RHEOLOGICAL METHODS FOR EVALUATION OF NANOCOMPOSITE HYBRID STRUCTURE

Prof. D.Sc. Rumiana Kotsilkova
Open Laboratory on Experimental Micro and Nano Mechanics (OLEM)
Institute of Mechanics, Bulgarian Academy of Sciences
E-mail: kotsilkova@imbm.bas.bg
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Molecular level dispersing of nanofiller in polymer

> Enormous surface area of nanofiller, thereby a lot of interfaces between the two intermixed phases

> Bound polymer layer at the interfaces

> Hybrid (supramolecular) structure of interpenetrating nanofiller/polymer network

> Extraordinary properties

DEPENDING ON THE INTERPHASE INTERACTIONS:

Class I - hybrid materials correspond to weak phase interactions such as: van der Waals, hydrogen bonding or simple mechanical blending of the inorganic and organic phases.

Class II - hybrid materials possess strong covalent or ionic-covalent bonds between the inorganic and organic phases.
Flocculated and Dispersed Hybrid Structure

- **Polymer–particle** and **particle–particle** interactions are key to the structure and properties of polymer nanocomposites;

- The preparation of well-defined systems **requires good control of particle aggregation and dispersion processes**, this determining the final material applications.

- Applications, such as electromagnetic, conducting and other physical properties, need paths of agglomerating particles for energy dissipation. Well-separated particles require for low-loss capacitive devices. (R. PELSTER, U. SIMON, Colloid and Polymer Science, 1999, 277,1,2)

- **Complex interfacial interactions reduce the molecular dynamics and suppress the relaxation processes in a polymer**, this improving mainly the mechanical performance of nanocomposites.

Schematic of local morphology and extent of interphase zone in the nanocomposites:

(a) **Flocculated systems** has local clustering of nanofillers, resulting in filler-rich/filler-poor regions;
(b) **Dispersed systems** has improved nanofiller dispersion and larger interphase zone of influence, resulting in a fully transformed matrix material.
Rheology of Nanocomposites

Three Rheological Methods for a Control on the Nanocomposite Structure and the Dispersion Process


**Rheology Method I**
Control of the Degree of Dispersion
Flow Index: \( \sigma_{12} \sim \dot{\gamma}^n \) or \( \eta \sim (\dot{\gamma}, \omega)^{n-1} \)
Terminal Zone Exponent: \( G' \sim \omega^m \)

**Rheology Method II**
Characterisation of the Superstructure
Scaling Exponent: \( G'_c \sim \phi^{\mu} \)
Yield Stress: \( \sigma_o \)
Two Percolation Thresholds: \( \sigma^*, \sigma^{**} \)

**Rheology Method III**
Polymer-Filler Interactions
Relaxation Time Spectra: \( G'_p, \tau_i \)
Mean Relaxation Time: \( \tau_m \)

**Rheological Experiments:**
- Dynamic Flow: \( G' \) and \( G'' (\omega) \) and \( \eta (\dot{\gamma}) \)
- Steady-Shear Flow: \( \eta (\dot{\gamma}) \) and \( \tau (\dot{\gamma}) \)
Rheology Method I: Control on the Degree of Nanofiller Dispersion

General Approach

Rheology method I proposes an approach that allows a control on the degree of nanofiller dispersion in polymer matrices by using experimental data from low-amplitude oscillatory shear and steady-state shear flow. If the nanofiller content and other variables are kept constant, the primary factor determining the rheological response of nanocomposites at low deformation rates will be the nanofiller dispersion/delamination/exfoliation etc.

Two rheological parameters are determined, using Power-Law Model:

- **shear thinning exponent** \((n, \text{flow index})\).

\[
\sigma = A\gamma^n \quad \text{and} \quad \eta = A\gamma^{(n-1)}
\]

- **terminal zone slopes** \((m,n)\) of Dynamic Storage \((G')\) and loss moduli \((G'')\):

\[
G' \sim \omega^m \quad \text{and} \quad G'' \sim \omega^n
\]

\(n = 1\) is indicative of a Newtonian flow system

\(m = 2\) is the value of the terminal flow behavior of fully relaxed polymers.

The values of the power law exponents, \(m\) and \(n\), are usually compared to the expectations: for neat polymer \(m = 2\) and \(n = 1\); for the liquid-crystal polymer (LCP) domain flow, \(n = 0.5\); and for systems with yield flow; \(n = 0\).
Power Law Model for Steady Shear Curves

Flow index \( (n) \)
(shear thinning exponent)
the slope of the flow curves calculated by the power-law models:

\[
\sigma_{12} = \gamma^n \\
\eta = \gamma^{(n-1)} \\
\eta' = \omega^{(n-1)}
\]

5% epoxy / smectite nanocomposites as varying the organoclay modifiers

\( n = 1 \) Newtonian flow
\( n < 1 \) Non-Newtonian flow

✓ Decreasing of Flow Index \( (n<<1) \) by varying of nanoparticles, modifiers or processing conditions indicates for increased degree of nanofiller dispersion.
Power-law model for Dynamic Flow

- Theoretical values of the terminal zone slopes of $G'(\omega)$ and $G''(\omega)$ are $m = 2$ and $n=1$, as predicted for the fully relaxed polymer chains.
- The values of $m < 2$ and $n < 1$ quantify the non-terminal regime behavior of the storage and loss moduli of polymer, caused by the presence of nanofiller.
- The function $G'(\omega)$ is usually more sensitive to the dispersion of nanofiller in the polymer matrix than is $G''(\omega)$. 

![Diagrams showing $G'(\omega)$ and $G''(\omega)$ with varying nanofiller concentrations and temperatures.](image)
SUMMARY

**Rheological Method** allows to select the **best processing conditions** and the **best dispersions** at an early stage of nanocomposite preparation. (*Easy and non-expensive method for a control on the dispersion*).

**Shear thinning exponent** \( (n) \) and the **terminal zone exponent** \( (m) \) can be used to compare the degree of nanofiller dispersion in different nanocomposite samples at fixed filler concentration. In general, \( n = 1 \) is indicative of a Newtonian flow system (typical for monomers and low-viscosity polymer samples), and \( m = 2 \) is the value of the terminal flow behavior of fully relaxed polymers.

- If a filled sample behave as the matrix polymer, essentially *Newtonian* \( (n = 1) \) or presenting a *terminal behavior* \( (m = 2) \), it is a *conventional composite*, and **not a nanocomposite**, and such behavior indicates the presence of microne size aggregates.

- In contrast, **nanocomposite samples** demonstrate a considerable *shear thinning* \( (n \approx 0) \) and a *solid-like behaviour* \( (m \approx 0) \) at a relatively small filler volume fraction, and thus usually comprise the morphology of smooth, finely dispersed nanoscale filler.

- Samples with moderate values of \( n \geq 0.5 \) and \( m \geq 1 \) are **not perfectly dispersed nanocomposites**.
Rheology Method II:

Scaling of Viscoelasticity and Rheological Percolation Threshold

Rheology method II stress on the nanofiller concentration dependence of the rheological characteristics.

The low shear rate test method determines the following main rheological parameters, which may be used as a practical tool to quantify the filler superstructure of nanocomposites:

• scaling characteristic of the storage modulus (scaling exponent, $\mu$);
• pseudo-solid-like response (yield stress, $\sigma_0$, and values of $G' > G''$);
• critical concentrations for structural transition (the flocculation and the percolation thresholds, $\phi^*$ and $\phi^{**}$)

The high shear rate test method might be used for modeling the flow behaviour of nanocomposites, (e.g. deflocculation, alignment) by increasing both the shear rate and the filler content.
Rheology Method II: Scaling of Viscoelasticity

The elastic characteristics of nanodispersions can be described as a function of volume fraction of filler by involving the fractal dimensions characteristics of the floccules, which is consistent with the scaling.

From this, an example model presented the Scaling of Viscoelasticity

\[ G'_0 \sim \Phi \mu \]

Where: \( G'_0 \) is the storage modulus (\( G' \)) at very low frequencies (e.g. \( \omega < 0.5 \text{ s}^{-1} \));

\( \Phi \) - volume fraction of filler;

\( \mu \) - scaling exponent, expressing the strength of the filler structure.

The Equation describes the change of floccules size, as the particle concentration increases.

The rapid change of the scaling exponent \( \mu \) characterize the transition of the nanofiller structure from dispersed to flocculated or to network (rheological percolation)
Rheological Transitions

Two Rheological Thresholds, $\phi^*$ and $\phi^{**}$

**$\phi^*$ - Flocculation threshold**
Formation of *fractal floccules* of interconnecting nanoparticles and infiltrated polymer matrix (conducting pathways)

**$\phi^{**}$ - Percolation threshold**
Formation of *infinite cluster (Network)* of contacting floccules

Concentration dependance of viscosity:

- *Einstein* relation for the relative viscosity of hard sphere suspensions:
  $$ \eta_r = \frac{\eta}{\eta_0} = 1 + [\eta] + O(\eta^2) $$
- *Frankel-Acrivos* equation predicted well the rapid rise of the viscosity:
  $$ \frac{\eta}{\eta_0} \approx \frac{9}{8} \left\{ \left( \frac{\phi}{\phi_m} \right)^{1/3} \right\} \frac{1}{1 - \left( \frac{\phi}{\phi_m} \right)^{1/3}} $$

Rhology Method III: Relaxation Time Spectra of Nanocomposites

The relaxation processes in polymer systems could be estimated by calculation of the relaxation time spectra using linear viscoelastic rheological data, $G'(\omega)$ & $G''(\omega)$, and Maxwell model, which provides the following relation between the discrete relaxation spectrum $(H_i \tau_i)$ and the linear rheological characteristics:

**Rhrelaxation Time Spectra Calculations: Maxwell Models:**

\[
G'(\omega) = G_0 + \int_{-\infty}^{+\infty} [H \omega^2 \tau^2 / (1 + \omega^2 \tau^2)] \, d\ln \tau \quad \text{(storage modulus)} \quad (1)
\]

\[
G''(\omega) = G_0 + \int_{-\infty}^{+\infty} [H \omega \tau / (1 + \omega^2 \tau^2)] \, d\ln \tau \quad \text{(loss modulus)} \quad (2)
\]

\[
G(t) = \int_{-\infty}^{+\infty} H \exp(-t/\tau) \, d\ln \tau \quad \text{(relaxation modulus)} \quad (3)
\]

For solution of Maxwell equation the dynamic modulus, $G'(\omega)$ and $G''(\omega)$ are described by $(n)$ Maxwell elements, each is characterized by weigh of spectra $H_i$ and relaxation time $\tau_i$:

\[
G'(\omega) = \sum_{i=1}^{n} G_i \omega^2 \tau_i^2 / (1 + \omega^2 \tau_i^2) \quad (4)
\]

\[
G''(\omega) = \sum_{i=1}^{n} G_i \omega \tau_i / (1 + \omega^2 \tau_i^2) \quad (5)
\]

\[
G(t) = \sum_{i=1}^{n} G_i \exp(-t/\tau_i) \quad (6)
\]

where $G_i$ is the elastic modulus for each element having a time constant $\tau_i$.


By including the experimental rheological data for $G'(\omega)$ and $G''(\omega)$ in eq. (3 and 4), and using the Advantage software we calculate the relaxation time spectra for the polymer and compare to those of the composites.

1). As nanofiller is added, if the mobility of the polymer chains is altered, the relaxation spectra can be broaden (to higher relaxation time) in comparison with that of the neat polymer (This means that the interface interactions creates only local changes in the relaxation behavior of polymer molecules. This appears below the percolation threshold or not so strong interactions).

2). If the spectra is shift vertically (it means that the polymer-filler interface interactions are strong and cause global changes in the polymer relaxation, i.e. in the whole volume of the sample. This usually appears above the percolation threshold).
Relaxation spectra can be transformed to theoretical prediction of all rheological characteristics. To do this we apply the Ferry equations that give the solution of the Maxell Models:

\[ G(t) = \sum_{i=1}^{n} G_i \exp\left(-\frac{t}{\tau_i}\right) \]

\[ G'(\omega) = \sum_{i=1}^{n} G_i \omega \tau_i^2 / \left(1 + \omega^2 \tau_i^2\right) \]

\[ G''(\omega) = \sum_{i=1}^{n} G_i \omega \tau_i / \left(1 + \omega^2 \tau_i^2\right) \]

\[ \eta E(t) = 3 \sum_{i=1}^{n} G_i \tau_i \left[1 - \exp\left(-\frac{t}{\tau_i}\right)\right] \]

\[ \eta' = 1 / G'' = \frac{1}{\sum_{i=1}^{n} G_i \omega \tau_i / \left(1 + \omega^2 \tau_i^2\right)} \]
Polymer-Nanofiller Interactions (suppressed relaxation)

The **Rheology Method III** proposes an approach to estimate the polymer-nanofiller interactions based on the relaxation time spectra. The relative mean relaxation time, $\tau_{m,\text{rel}}$ is proposed as the *characteristic rheological parameter for polymer-filler interactions*, which presents namely the ‘additional relaxation’ of nanocomposites associated with the presence of hybrid structure.

### Sample | Carbon content (wt. %) | Carbon content (vol. %) | Mean relaxation time
| --- | --- | --- | --- |
| Epoxy resin | 0 | 0 | $\tau_m$ (s) | $\tau_{m,\text{rel}}$
| 1% GD(*) | 1.68 | 1 | 0.12 | 1
| 2% GD | 3.34 | 2 | 0.14 | 1.17
| 4% GD | 6.58 | 4 | 0.16 | 1.33
| 6% GD | 9.74 | 6 | 0.33 | 2.75
| 8% GD | 12.82 | 8 | 1.03 | 8.58
| 10% GD | 15.82 | 10 | 5.82 | 48.5

- **Shift of the relaxation time spectra to higher times by nanofiller**
- **Polymer-nanofiller interactions at the interfaces produces a suppressed relaxation** (retardation of polymer relaxation by nanofiller)
GENERAL CONCEPT of the Rheology–Structure–Property Relationship

First PERCOLATION (fractal flocs) \( \phi^* \)

Second PERCOLATION (network of flocs) \( \phi^{**} \)

RHEOLOGICAL PERCOLATION TRESHOLDS, \( \phi^*, \phi^{**} \)

Prognostic window
CONCLUSIONS on Rheology of Nanocomposites

The proposed Rheology Methods are very useful practical tool for a short-time consuming synthesis of novel nanocomposite materials, as well as a tool for a control on the optimal structure and properties.

- Three Rheological Methods allow:
  (i) rapid control of the degree of nanofiller dispersion;
  (ii) control on supramolecular structure of nanofiller in polymer;
  (iii) evaluation of the polymer–nanofiller interactions.

Advantages of the Rheological Methods:
- based on routine rheological experiments and modelling;
- easy and non-expensive methods for nanocomposite design;
- applicable for control on the technology and structure of nanocomposites of either thermoset, or thermoplastic polymers incorporating nanofillers.
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