Quiz 8 Polymer Properties March 29, 2019

McEwan et al.¹ measure the structure factor, S(q), for polymer grafted nanospheres (*N* is the degree of polymerization of the graft and *P* is the degree of polymerization of the matrix chains.) and state: "In general, both S(q) and g(r) characterize the particle micro-structure as they relate the local particle density to the probability of finding nearest and subsequent particle neighbors."

- a) Define S(q) and g(r). How do they describe micro-structure?
- b) Explain Equation 1: $I(q) = f_c V_p(\Delta \rho)^2 P(q) S(q)$. How can you experimentally find the form factor, P(q) and the structure factor S(q)?

c)
$$S(q) = 1 + 4\pi\rho_p \int_0^{\infty} (g(r) - 1)r^2 \frac{\sin(qr)}{qr} dr$$
 (2)

Figure 4 shows the behavior of S(q) as a function of concentration of grafted spheres. Explain this behavior.

- d) Figure 5 shows the behavior of g(r), the correlation function, for short and long chain grafts (*N*). For low graft density, $\sigma \sim 0.008$, in figure 1 explain this behavior of g(r).
- e) McEwan et al. use the Ornstein-Zernike function,

$$\gamma(r) = h(r) - c(r) = \rho_{\rm p} \int h(r') c(|r - r'|) dr'$$
(5)

to calculate g(r). They state, "Successful application of the theory rests upon the analysis of correlation functions that relate the interactions, U(r), between two particles in the presence of the N - 2 remaining particles through the Ornstein–Zernike (OZ) relation which decomposes the total correlation function, h(r) = g(r) - 1, into direct and indirect contributions, c(r) and $\gamma(r)$, respectively. Explain what $\gamma(r)$, and c(r) correspond to.



Fig. 1 Theoretical wetting phase diagram of dimensionless graft density σ versus swelling ratio *P*/*N* for homopolymer melt in contact with a chemically identical grafted brush.



Fig. 2 (a) A schematic of polymer-grafted particles of center-to-center separation distance r, surface-to-surface separation h, brush height L and core radius a_c . (b) The potential energy per lattice site of two grafted particles modeled through SCF calculations between flat plates. Schematics are not to scale.



Fig. 4 Comparison of experimental and theoretical structure factors S(q) for radius $R \approx 100$ nm silica nanoparticles grafted with 25 kg mol⁻¹ PDMS in 13 kg mol⁻¹ PDMS with varying core volume fractions $\phi_c = 0.09-0.47$. Thin solid lines are predictions of S(q) from Percus–Yevick closure from eqn (13) for particles with a size distribution of 109 ± 13 nm obtained from analysis of USAXS intensities.



Fig. 5 Comparison of the magnitude of peak in radial distribution function g(r) at a silica core volume fraction of $\phi_c = 0.27$ to the storage modulus, G', taken at an angular frequency of $\omega = 1$ rad s⁻¹: (a) experimentally extracted g(r) of $R \approx 100$ nm silica nanoparticles grafted with 25 kg mol⁻¹ PDMS in 2 kg mol⁻¹ PDMS (black) and 13 kg mol⁻¹ PDMS (gray); and (b) storage modulus, G', versus ϕ_c with concentration corresponding to (a) encircled. Higher magnitude of peak in g(r) in 2 kg mol⁻¹ PDMS corresponds to increased particle ordering due to brush stretching, leading to enhancement in G' in the lower molecular weight melt.

¹ McEwan ME, Egorov SA, Ilavsly J, Green DL, Yang, Y Mechanical reinforcement of polymer nanocomposites: theory and ultra-small angle X-ray scattering (USAXS) studies *Soft Matter* **7** 2725 (2011).

² McEwan ME, Green DL Rheological impacts of particle softness on wetted polymer-grafted silica nanoparticles in polymer melts *Soft Matter* **5** 1705 (2009).

ANSWERS: Quiz 8 Polymer Properties March 29, 2019

- a) S(q) is the structure factor and reflects the organization of matter. The peak in S(q) occurs at q* = 2π/d for the spacing of the material.
 g(r) is the binary correlation function. The probability of finding matter at a distance "r" from matter integrated over all of the positions where matter exists. It reflects the average probability of finding matter separated at a distance "r".
- b) $I_0(q)/\phi_{c,0}$ at low concentrations is P(q). $(I(q)/\phi_c)/(I_0(q)/\phi_{c,0}) = S(q)$.
- c) As the concentration increases the organization of matter becomes sharper and the peak becomes narrower and larger. A second order peak appears at high concentration indicating long range order of the material as it begins to crystallize. Each order of reflection occurs at nq^* where *n* is an integer.
- d) The chains are in the "complete wetting" regime of Figure 1 for the 2,000 g/mole chains. When the molecular weight of the grafts, N, increases to 13,000 g/mole the chains de-wet and the organization of the spheres decreases. The transition is driven by the conformational change of the grafted chains. Normally one would expect that ordering should increase with N as is shown in Figure 2. However, with N >> P the grafted chains are not as compatible with the matrix chains and they are not swollen to the extent that they are fully extended as in Figure 2.
- e) The direct correlation function c(r) corresponds to the correlation function for nearest neighbor binary interactions. The indirect correlation function, χ(r), corresponds to the impact of non-binary interactions on binary interactions. For three particles, 1, 2, 3, interactions between 1 and 2 can be influenced by interactions between 2 and 3. χ(r) describes this influence. c(r) describes the low concentration behavior where there are only 1-2 interactions.