stress at moderate strains. This elastic does not seem to display elastic behavior.

e) You see a paper where stress strain data for filled elastomers is plotted as $\sigma/(\lambda - \lambda^{-2})$ versus $1/\lambda$.

2) a) Explain why a rubber that obeys the rubber elasticity equation is called an ***ideal*** rubber. (Draw an analogy to an ideal gas.)

b) Explain the role of entropy and enthalpy in rubber elasticity and in the ideal gas law.

c) Write the ideal gas law and the equation for elasticity of a single chain. Show that the two equations are basically the same.

3) a) Give the relationship between engineering tensile stress and extension ratio, λ, for an ideal rubber.

b) List 6 assumptions on which this equation is based.

c) Determine the modulus from the equation given in part a).

d) How does this modulus depend on molecular weight between crosslinks?

e) If an ideal rubber were used as a shock absorber how would the flexibility of the rubber change with temperature.

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1) a) The gas expands as approximated by the ideal gas law, P=T (nk/V) where n, k and V are held constant. The force on the rubber follows the ideal rubber law, $F/R = T (3k/nl^2)$, where k, n and l are constant. As the pressure increases linearly with absolute temperature the constraining stress equally increases linearly so the balloon does not expand or contract.

b) $F/R = T (3k/nl^2)$ The force increases with temperature and crushes the thin glass tube.

c) The modulus of an ideal rubber follows 3ρkT. Where $\rho = \rho_{Mass} N_A/M_c$. M_c is the molecular weight between crosslinks. As the molecular weight increases the modulus drops.

d) The engineering stress is non-linear in strain and follows the rubber elasticity equation,

$$\sigma = \rho kT \left[\frac{(\varepsilon + 1)^3 - 1}{(\varepsilon + 1)^2} \right]$$

e) This is a Mooney-Rivlin plot which takes into account the ideal rubber equation and the expected non-linearity in stress.

2) a) For an ideal gas the gas molecules are governed only by entropy and move by Brownian motion to create pressure so that the pressure is proportional to nkT. For an ideal rubber the chain motion is analogous to the motion of ideal gas molecules, the force exerted on the chain is due to entropy of the chain and random motion of the mer units. This motion is entirely thermal so the force is proportional to kT.

b) Both the ideal gas law and the ideal rubber law do not consider enthalpy at all. They are both due solely to entropy, hence the linear dependence on temperature.

c) For an ideal gas P = F/A = (n/V) kT = ρ kT. For a single chain, $F/R = 3kT/nb^2$, then the issue becomes how is 1/n like density where n is the chain molecular weight. There are several ways to consider this. One is that 1/n is basically a count of the end group contribution in terms of the end group density, so there is an analogy between end group density and gas molecule density.

3) a)

$$\sigma = \rho kT \left[\lambda - \frac{1}{\lambda^2} \right]$$

b) Assumptions:

1) fixed junction points
2) unimodal chain length
3) affine deformation
4) Gaussian Chain statistics are followed
5) Incompressible
6) Isotropic

c) $E \equiv \left(\frac{\partial \sigma}{\partial \varepsilon}\right)_{\varepsilon \to 0} = 3\rho kT\left[3 - \left(2 - \frac{2}{(\varepsilon + 1)^3}\right)\right]_{\varepsilon \to 0} = 3\rho kT$

d) ρ is proportional to $1/M_c$.

e) The rubber becomes stiffer in proportion to absolute temperature so the shock absorber would be less flexible at high temperature.