Composite Technology course: exercises on nanocomposites, December 2024

Christopher Plummer, LMOM-IMX

Question 1.

A polymer contains 10 volume % of roughly spherical clay agglomerates with a radius of 10 microns. Estimate the interfacial area between the polymer and the clay per unit volume.

Suppose the clay is now exfoliated, so that it takes the form of 10 micron radius, 1 nm thick circular platelets. What is the interfacial area per unit volume now?

Suppose now that the presence of the clay modifies the matrix properties over a distance of about 5 nm from the interface. Estimate the volume fraction of the matrix whose properties are modified in each case (i.e. for agglomerates and exfoliated clay).

Question 2.

The Halpin Tsai equations may be used to estimate the modulus, E, of a polymer nanocomposite containing aligned disc-shaped inclusions (such that E is measured in the direction of the alignment) with an aspect ratio α (ratio of the diameter to the thickness)

$$\eta = \frac{E_1 / E_0 - 1}{E_1 / E_0 + \zeta}$$

$$E \approx E_0 \left(\frac{1 + \zeta \eta \phi_1}{1 - \eta \phi_1} \right)$$

E_o: matrix modulus

 E_1 : modulus of the inclusions

 ϕ_1 : volume fraction of the inclusions

 $\zeta = 2\alpha$

Suppose we have a dispersion of aligned exfoliated clay particles with a diameter of 1 micron and a thickness of 1 nm. What is ζ in this case ?

The modulus of a clay particle is about 200 GPa. Suppose the polymer is an elastomer, with a modulus E_o of about 3 MPa. Show that in this limit, the Halpin-Tsai equations imply

$$E \approx E_0 (1 + 2'000\phi_1)$$

for small ϕ_1 . Why is the modulus effectively independent of that of the reinforcing particles? Would you expect this degree of reinforcement for a glassy polymer matrix (modulus of the order of 1 GPa)?

Question 3.

In a randomly oriented nanocomposite *E* is predicted by the Halpin-Tsai equations to be approximately half that in the aligned nanocomposite for a given volume fraction of clay, i.e.

$$E \approx 0.5E_0(1 + 2'000\phi_1)$$

for the nanocomposite in the previous question.

Why does this model break down for high aspect ratio particles as ϕ_1 increases above a critical particle volume fraction?

Above this volume fraction the effective particle aspect ratio is $\alpha_{eff} \approx 1.5/\phi_1$ owing to crowding effects. Assuming as previously E_o of about 3 MPa, estimate E for our nanocomposite if it contains 10 vol% randomly oriented clay particles and 20 vol% randomly oriented clay particles. Comment on your result.

Question 4.

The viscosity of a suspension of spherical particles in a liquid matrix is expected to tend to infinity as their volume fraction approaches the maximum random close packing fraction of about 64 %.

A liquid epoxy resin contains spherical nanoparticles with a diameter of 10 nm. Suppose a 5 nm thick layer of the epoxy at the nanoparticle surfaces is immobilized owing to interfacial interactions (i.e. behaves as a solid). Estimate the critical volume fraction of such nanoparticles above which the nanocomposite is no longer able to flow.

In the case of random dispersions of disc-shaped nanoplatelets (e.g. exfoliated clay), solid-like behaviour may occur when spheres with a diameter equivalent to that of the platelets reach their critical volume packing fraction. At about what volume fraction would you expect a suspension of platelets with a thickness of 1 nm and a diameter of 1 micron to begin to show solid-like behaviour?

In fact, the elastic networks formed by exfoliated clay particles are relatively weak and readily broken up at high stresses. Hence explain why the formation of such networks is generally less problematic for the processing of thermoplastics than for liquid thermoset resins.