Polymer Physics
HW 10
March 25, 2022 (Due March 29)

Epoxy resin is used to make surf boards, sailboats, and fighter jets. Epoxys are network glassy polymers that have a low viscosity allowing fiberglass layouts that can be thermally cured to a glassy fiber reinforced composite. Epoxy has been known since the 1930s but the curing kinetics are complex and there are still issues of interest to be explored. A group from the AFRL in Dayton and NSLS II in Brookhaven NY recently studied the curing kinetics of an amine cure epoxy resin using a difunctional amine (DDM) a monofunctional amine (ptol) and a bisphenol A resin (EPON826) using X-ray photon correlation spectroscopy (XPCS) which is similar to dynamic light scattering, Trigg EB, Wiegart L, Fluerasu A, Koerner H *Dynamics of Polymerization and Gelation in Epoxy Nanocomposites via X-ray Photon Correlation Spectroscopy* Macromolecules **54** 6575−6584 (2021). The network structure doesn't have an X-ray scattering signal so Trigg used probe particles, similar to diffusive wave spectroscopy (DWS) but with X-rays, to probe the micro-rheology during cure. Trigg also performed NMR and IR to obtain cure kinetics, modulated DSC, thermal gravimetric analysis (TGA), multiwave oscillatory rheology, and he performs a simple Monte-Carlo simulation to obtain cure kinetics using the NMR data for the kinetic reaction constants. The result of the study is a comprehensive and consistent description of the network formation, gel point and dependence on network functionality. The networks appear to be surprisingly homogeneous by Trigg's analysis which contradicts the usual understanding of these complex systems. It is worth considering Trigg's work in some detail since it covers many of the important modern characterization techniques used in polymer science. We can only look at a few of the points in this homework.

a) The XPCS measurement on a curing system requires a "two-time" correlation function, Bikondoa O, *On the use of two-time correlation functions for X-ray photon correlation spectroscopy data analysis* J. Appl. Cryst. **50** 357-368 (2017) and Sutton M, Laaziri K, Livet F, Bley F *Using coherence to measure two-time correlation functions* Optics Express **11** 2268-2277 (2003). Trigg uses a one-time correlation function. Explain under what condition this is appropriate for this curing system.

b) Equation (1) is similar to the equation for the correlation function in DLS except that this is a "scaled exponential", Williams G, Watts DC, *Non-Symmetrical Dielectric Relaxation Behaviour Arising from a Simple Empirical Decay Function* Trans. Faraday Soc. **67** 80-85 (1971). Trigg calls the scaling factor a "compression exponent" γ. This is a factor that can determine the "fragility" of a transition but is essentially a fudge factor for this study. The "relaxation rate", Γ, is dependent on the size scale by a scaling factor "p". Explain why p has expected values of 2 and 1.

c) The complex viscosity, equation (3) and the storage and loss moduli Figure (S14) in the Supplemental Data can be obtained from XPCS, Squires TM, Mason TG, *Fluid Mechanics of Microrheology* Annu. Rev. Fluid Mech. **42** 413-438 (2010). This is compared with multiwave oscillatory rheology, *Rheology – Multi-Wave Oscillation* Thermal Instruments technical bulletin RH096. Explain in a short paragraph how the dynamic viscosity and modulus can be obtained from probe particles and why a multi-wave rheometer must be used to study curing kinetics.

d) Figure 8 compares changes in the exponent p, the crossover time for oscillatory rheology, and the prediction for the gel point from the MC simulation for various fractions of difunctional/monofunctional curing agent. Why is there no change in the gel point for the 0% ptol sample while there is a frequency dependence for the 100% ptol sample? How is the gel point calculated using the Flory-Stockmeyer theory using the results of the MC simulations? (https://en.wikipedia.org/wiki/Flory–Stockmayer_theory).
e) Figure 4 compares the oscillatory complex rheology at the five frequencies with the XPCS values obtained from equation (3). The values agree for high crosslink density (low ptol fraction) but diverge at longer cure times and at lower crosslink density. Two reasons for this behavior are given in the paper. Explain these two reasons.