



Rheological behaviour of oil-filled polymer nanoparticles in aqueous dispersion



Hesam Taheri^{a,b}, Dirk Stanssens^c, Pieter Samyn^{a,b,*}

^a University of Freiburg, Freiburg Institute for Advanced Studies (FRIAS), Faculty of Environment and Natural Resources, Chair for Bio-based Materials Engineering, Habsburgerstrasse 49, 79104 Freiburg, Germany

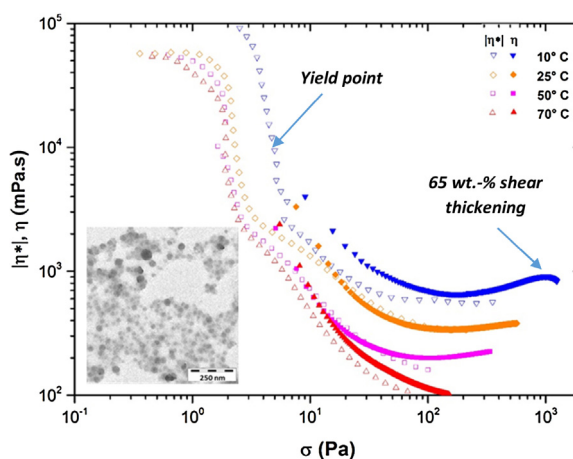
^b Freiburg Materials Research Center, Stefan-Meier-Straße 21, 79104 Freiburg, Germany

^c Topchim N.V., Nijverheidstraat 98, B-2160, Wommelgem, Belgium

HIGHLIGHTS

- Aqueous SMI/oil dispersions behave as a viscoelastic medium at low stresses and become purely viscous at high stresses.
- Presence of oil reduces viscosity and enhances viscoelastic properties of dispersion.
- Overlap between rotational and oscillatory data for SMI/oil dispersions was found by considering the dynamic viscosity and shear viscosity as a function of shear stress.
- Transition of viscosity with shear stress indicates yield point.

GRAPHICAL ABSTRACT



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ABSTRACT

Hybrid organic nanoparticles of poly(styrene-co-maleimide) with 70 wt.-% incorporated palm oil (SMI/oil) were provided in aqueous dispersion for use in industrial coating processes. The rheological characteristics of dispersions with 65 wt.-% and 35 wt.-% solid content have been determined by creep, oscillatory and rotational testing under different shear stresses, shear rates, frequencies and temperatures. The effects of oil on viscoelastic properties have been demonstrated by comparative tests on a 35 wt.-% pure SMI nanoparticle dispersion. The creep and strain recovery data show viscoelastic responses only for 65 wt.-% SMI/oil dispersions at low stresses, as further detailed by the calculated Burger model parameters. The 65 wt.-% SMI/oil dispersion at higher stresses and 35 wt.-% SMI/oil dispersion over the full stress range become viscous. From strain sweep tests, the cross-over of G' and G'' demonstrates linear features at low strain and a transition into viscoelastic properties at high strain. The frequency sweep test indicates a linear solid-like behaviour with storage and loss modulus independent of frequencies at temperatures up to 70 °C. From rotational tests, the sensitivity of shear-viscosity properties to concentration and temperature has been demonstrated. The oscillatory and rotational data can be fitted

* Corresponding author at: University of Freiburg, Freiburg Institute for Advanced Studies (FRIAS), Faculty of Environment and Natural Resources, Chair for Bio-based Materials Engineering, Habsburgerstrasse 49, 79104 Freiburg, Germany.

E-mail address: pieter.samyn@outlook.be (P. Samyn).

by the Cox-Merz rule using dynamic viscosity and shear viscosity as a function of frequency or shear stress, while a yield point has been detected as a function of shear stress for both 65 and 35 wt.-% SMI/oil dispersions.

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1. Introduction

The interest in aqueous dispersions containing oil-filled nanoparticles relates to their ability for delivering encapsulated vegetable oils as hydrophobic moieties in aqueous environment. In our previous work, different vegetable oils have been incorporated into organic nanoparticles of poly(styrene-*co*-maleimide) or SMI during an imidization reaction of poly(styrene-*co*-maleic anhydride), forming a stable aqueous dispersion of SMI/oil nanoparticles with high solid content. The stability of SMI/oil nanoparticle dispersions is favourably governed by a fraction of ammonolyzed maleic anhydride that fulfills the role of surfactant [1]. The oil-filled nanoparticles can be applied as a dispersion coating improving hydrophobicity and water repellence on paper [2], or wood [3]. A better insight in the rheological properties of the nanoparticle dispersions could help in further optimizing their processing conditions.

The rheological features of organic nanoparticles in aqueous medium depend on the volume fraction of dispersed particles, particle size distribution, or pH and ionic strength of the medium [4–6]. The rheological behaviour and linear viscoelasticity of suspensions with nanosized particles strongly depend on the aspect ratio and structuration by network formation through interparticle interactions [7]. For a polystyrene latex, steady shear and oscillatory rheometry indicated that long-ranged polymeric forces between particles governed the variation of viscosity and storage modulus with applied stress, which could be altered by surface grafting [8]. The polystyrene particles in dilute suspensions under shear flow aligned and formed uniformly spaced strings [9]. At a critical concentration for polystyrene latex particles, a transition in the rheological characteristics over a narrow range of polymer volume fractions was observed [10]: remarkably, the Cox–Merz rule was not followed at high concentrations. For concentrated polystyrene latex dispersions, the system became predominantly elastic and significant interpenetration and compression of the chains occurred in parallel with an increase in moduli and dynamic viscosity [11]. The rheology of polystyrene particles was strongly influenced by intramolecular crosslinking and molecular mass [12]. The aqueous dispersions of organic nanoparticles could show gelling in presence of vaseline and almond oil [13]. The gelled oil particle formulations were stabilized by electrostatic interactions between positively charged polyethyleneimine and stearic acid [14]. The core-shell nanoparticles with crosslinked polystyrene shell showed nonlinearities assigned to disentanglement of polystyrene macromolecules in the matrix [15].

The rheological properties of dilute and semi-dilute emulsions with immiscible fluids have been generally studied [16,17], in particular considering oil-in-water emulsions as a system of stabilized oil droplets in aqueous medium [18]. With increasing volume fraction of dispersed oil phase, the contact between the droplets tends to break the stability of the medium resulting in flocculation or coalescence due to thermodynamic instabilities and interfacial tension between the dispersed components [19]. In parallel, the change in effective hydrodynamic volume of the dispersed phase affects the rheological properties and results in higher viscosity [20], which is proportional to interfacial tension and inversely proportional to drop size [18]. The stability can be improved by reducing the

concentration below the critical flocculation concentration [21]. However, high volume fractions of oil and high solid contents are required for coating applications, but they might show remarkable elasticity due to the interfacial energy associated with the deformation of the medium. Studies on creep and strain recovery of a dispersed oil phase in water can provide better insights in the elastic, viscous or viscoelastic properties: the degree of elasticity and viscoelasticity is sensitive to the oil phase, particle dispersion, volume fraction and shear stress [22]. The aqueous phase helps in minimizing emulsion deformation: the recovery seems to be larger at high water cuts due to the inherent recoverable nature of water [23,24]. According to creep and strain recovery data of oil-in-water emulsions, the viscous features were dominant and the elasticity decreased under high stresses [25], which manifested as break-up and reformation of bonds. The rheology and stability of oil-in-water systems can be influenced by surfactants or additives. In one approach, surfactants stabilize the interfaces and allow the formation of highly concentrated homogeneous emulsions. The surfactants enhance gelling at a critical concentration: e.g., in presence of maltodextrin, the oil emulsions form a viscous system with strong shear thinning above the critical flocculation concentration [26]. In another approach, the addition of small particles alters the viscosity depending on volume fraction, wettability and stabilizing effect of the particles [27]. The rheological properties and viscosity of oil-in-water emulsions with solid particles was mostly affected by the particle concentration and not by the water content, at water fractions below 30% [28]. The oil droplets affect the interaction between the dispersed solid particles to reach a stable viscosity at higher volume fractions of particles. The dispersions stabilized by particles behave as a single homogeneous phase, where the increment in viscosity depends on the concentration of solid particles, while there was no correlation between viscosity effects of the oil and particles [29].

In this paper, a detailed rheological study on the stability, creep recovery and flow properties of SMI/oil nanoparticle dispersions under different conditions of shear rate, shear stress, concentration and temperature will be presented. In particular, the creep modeling of SMI/oil dispersions will be emphasized to evaluate the viscoelastic features in presence of oil. The effects of oil on the rheological properties of a SMI/oil dispersion will be confirmed by comparing with previous rheological data of a pure SMI nanoparticle dispersion [30].

2. Materials and methods

2.1. SMI/oil organic nanoparticle dispersion

An aqueous dispersion of SMI/oil nanoparticles was delivered by Topchim N.V. (Wommelgem, Belgium) following synthesis by a previous protocol [31], which includes the imidization of poly(styrene-*co*-maleic anhydride) or SMA into poly(styrene-*co*-maleimide) or SMI nanoparticles in presence of 70 wt.-% palm oil. In brief, an SMA copolymer (26 mol.-% maleic anhydride, $M_w = 80,000$ g/mol) was loaded in a 1 L autoclave together with palm oil, water and ammonium hydroxide (the weight ratio of ammonium hydroxide to maleic anhydride was 1:1.01). After 5 h reaction time under continuous stirring at a maximum temperature

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