

RHEOLOGICAL CHARACTERIZATION OF A WATERBORNE ORGANIC NANOPARTICLE DISPERSION

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ABSTRACT:

Organic nanoparticles of poly(styrene-co-maleimide) or SMI were synthesized in aqueous dispersion with a maximum concentration of 35 wt.% and are favorably applied in industrial coating processes. In order to evaluate the further processability and flow behavior of these nanoparticle dispersions, general rheological characterization under creep, oscillatory and rotational testing was done by applying various shear stresses, shear rates and frequencies on an air-bearing cylindrical rheometer. Creep tests at different stresses show that the nanoparticle dispersions behave like a viscous material. The crossover of G' and G'' according to oscillatory experiments also demonstrates a transition to viscoelastic behavior at high frequency. The sensitivity of shear-viscosity behavior to concentration and temperature of the dispersions has been evaluated. In parallel, the influences of gap size, repeatability and water evaporation have been statistically evaluated and could be successfully controlled. By comparing oscillatory and rotational rheometry data, flow curves under low shear rates were reconstructed.

KEY WORDS:

Nanoparticles, polymer, aqueous dispersion, rheometry, shear, viscosity

1 INTRODUCTION

Aqueous dispersions of polymer nanoparticles have demonstrated favorable features as sizing or coating agents for papers, cardboard and textiles controlling specific properties such as permeability, wettability, or printability [1]. The availability of nanoparticles in aqueous dispersion with high solid content is encouraged as volatile organic solvents should be avoided because of processing incompatibilities, cost and ecological concerns [2]. In order to extend the application range and enhance the processing of such nanoparticles, better understanding of the rheological characteristics and colloidal stability is needed.

The rheological characteristics of nanoparticles in aqueous medium relate to the behavior of complex fluids [3]. Suspensions are generally classified as heterogeneous mixtures of relatively large particles that settle down over time under the influence of gravity, if it remains undisturbed. Colloidal dispersions, on the contrary, are equally divided suspensions with smaller particles that do not aggregate or separate upon standing.

However, the colloidal stability can be altered by perturbations and/or under specific processing conditions. The stability and/or sedimentation of colloidal particles is generally determined by a balance of Brownian forces, gravity, electrical, thermal and magnetic fields. The Brownian motion causes random particle orientation in dilute systems without inter-particle interactions, but orientation may happen at high Péclet numbers. The particle orientation and rotation depend on the particle shape and may alter flow characteristics, because of shear thinning effects reducing the viscosity and causing non-linear rheological properties [4]. In addition, the non-linear effects are influenced by wall slip as interfacial slippage [5]: The shear rate at the boundary is consequently higher than in the core of the medium and the viscosity is artificially increased [6]. The effects of wall slip and related flow instabilities have been systematically overcome by roughening the wall of the testing geometry, although it could not be fully prevented [7]. The contributions of wall slip can be understood by changing the gap distance, as it affects flocculation at high shear rates [3]. In general, a gradual increase in

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100 rad/s. Under stable flow conditions, dynamic formation and desintegration of some clusters and specific flow patterns were preliminary observed.

The shear-viscosity behavior of the nanoparticle dispersions is very sensitive to concentration and temperature: Therefore, even small amount of water evaporation affects to the rheological behavior of dispersion. In this regard, water evaporation has been successfully controlled during ascending and descending testing, where different viscosity trends have been duplicated at ascending/descending shear stresses or shear rates and may be most likely related to the intrinsic dispersion nature and two-phase behavior. The effects of gap size (on fresh samples) and reproducibility (on single samples loaded for different number of cycles) were extensively evaluated and present low coefficients of variation. Comparing oscillatory and rotational rheometry data provides viscosity shows some differences under low shear rate regimes, where a two-phase behavior may occur. Finally, the stability of the dispersions after high-shear rate experiments and over a longer time is illustrated by only small variations in nanoparticle size (between 100 to 120 nm diameter) that are mostly due to small changes in hydrodynamic radius during processing and storage.

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REFERENCES

- [1] Doeren K, Freitag W, Stoye D: Water-borne Coatings: The Environmentally-Friendly Alternative, Hanser Verlag, München (1994).
- [2] Samyn P, Schoukens G, Stanssens D, Vonck L, Van den Abbeele H: Incorporating different vegetable oils into an aqueous dispersion of hybrid organic nanoparticles, *J. Nanopart. Res.* 14 (2012) 1075.
- [3] Larson RG: The Structure and Rheology of Complex Fluids, Oxford University Press, New York (1999).
- [4] Mewis J, Wagner NJ: Colloidal Suspension Rheology, Cambridge University Press, New York (2012).
- [5] Barnes HA: A review of the slip (wall depletion) of polymer solutions, emulsions and particle suspensions in viscometers: its cause, character, and cure, *J. Non Newton Fluid Mech.* 56 (1995) 221–251.
- [6] Saarikoski E, Saarinen T, Salmela J, Seppälä J: Flocculated flow of microfibrillated cellulose water suspensions: An imaging approach for characterisation of rheological behaviour, *Cellulose* 19 (2012) 647–659.
- [7] Nechyporchuk O, Belgacem MN, Pignon F: Rheological properties of micro-/nanofibrillated cellulose suspensions: Wall-slip and shear banding phenomena, *Carbohydr. Polym.* 112 (2014) 432–439.
- [8] Tseng WJ, Lin KC: Rheology and colloidal structure of aqueous TiO₂ nanoparticle suspensions, *Mater. Sci. Eng. A* 355 (2003) 186–192.
- [9] Kaydanova T, Miedaner A, Perkins JD, Curtis C, Alleman JL, Ginley DS: Direct-write inkjet printing for fabrication of barium strontium titanate-based tunable circuits, *Thin Sol. Films* 515 (2007) 3820–3824.
- [10] Nersisyan HH, Lee JH, Son HT, Won CW, Maeng DY: A new and effective chemical reduction method for preparation of nanosized silver powder and colloid dispersion, *Mater. Res. Bull.* 38 (2003) 949–956.
- [11] Sarkar A, Kapoor S, Mukherjee T: Preparation, characterization, and surface modification of silver nanoparticles in formamide, *J. Phys. Chem. B.* 109 (2005) 7698–7704.
- [12] Sudeep PK, Kamat PV: Photosensitized growth of silver nanoparticles under visible light irradiation: A mechanistic investigation, *Chem. Mater.* 17 (2005) 5404–5410.
- [13] Yin H, Yamamoto T, Wada Y, Yanagida S: Large-scale and size-controlled synthesis of silver nanoparticles under microwave irradiation, *Mater. Chem. Phys.* 83 (2004) 66–70.
- [14] Lengálová A, Pavlínek V, Sába P, Quadrat O, Stejskal J: The effect of dispersed particle size and shape on the electrorheological behaviour of suspensions, *Colloids Surf. A* 227 (2003) 1–8.
- [15] Vicent M, Sánchez E, Mallol G, Moreno R: Study of colloidal behaviour and rheology of Al₂O₃-TiO₂ nanosuspensions to obtain free-flowing spray-dried granules for atmospheric plasma spraying, *Ceram. Int.* 39 (2013) 8103–8111.
- [16] Taylor ML, Morris GE, Smart RSC: Polyphosphate interaction with aluminium-doped titania pigment particles, *Colloids Surf. A* 190 (2001) 285–294.
- [17] Knauert ST, Douglas JF, Starr FW: The effect of nanoparticle shape on polymer-nanocomposite rheology and tensile strength, *Polym. Eng. Sci.* 53 (2013) 1512–1528.
- [18] Tshilumbu NN, Masalova I: Effect of nanoparticle hydrophobicity on the rheology of highly concentrated emulsions, *Appl. Rheol.* 23 (2013) 62835–62846.
- [19] Turian RM, Ma TW, Hsu FLG, Sung DJ: Characterization, settling, and rheology of concentrated fine particulate mineral slurries, *Powder Technol.* 93 (1997) 219–233.
- [20] Morris GE, Skinner WA, Self PG, Smart RSC: Surface chemistry and rheological behaviour of titania pigment suspensions, *Colloids Surf. A* 155 (1999) 27–41.
- [21] Bach U, Lupo D, Comte P, Moser JE, Weissörtel F, Salbeck J, Spreitzer H, Grätzel M: Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies, *Nature* 395 (1998) 583–585.
- [22] Richmond WR, Jones RL, Fawell PD: The relationship between particle aggregation and rheology in mixed silica-titania suspensions, *Chem. Eng. J.* 71 (1998) 67–75.
- [23] Tielemans M, Roose P: Study of the rheology of aqueous radiation curable polyurethane dispersions modified

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<http://www.appliedrheology.org>

- with associative thickeners, *Prog. Org. Coat.* 63 (2008) 182–188.
- [24] Sauer F: A new approach to the understanding of rheological additives, *Proceedings of the Eurocoat 2* (2003) 303–317.
 - [25] Samyn P, Deconinck M, Schoukens G, Stanssens D, Vonck L, Van den Abbeele H: Modifications of paper and paper-board surfaces with a nanostructured polymer coating, *Prog. Org. Coat.* 69 (2010) 442–454.
 - [26] Samyn P, Deconinck M, Schoukens G, Stanssens D, Vonck L, Van den Abbeele H: Synthesis and characterization of imidized poly(styrene-maleic anhydride) nanoparticles in stable aqueous dispersion, *Polym. Adv. Technol.* 23 (2012) 311–325.
 - [27] Schmidt M, Münstedt H: On the elastic properties of model suspensions as investigated by creep recovery measurements in shear, *Rheol. Acta* 41 (2002) 205–210.
 - [28] Hyun K, Wilhelm M, Klein CO, Cho KS, Nam JG, Ahn KH, Lee SL, Ewoldt RH, McKinley GH: A review of nonlinear oscillatory shear tests: Analysis and application of Large Amplitude Oscillatory Shear (LAOS), *Prog. Polym. Sci.* 36 (2011) 1697–1753.
 - [29] Rossano M, Hucher N, Picard C, Colletta D, Le Foll F, Grisel M: Effects of aging on structure and stability of TiO₂ nanoparticle-containing oil-in-water emulsions, *Int. J. Pharm.* 461 (2014) 89–96.
 - [30] Bröckel U, Meier W, Wagner G: *Product Design and Engineering: Formulation of Gels and Pastes*, Wiley-VCH Verlag, Heidelberg (2013).
 - [31] Møller PCF, Mewis J, Bonn D: Yield stress and thixotropy: on the difficulty of measuring yield stresses in practice, *Soft Matter* 2 (2006) 274–283.
 - [32] Bender JW, Wagner NJ: Reversible shear thickening in monodisperse and bidisperse colloidal dispersions, *J. Rheol.* 40 (1996) 899–916.
 - [33] Barnes HA: Shear-thickening ('dilatancy') in suspensions of nonaggregating solid particles dispersed in Newtonian liquids, *J. Rheol.* 33 (1989) 329–366.
 - [34] Brady JF, Morris JF: Microstructure of strongly sheared suspensions and its impact on rheology and diffusion, *J. Fluid Mech.* 348 (1997) 103–139.
 - [35] Faith AM: *Understanding Rheology*, Oxford University Press, New York (2001).
 - [36] D'Haene P, Mewis J: Rheological characterization of bimodal colloidal dispersions, *Rheol. Acta.* 33 (1994) 165–174.

