Origins of Mechanical and Rheological Properties of Polymer Nanocomposites

Venkat Ganesan

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Megha Surve, Victor Pryamitsyn

Department of Chemical Engineering
University of Texas@Austin
Polymer Nanocomposites

Polymers (Blends, Block copolymers) + Nano-Fillers → Nanocomposites

- Single- and Multi-Walled Carbon Nanotubes
- Fullerenes/Buckyballs
- Montmorillonite Clays
Polymer Nanocomposites

Polymers (Blends, Block copolymers) + Nano-Fillers → Nanocomposites

- Processing nanocomposites requires understanding their flow behavior.
- Flow fields provide a versatile approach for controlling dispersions of nanocomposites.
Objective: To model the flow dynamics and structure of nanoparticle-polymer mixtures.

Challenges

Interplay of hydrodynamics and friction in a viscoelastic medium

Flow-induced orientation

Effect of molecular interactions

Flow-induced gelation

Flow-induced Jamming

(Schmidt)

(Schmidt Vermant)

(Galgali)
The Approach

Explicit Solvent Method
(Molecular dynamics)

- Captures hydrodynamics and other interactions.
- Due to size asymmetry, is computationally expensive.

Continuum Methods
(Stokesian dynamics, Lattice-Boltzmann)

- Captures hydrodynamics and is computationally tractable.
- Can't include interactions with the solvent.
- Not developed for Non-Newtonian flows.
The Approach

Explicit Solvent Method

Coarse-Grained Explicit Solvent Method

Collection of microscopic solvent units

- Particle and solvent units interact by coarse-grained potentials.
- $U_{pc}(r), U_{pp}(r)$ are derivable from more atomistic representations.
The Approach

Explicit Solvent Method

Coarse-Grained Explicit Solvent Method

Particles interact by momentum conserving thermostat (preserves hydrodynamics).

Involves (central) dissipative forces dependent upon the normal component of the velocity differences.

Similar to Dissipative Particle Dynamics.
The Approach

Explicit Solvent Method

Coarse-Grained Explicit Solvent Method

- Does not capture local hydrodynamics.
- Requires tangential (not central) velocity-dependent forces.

\[ F_D^T \propto v_P^T - v_C^T \]
The Approach

Explicit Solvent Method

Coarse-Grained Explicit Solvent Method

- Does not capture local hydrodynamics.
- Requires tangential (not central) velocity-dependent forces.

Composite Particles
The Approach

Explicit Solvent Method

Coarse-Grained Explicit Solvent Method

Our proposal

- Directly incorporate tangential velocity-dependent forces.
Hydrodynamic Friction Forces

- Conserves linear and angular momentum
- Preserves hydrodynamical phenomena
- Includes tangential friction
- Brownian dynamics + Dissipative forces
- Computationally tractable (for size asymmetric systems)

(Espanol, 1998; Pryamitsyn and Ganesan, JCP, 2005)
Coarse-Grained Colloidal Suspension

- Mixture of colloid and solvent
- Colloid:Solvent Radius = 5:1.

\[ U_{CC} \approx U_{CP} \approx U_{PP} \]

\[ U_{CC} \approx U_{CP} \approx U_{PP} \]

(Pryamitsyn and Ganesan, JCP, 2005)
Hydrodynamic Interactions: Zero-Shear Viscosity

- Coarse-Grained solvent method captures hydrodynamical interactions
Rheology is sensitive to lubrication forces.
Provides a sensitive test of explicit solvent model.

Agrees to within 20% of Stokesian dynamics results.
Summary So Far..

• Outlined a coarse-grained explicit solvent method to simulate hydrodynamical phenomena involving particles in complex fluids.

• Provided evidence that both hydrodynamical and other interactions can be faithfully captured.

• Results on hard sphere suspensions provided new insights into the interplay between glass transition, hydrodynamics and rheology.
Why Polymer Nanocomposites?

Polymers (Solutions, Blends) + Nano-fillers (Clay, Nanotubes, Fullerenes) → Nanocomposites

Reinforcement even at \( \eta \sim 2\% \)

Addition of small particles – Significant property enhancement!!

- Elastic modulus doubles
- Viscosity increases by an order of magnitude
- Microsized particles vol ~ 30%
- Nanoparticles vol ~ 1-5%

Silica + PEO#

\# Zhang and Archer, Langmuir, 2002

✓ Addition of small particles - Significant property enhancement!!
Issues and Questions

- How do nanoparticles modify the mechanical properties of polymer matrices?
- What are the mechanisms underlying the above effects?
- What are the parameters governing the mechanisms?
Rheology of PNCs: Linear Viscoelasticity

- Significant enhancements in elasticity at extremely low loadings
- Change of viscoelastic response to “solid-like” behavior.

Polycaprolactone + Montmorillonite Clays*
PC + Nanotubes**

*: Krishnamoorti and Giannelis; **: Fornes and Paul
Rheology: Explanations

Particle Jamming/Percolation (Krishnamoorti)

\[ 2R \gg d \]

\[ \phi R^3 \approx 1 \]

- Jamming/percolation occurs at low \( \phi \)
- Leads to solid behavior and the enhancements in modulus.
Rheology: Explanations

Polymer Network Mechanism (Kumar and Douglas)

- Elasticity due to transient network formation.
- Plateau modulus due to bridges.

Immobilized Monomers
Rheology of PNCs: Model System

- Mixture of spherical nanoparticles in polymer matrices

\[
\frac{2R_g^P}{\sigma_{CC}} \approx O(1)
\]

\[
\frac{h}{R_g} \approx O(1)
\]

- Advantage: A lot is known about spherical colloidal dispersions
- Disadvantages: Orientational effects are absent. Need much higher loadings.
Model of Polymer Nanocomposites

- Mixture of colloid and polymeric melt

\[
\begin{align*}
U_{CC} & = \sigma_{CC} \\
U_{CP} & = \sigma_{CP} \\
F_{PP} & = b_{PP}
\end{align*}
\]

\[
\begin{align*}
\frac{\sigma_{CC}}{\sigma_{PP}} & = 5.0 \\
\frac{\sigma_{CP}}{\sigma_{PP}} & = 3.0
\end{align*}
\]

(VP & VG: Macromolecules, 2006; J. of Rheology)
Rheology of PNCs: Linear Viscoelasticity

- **Lower Loadings**: Enhancement in modulus but no apparent change in relaxation behavior.
- **Higher Loadings**: Significant enhancement in modulus and a solid-like behavior.
Rheology of PNCs: Linear Viscoelasticity

Polycaprolactone + Montmorillonite Clays*

- Significant enhancements in elasticity at extremely low loadings
- Change of viscoelastic response to “solid-like” behavior.

PC + Nanotubes**

*: Krishnamoorti and Giannelis; **: Fornes and Paul
Rheology of PNCs: Linear Viscoelasticity

- Enhancement in modulus but no apparent change in relaxation behavior at lower loadings: Why?
- Significant enhancement in modulus and a solid-like behavior at higher loadings: Why? (Not in this talk)
Impact on Polymer Dynamics

- Significant impact upon glass transition temperature and polymer dynamics on adding nanoparticles.  

How does the polymer dynamics change due to addition of nanoparticles?

For unentangled polymers,

\[
\langle X_m(t)X_m(0) \rangle \approx \exp(-t/\tau_m)
\]

\[
\tau_m \propto m^{-2} \quad \tau_1 N_p^{-2} \propto \xi
\]

Related to viscosity of media

Simulation Features
- No glass transition
- Coarse-grained model

### Equations:

\[
R(t) \xrightarrow{\text{Normal modes}} X_m(t) \\
\langle X_m(t)X_m(0) \rangle
\]

Effect of Particles on Polymer Dynamics

\[ \langle X_p(t) X_p(0) \rangle \approx \exp(-t / \tau_p) \]

Overall Slowing of Polymer Relaxations

\[ (p-1) / (N_p - 1) \]
Effect of Particles on Polymer Dynamics

\[ \langle X_p(t)X_p(0) \rangle \approx \exp(-t / \tau_p) \]

- Simulations of Grant Smith: Attractions lead to only a weak slowing down in melts.
- Different monomers of a chain access the slower regions: Overall slowing down of the polymers

Slowed Monomers
Effect of Particles on Polymer Viscoelasticity

\[ \langle X_p(t)X_p(0) \rangle \approx \exp(-t/\tau_p) \Rightarrow G(t) \propto \sum_{p=1}^{N_P} \exp(-2t/\tau_p) \]

Modified \( G'_\text{pol} \) due to changes in relaxation times
Effect of Particles on Polymer Viscoelasticity

\[ \langle X_p(t)X_p(0) \rangle \approx \exp\left(-t/\tau_p\right) \Rightarrow G(t) \propto \sum_{p=1}^{N_P} \exp(-2t/\tau_p) \]

Modified \( G'_\text{pol} \) due to changes in relaxation times

\( G'_\text{pol}(\omega) \)

\( \omega \)

\( N_P = 24 \)
Effect of Particles on Polymer Viscoelasticity

\[
\langle X_p(t)X_p(0) \rangle \approx \exp(-t / \tau_p) \Rightarrow G(t) \propto \sum_{p=1}^{N_p} \exp(-2t / \tau_p)
\]

Modified \( G'_\text{pol} \) due to changes in relaxation times

\[
\begin{align*}
G'_\text{pol}(\omega) & = \phi = 0.01 \\
G'(\omega) & = \phi = 0.11 \\
G'(\omega) & = \phi = 0.33
\end{align*}
\]
Physical Picture of Polymer Rheology at Low Loadings

• Particle-induced changes in polymer dynamics is responsible.

• For the weakly attractive particles, the above manifests as just a change in relaxation times.

• For strongly attractive particles, the above manifests as the modulus due to polymer-bridged networks.
Comparisons to Experiments

- (Kropka, Green and Ganesan, Macromolecules, In Press)

Comparison of the relaxation times in nanocomposites to the bare relaxation times.
Comparisons to Experiments

- (Kropka, Green and Ganesan, Macromolecules, in Press)
  Superposition of mechanical moduli after renormalization of relaxation times.
Rheology of PNCs: Issues and Questions

• How do nanoparticles modify the rheology of polymer matrices?

• What are the mechanisms underlying the above effects?

• At low particle loadings, polymer-bridging of particles is the responsible mechanism.

• What are the parameters governing the mechanisms?

• What are the elastic and structural properties of the gels?

• Why do nanoparticles lead to prevalent gelation?

• How does the concentration of particles and polymer affect the gelation, stability characteristics of the mixture?
Outline of Approach

Integrate out polymer degrees of freedom

Monte Carlo and Equilibration

Effective Interactions

Thermodynamics, Phase Behavior

Gelation, Elastic Modulus

Analogous to density functional theories used to obtain interatomic potentials in quantum chemistry

Effective Interactions

Cluster Counting

Effective Interactions

Thermodynamics, Phase Behavior

Gelation, Elastic Modulus

Analogous to density functional theories used to obtain interatomic potentials in quantum chemistry
Integrating Out the Polymer By Mean-Field Theory

N segment chain

- Self avoiding random walk
- Charge effects

Bead-spring model of polymer

Idea behind mean-field theory*

\[ W(r) \]

* Single chain in a potential field \( W(r) \).
* \( W(r) \) determined self-consistently to match statistical properties of polymers, say, the volume fraction.

*: Helfand (1975)
Integrating Out the Polymer By Mean-Field Theory

N segment chain

- Self avoiding random walk
- Charge effects

Bead-spring model of polymer

Mean Field Approach

Presence of other chains
Self consistent potential field \( w(r) \)

Configurations of a chain subjected to \( w(r) \)

\[
\frac{\partial G(r, r'; n)}{\partial s} = \nabla^2 G(r, r'; n) - iw(r)G(r, r'; n) \quad G(r, r'; 0) = \delta(r - r')
\]

BCs:
Polymer - particle interactions

\( G(r, r'; n) \)
Field-Theory Model For Polymers

Density distributions for polymer → Polymer mediated effective interactions

Numerical solution

Bispherical coordinates

Configurations of a chain subjected to $w(r)$

\[
\frac{\partial G(r, r'; n)}{\partial s} = \nabla^2 G(r, r'; n) - iw(r)G(r, r'; n) \quad G(r, r'; 0) = \delta(r - r')
\]

Curvature of particles accounted exactly!!!

Number and probability distribution

Tail

Loop

Bridge

Field-Theory Model For Polymers
Adsorbed Layer: Particle Size Effects

Fraction of segments in loops & tails

Radius of the particle, \( R / R_g \)

\( \phi = 2.58 \)

Tails dominate! → Loops dominate!

Smaller particles - tails dominate
Smaller particles - More number of bridges

Bridging: Particle Size Effects

# of bridges/area

Interparticle distance, $r/R$

- $R/R_g = 0.5$
- $R/R_g = 1.0$
- $R/R_g = 2.0$

Bridge
Cluster Statistics and Gelation

Effective interactions

Bonds generation \sim \text{bridging probability}

Monte Carlo Moves & Equilibration

Cluster formation

Volume fraction at which a space spanning cluster is observed

# & size of clusters, Percolation thresholds
Cluster Statistics and Gelation

Smaller particles - Gel much earlier!

\[ \frac{R}{R_g} = 2.0 \quad \frac{R}{R_g} = 1.0 \quad \frac{R}{R_g} = 0.5 \]

\[ \eta = 8\% \]

\[ \phi = 5.16 \]

Polymer melt

Percolation threshold

Particle size ratio, \( \frac{R}{R_g} \)
Determining Elastic Properties

Post-gel systems

Identification of backbone

Simple Network Theories: Elastic Modulii = Number of Bridges in backbone
Smaller particles → stronger reinforcement.

Smaller quantities of nanoparticles are required.

Bridging induced clustering of particles responsible for reinforcement.

Scaling of Elastic Moduli of Gels

\[ G' \sim (\eta - \eta_c)^{1.799} \]

Simulation results

Experimental data

Universal scaling of elastic modulus

Gelation

For smaller particles, gelation occurs at very low volume fractions

Small particles -> dense networks

Small particles -> Much stronger enhancements in modulii