Unusual Dynamic Processes in Polymer Nanocomposites

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Dynamics are important for polymer processing …

- Dispersion/orientation of nanoparticles during processing depends on dynamics of polymers and nanoparticles

- Dynamics characterised by the viscosity and the diffusion coefficient
Morphology evolution of PS-C$_{60}$ composites along the barrel of a twin screw extruder
Does sample preparation impact on the morphology?

Formulation:
1.0% C$_{60}$/ 99.0% PS

- Solvent-processed composite
- Mechanically mixed powders
Solvent processed mixture evolves toward that from mixed powder.
Morphology of PS-C$_{60}$ composites is determined by coupling between thermodynamics of mixing and rheology.

Dynamics characterised by viscosity

Dynamics characterised by diffusion coefficient

Bernando et al, Macromolecules 2017, 50, 3301–3312
Viscosity and diffusion strongly correlated in polymer melts

- Diffusion represents chain motion but is difficult to measure
- Viscosity is easy to measure

"Entangled" polymers
- effect of surrounding polymers modelled by motion in a tube

Viscosity scales with molecular weight

Polymer viscosity scales with molecular weight

From Colby and Rubinstein: Polymer Physics

- Viscosity $\sim M^3$
- Diffusion $\sim M^{-2}$
Viscosity/diffusion in CNT nanocomposites

- Nanoparticle dispersion and orientation dependent on dynamics not stress relaxation
- Diffusion becomes a more important characteristic
- Impacts upon polymer – polymer welding
- Can processing be used to manipulate dispersion/orientation?
SWCNTs slow polymer diffusion at low volume fractions

- Maxwell model
  - decrease in diffusion due to presence of obstacles
- Polymer diffusion decreases more significantly than Maxwell model prediction

Mu et al, Macromolecules 2011, 191, 44, 191
Tracer diffusion recovers above critical volume fraction

- $D_{\text{min}}$ at critical volume fraction of SWCNT 0.4 vol%  
  - independent of polymer molecular weight  
  - correlates with SWCNT percolation  
- SWCNTs have a more dramatic influence on $D$ of shorter tracers
Diffusion is decoupled from viscoelasticity in nanocomposites.

SWCNT/480k PS, 200 °C

Plateau modulus $M_e = \text{constant}$

Relaxation time $\sim 8$ sec independent of SWCNT concentration

Low frequency modulus scales with square of nanotube concentration
The glass transition temperature

- No significant change in $T_g$ as measured by DSC

- Width of transition, 6 - 7°, also independent of CNT concentration
A phenomenological trapping model for diffusion

- SWCNT (blue) creates a trap region
- Inside and outside traps
  - probability of hopping between sites constant, $p_o$
- Jump probability smaller for hop into or out of trap, $p_1$
- Consistent with both viscoelasticity and diffusion observations

Jump probability: $p_o > p_1$

Mu et al, Macromolecules 2011, 191, 44, 191
A phenomenological trapping model for diffusion

Jump probability: \( p_0 > p_1 \)

Is there a molecular basis?
What can we learn from molecular dynamics simulations?

- Bead-Spring model
  ![Bead-Spring model](image1)

- Atomistic model for SWCNT
  ![Atomistic model for SWCNT](image2)
  - SWCNT diameter ~ Kuhn length
  - Fixed SWCNT spans simulation box
  - Volume fraction of SWCNT ~ 0.4%

Unconnected beads interact through Lennard-Jones potential

\[ U(r) = 4\varepsilon \left( \frac{\sigma_{ij}^{12}}{r^{12}} - \frac{\sigma_{ij}^6}{r^6} \right) \]

Connected beads interact through harmonic potential

\[ U(r) = \frac{K}{2}(r - r_0)^2 \]
Local structure: radial distribution function $g(r)$

Zero attractive energy

Increasing radius of SWCNT

~ 2 bead diameters

Attractive interactions

Fixed $N$
Impact of curvature

- For a fixed degree of polymerisation, the interfacial volume per SWCNT decreases with increasing radius of SWCNT.
Affect of SWCNT on chain dimensions

- Both radius of gyration and r.m.s. end-to-end distance unaffected by a single SWCNT
  - Equivalent to nanocomposite with 0.4% volume fraction SWCNTs
  - overall chain configuration well described by Gaussian statistics

Chain confirmation is anisotropic

- If CNTs randomly aligned
  - Experiments average over all orientations
  - Cannot distinguish behaviour parallel and perpendicular to individual CNTs
- Use an aligned mesh of CNTs

Tung et al. *ACS Macro Letters*, 4, 916, 2015
The impact of interactions on polymer dynamics in the presence of a SWCNT

- Reduction in $D$ for higher molecular weight chains when $k_B T$ attractive interaction between polymer and SWCNT
Dynamic anisotropy

FIG. 2: Mean square displacement of polymer chains, with attractive \((k_B T)\) interaction (green) parallel (solid lines) and perpendicular (dashed lines) to SWCNT \((r_{SWCNT} = 0.66)\) for three different lengths.

For comparison we show the MSD in the case of 60mers with no attractive interaction with the SWCNT surface (black).

In the case of weak interaction \((k_B T/2)\) between the polymer and the nanotube surface, the polymer chain regains its bulk value at a distance of \((R_g + \sigma_m)\) from the nanotube surface. Interestingly, at a greater distance, the polymer chain diffusivity is slightly enhanced. A further increase in the interaction strength causes the dynamics of the first layer (bound layer) to slow down drastically.

In particular, a polymer – nanotube attraction of the order of \(k_B T\) induces a near immobilization of the in contact polymer chains in agreement with results from spherical nanoparticle composites \([29, 35, 66–69]\) and polymer melt at attractive surfaces \([70]\). Thus, as can be seen from Fig. 3, the parallel to SWCNT dynamics parallel to SWCNT perpendicular to SWCNT
Proximity to surface impacts diffusion

Reduced diffusion coefficient dependence on distance of chain from SWCNT surface
Karatrastos et al, Macromol 2012

Experimental diffusion coefficient near flat substrate surface
Choi et al, Macromol 2017
Concentrated well-entangled SWCNT nanocomposites: dissipative particle dynamics

- Soft potential replaces LJ potential
  \[ U(r) = \frac{\alpha}{2} (\sigma - r)^2 \]
- Increases time step
Dynamics in polymer/silica nanocomposites

- Observed ‘Master Curve’ of polymer dynamics in presence of spherical nanoparticles
  - Well dispersed up to 50% nanoparticle
  - Reduced diffusion coefficient vs interparticle distance scaled with radius gyration

Physical mechanism?

- MD simulations by Liu et al of unentangled polymers does not reproduce collapse
- Is explanation related to entangled polymer dynamics?

From Liu et al, Soft Matter 2014
Molecular Dynamics of spherical nanoparticle/polymer mixtures: diffusion

- For unentangled polymers:
  - At 5% diffusion obeys Maxwell geometric model for diffusion
  - Above 5% diffusion is more strongly affected than geometric model predicts

- For weakly entangled ( < 2 entanglements) polymers
  - Similar behaviour at 5%
  - Above 5% trend similar to the experimental data for more entangled chains

\[ \frac{D}{D_0} = \frac{1}{\epsilon^2 \phi} \]

\[ \epsilon = \frac{R_i}{R} \]

\[ R = \frac{d_{NP}}{\sqrt{\phi}} \]

\[ D/D_0 = f(\phi) \]

\[ \phi = \frac{V_{NP}}{V_0} \]

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A very coarse – grained model of polymer dynamics

- Develop a simple simulation in which obstacles are regularly spaced walls with holes
- Inspired by Muthukumar work on single chain translocation through pores

From Saltzmann and Muthukumar, J Chem Phys, 2009, 131, 214903

From Liu et al, Soft Matter 2014
Are dynamics controlled by the presence a very few small "pores"? Monte Carlo modelling of chain diffusion in a constrained environment

- Dynamics in nanocomposites complicated by complex structure
  - Wide range of lengthscales associated with distances between particles
- Consider motion through uniformly sized chambers with holes
  - Geometry of constraints well defined
- Reptation from the Evans-Edwards MC model
The Evans – Edwards Monte Carlo model for reptation

• Highly coarse-grained
  – Each segment represents an entanglement segment

• Motion occurs by
  – End segments
  – Hairpins

Taken from Baumgärtner et al, J Stat Phys, 1998, 90, 1375
A Master Curve?

Collapse onto a single curve almost observed

Difference due to regular vs dispersed structures?
The constraint diffusion coefficient

The constraint has an effective width equal to $R_g$
- once the chain has escaped through hole it has diffused $\sim R_g$

Assume that we can treat as a 1D problem

$$\frac{1}{D} = \frac{f}{D_t} + \frac{1-f}{D_0}; \quad f = \frac{R_g}{ID}$$
The constraint diffusion coefficient

- Overall diffusion due to two processes
  - Diffusion within chambers, $D_0$
  - Diffusion between chambers, through holes, $D_t$

- $D_t$ scales with chain size as $N^{-3}$
  - Suggests physical mechanism

- $D_0$ scales with chain size as $N^{-2}$
The Classic ruin problem: an explanation for scaling?

- Each turn player wins or loses one dollar with equal probability
- Given an initial stake $z$ dollars, and a goal $a$ dollars
  - probability of win
    \[ p(\text{win}) = \frac{z}{a} \]
  - average duration given win
    \[ \langle \text{duration} \rangle = \frac{1}{2} \left( a^2 - z^2 \right) \tau_0 \]
    time for each turn
Gambler’s ruin and reptation

- Reptation is a series of random walks along the tube
  - equal probability of walking one entanglement in either direction along tube
- Combine physics with statistics of gambler’s ruin:
  \[ D_t = \frac{R_g^2}{\langle \text{duration of escape} \rangle} \approx \left( \frac{1}{N^{(MC)}} \right)^3 \]

Scaling observed from MC simulations
Diffusion in cylindrical confinement

Figure S1 shows the SEM images of the top view and the cross section view of the AAO membranes used in ERD experiments.

Figure S1. SEM images of the top view and the cross section view of the AAO membranes with four different diameters (18nm, 35nm, 55nm, 80nm).

MD simulations

Evans–Edwards model

Experiment
Towards a universal picture for both spherical and rod-like nanoparticles

- A minimum is observed when two geometric characteristics are met:

\[ d < 2R_g \text{ and } L > 2R_g \]

Choi et al, ACS Macro Lett. 2014
Successes and open questions

- Mesoscale models demonstrate how decoupling between diffusion and viscosity can be rationalised
- Structure predictions can help elucidate nature of surface interactions
- What is the molecular mechanism for a minimum in the diffusion coefficient in SWCNT/polymer mixtures?
- How should entanglements be defined in polymer/nanoparticle matrices?
The role of nanoparticle aspect ratio

- SWCNT have very large aspect ratio: L/D >> 1
- Silica nanoparticle have aspect ratio: L/D = 1
- Is behavior difference due to aspect ratio?
  - Test by synthesizing ‘intermediate’ aspect ratio nanoparticles