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# Rheology and applications of highly filled polymers: A review of current understanding

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## ARTICLE INFO

## ABSTRACT

This paper reviews current knowledge about the rheology and applications of highly concentrated molten polymers, focusing on hard particles with sizes ranging from several 100 s nm to a few microns. Understanding the rheological properties should assist the formulation and processing of such polymeric materials. The main factors affecting the rheological behavior of these composites are discussed, such as size distribution, nature and shape of the particles, interactions, maximum packing fraction and matrix viscosity. The matrix viscosity is a key parameter that has to be optimized to be low enough to enable the material processing and high enough to improve the dispersion. The size polydispersity of the fillers facilitates higher filling levels and decreases the melt mixture viscosity for a given filler content. The different types of interactions (viz. particle-particle, particle-matrix) are described to interpret the phenomena arising during processing better. On the other hand, mixing is of particular importance to reach high-quality dispersion and distribution of the particles in the matrix in order to obtain a homogenous mixture and desirable properties. The mixing methods and tools to characterize the degree of mixing are reviewed. The use of organic dispersants is generally necessary to improve and control the dispersion degree and flow properties. Mathematical models relating the viscosity as a function of the filler content for unimodal and bimodal highly filled suspensions are summarized. Constraints and flow instabilities often lead to non-linear rheological behavior such as wall slip, particle-binder segregation, swelling and surface instabilities phenomena; these are discussed. Finally, the latest applications for highly filled systems (such as solid propellants, flame retardancy, magnetic materials, ceramic materials, batteries, etc.) are presented as a source of inspiration for industrial improvements.

## Contents

## Nomenclature

| | |
|---|---|
| AIN | Aluminium nitride |
| BN | Boron nitride |
| BSE | Back-scattered electrons |
| CB | Carbon black |
| CIM | Ceramic injection molding |
| CNF | Carbon nanofibers |
| CNT | Carbon nanotubes |
| CTE | Coeffcient of thermal expansion |
| EDX | Energy dispersive X-ray |
| EVA | Ethylene-vinyl acetate block copolymer |
| GRT | Ground rubber type |
| hBN | Hexagonal boron nitride |
| HDPE | High density polyethylene |
| HF | Highly filled |
| HP | Hot press molding |
| HPIM | High pressure injection molding |
| HTPB | Hydroxyl terminated polybutadiene |
| iPP | Isotactic polypropylene |
| KCl | Potassium chloride |
| LDPE | Low-density polyethylene |
| LLDPE | Linear low density polyethylene |
| LPIM | Low pressure injection molding |
| LTEG | Low temperature expandable graphite |
| LVR | Linear viscoelastic region |
| MI | Mixing index |
| MIM | Metal injection molding |
| MR | Magnetic resonance |
| OMMT | Organically modified montmorillonite |
| PBAN | Polybutadiene acrylonitrile |
| PBT | Polybutylene terephthalate |
| PDMS | Polydimethylsiloxane |
| PEG | Polyethylene glycol |
| PIB | Polyisobutene |
| PIM | Powder injection molding |
| PIV | Particle image velocimetry |
| PM | Particle migration |
| PMMA | Polymethyl methacrylate |
| PP | Polypropylene |
| PS | Polystyrene |
| PSD | Particle size distribution |
| PVA | Poly(Vinyl alcohol) |
| PVDF | Polyvinylidene fluoride |
| SEM | Scanning electron microscopy |

| | |
|---|---|
| TEM | Transmission electron microscopy |
| UHMWPE | Ultra-high-molecular-weight polyethylene |
| VdW | Van der waals |

*Symbols in Arabic letters*

| | |
|---|---|
| A | Hamaker constant $[-]$ |
| $A_r$ | aspect ratio equal to $d_{max}/d_{min}$ $[-]$ |
| c | crowding factor $[-]$ |
| D | diameter of the particle [m] |
| $D_i$ | inter-particle spacing parameter [m] |
| $\bar{D}$ | particle mean diameter [m] |
| $D_{dep}$ | Diameter of the depletent particle |
| $D_{ro}$ | rotary diffusivity $[s-1]$ |
| $D_x$ | the x-th moment of the particle size distribution $[-]$ |
| $d_{50}$ | median diameter of the particle size distribution [m] |
| $d_{max}$ | particle longest characteristic distance [m] |
| $d_{min}$ | particle smallest characteristic distance [m] |
| $f_i$ | number fraction of the i-th component $[-]$ |
| $G'$ | storage modulus [Pa] |
| $G''$ | loss modulus [Pa]h: minimum separation between particles [m] |
| $H(\phi)$ | unimodal concentration function, Stiffening function $[-]$ |
| $k_b$ | Bolztmann constant [-] |
| $k_{ij}$ | function of the fraction of small particles in a $b_i$-dispersed system $[-]$ |
| L | length of the particle [m] |
| $M_w$ | molecular weight [kg/mol] |
| $N_1$ | first normal stress difference [Pa] |
| $N_2$ | second normal stress difference [Pa] |
| $n_b$ | power law or Ostwald de Waele index $[-]$ |
| $Pe$ | Peclet number = $\dot{\gamma}/D_r$ $[-]$ |
| $p$ | aspect ratio according to the axis of symmetry $[-]$ |
| $s$ | standard deviation [u] |
| $s_o$ | maximum variance for a completely segregated system [u] |
| T | temperature [K] |
| $U_{dep}$ | depletion potential [J] |
| $U_r^{el}$ | repulsive electrostatic potential [J] |
| $U_r^s$ | repulsive steric potential [J] |
| $U_s$ | wall slip velocity [m.s-1] |
| $U_T$ | total interparticle potential [J] |
| $U_{VdW}$ | attractive Van der Waals potential [J] |