# Composite Technology course: Nanocomposites

Christopher Plummer, LMOM-IMX

## 1. What you should know for the exam

You will be examined only on what was presented in the lecture and corresponding slides (so not the last few slides, which were not covered in the lecture). The recorded lecture on Moodle covers exactly the same material.

You should know:

a) Why the interfacial region may gain in importance for physical properties as we progressively reduce filler particle sizes at constant particle volume fractions (see also the exercises, Q1 and Q4)
b) Structure of *montmorillonite clay*, concepts of *exfoliation* and *intercalation* as applied to clay-based nanocomposites, morphology of an individual montmorillonite clay platelet.
c) How montmorillonite clay is usually modified to render it compatible with hydrophobic polymer matrices
d) The *in-situ* route to preparation of exfoliated PA6-montmorillonite nanocomposites and its limitations.
e) The melt mixing route to preparation of nanocomposites and its advantages.
f) Some of the properties that are typically improved in montmorillonite-polymer nanocomposites with respect to the pure matrix.
g) Why we get very large stiffness improvements in fully exfoliated nanocomposites even at very low volume fractions (cf. the exercises, Q2 - you don't need to be able to reproduce the Halpin-Tsai equations, but you should be able to use them to estimate the modulus for different platelet aspect ratios). Hence why the property improvements seen at low montmorillonite contents may require much higher loadings of conventional particle or short-fibre reinforcements.
h) Why stiffness improvements tend to be a lot less at high montmorillonite contents in randomly oriented nanocomposites than you would predict on the basis of the Halpin-Tsai equations and the aspect ratio of an isolated platelet (crowding effect, local stacking or folding or platelets reduces their effective aspect ratios) – and hence why manufacturers generally stick to low montmorillonite contents in practice.
i) Why highly dispersed nanoparticles, and exfoliated montmorillonite in particular, may lead to processing problems in the case of thermosets, but not usually for thermoplastics
j) How nanocomposites in general may improve burning resistance.
k) How montmorillonite nanocomposites may reduce permeability and hence improve barrier properties.

## 2. Exercises on nanocomposites, December 2024, Solutions

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.

There are $0.1/V_a$ agglomerates per unit volume, and hence an interfacial area per unit volume equal to $0.1\ S_a/V_a = 0.1 \times 3 \times 10^5 = 3 \times 10^4\ m^2/m^3$.

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?

In this case, $0.1\ S_a/V_a \approx 0.1 \times 2 \times \pi \times (10^{-5})^2/(\pi \times (10^{-5})^2 \times 10^{-9}) = 2 \times 10^8\ m^2/m^3$ or 200 $m^2$/cc. Thus, the interfacial area contained within 1 cc of the exfoliated nanocomposite is roughly equal to the surface area of a tennis court!

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).

In the case of the agglomerates, the immobilized volume per agglomerate is given by $4/3\ \pi\ ((r + d)^3 - r^3)$ where $r = 10^{-5}$ m and $d = 5 \times 10^{-9}$ m is the supposed thickness of the immobilized layer. The volume fraction of immobilized matrix is then $0.1 \times 4/3\ \pi\ ((r + d)^3 - r^3)/(4/3\ \pi\ r^3) = 1.5 \times 10^{-4}$.

In the case of the exfoliated platelets, we can estimate the volume fraction of the immobilized matrix from $0.1 \times 2 \times d/t = 0.1 \times 2 \times 5 = 1$, which turns out to be more than the actual volume fraction of matrix of 0.8! In other words, the matrix is expected to be totally immobilized under these conditions. *In the solid state the matrix is in any case immobile, but in the liquid state, restricted mobility over distances of a few nm may make a significant difference to the flow properties of an exfoliated nanocomposite.*

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 $\alpha$ (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*

*$\phi_1$ : 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 $\zeta$ in this case? $\alpha = 10^3$ and so $\zeta = 2 \times 10^3$.

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

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

for small $\phi_1$. $E_1 >> E_0$, so $\eta \approx 1$. For small $\phi_1$, then, $E \approx E_0(1 + \zeta\phi_1) = E_0(1 + 2 \times 10^3 \phi_1)$.

Why is the modulus effectively independent of that of the reinforcing particles? Because the modulus of the reinforcing particles is very much greater than that of the elastomer matrix, their deformation becomes negligible and they may be considered to be infinitely stiff. In fact, Halpin-Tsai is not very realistic in this limit because of the very inhomogeneous strain distribution in the matrix, and the possibility of particle-matrix debonding even at low overall strains.

Would you expect this degree of reinforcement for a glassy polymer matrix (modulus of the order of 1 GPa)? In the case of a glassy polymer, $E_1/E_0$ is no longer >> $\zeta$ and the degree of reinforcement will be sensitive to both $E_1$ and $E_0$.

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.

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

for the nanocomposite in the previous question.

Why does this model break down for high aspect ratio particles as $\phi_1$ increases above a critical particle volume fraction? Have a look at the corresponding slide in the nanocomposites lectures. In a randomly oriented nanocomposite, particles with large aspect ratios will begin to overlap above some critical volume fraction, $\phi_{max} \approx 1.5/\alpha$. They are therefore forced either to bend or to form locally aligned stacks as shown schematically in the slides.

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. In both cases, $\phi_1 >> 1.5/\alpha$. We can hence try using $E = E_0(1 + 2\ \alpha_{eff}\ \phi_1)$, with $\alpha_{eff} \approx 1.5/\phi_1$, which implies $E = E_0(1 + 2 \times 1.5) = 4\ E_0$ regardless of whether the particle content is 10 or 20 vol%! While this is rather simplistic, it illustrates why you can only make efficient use of randomly dispersed exfoliated clay platelets to reinforce a polymer matrix at very low volume fractions.

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. The volume of a particle plus the immobilized layer is 4/3 $\pi$ $((r + d)^3$ as in question 1 where r in this case is 5 nm. The fraction of this volume occupied by the particle is $r^3/(r + d)^3$ and hence the particle volume fraction at which the nanocomposite can no longer flow is $0.64 \times r^3/(r + d)^3 = 0.64 \times (5/10)^3 = 0.08$, i.e. 8 vol%, which might seem surprisingly low.

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?

Here we may estimate the critical volume fraction from $0.64 \times 10^{-9} \times \pi r^2/(4/3 \pi r^3) = 0.64 \times 3 \times 10^{-9}/(4 r) = 0.64 \times 3 \times 10^{-9}/ (4 \times 5 \times 10^{-7}) \approx 0.001$ or 0.1 vol%! In this case the effect is not due to an immobilized layer (which would not make much difference here unless it was very much thicker than the discs) but to the high aspect ratio of the discs, which means they will begin to interact with each other even at very low volume fractions.

In fact, the elastic networks formed by exfoliated clay particles are relatively weak and readily broken up at high stresses. Hence explain why they are generally less problematic for the processing of thermoplastics than for liquid thermoset resins. The viscosity of thermoplastics is already very high, so that the stress required to break up the network of particles is negligible compared with the stress needed to cause the matrix to flow. On the other hand, the viscosity of a thermoset resin may be very low, in which case the nanoparticles will have a significant influence on the flow behaviour, particularly at low shear rates.