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Rheological characterization of Poly(ethylene oxide) and carboxymethyl cellulose suspensions with added solids

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ABSTRACT

Many foods are suspensions of solid particles randomly distributed in a non-Newtonian polymeric fluid. The rheological properties of high molecular weight poly(ethylene oxide) (PEO) and carboxymethyl cellulose (CMC) suspensions by adding micro-metric solid particles such as fibres or spheres were studied. The particle volume fraction, Φ, was varied between 0 and 0.4. Their rheological properties were obtained after fitting a Cross model. Rheological behaviour of the solutions was compared with rheological behaviour of food reported in the literature. For PEO and CMC solutions with spherical particle, the behaviour of the normalized steady shear viscosity, μ/μ_0, as function of the fraction volume was compared with a Thomas model. However, for PEO the multibody interactions were not well represented and for CMC suspensions, μ/μ_0 seems to be lineal with Φ. To observe and explain more the influence of the particle concentrations on the rheological behaviour, dynamic rheological measurements (upon verification of the linearity limit) were also performed. A transition from a dominantly viscous fluid to a dominantly elastic material was observed when Φ was increased.

1. Introduction

Many foods are suspensions of solid particles randomly distributed in a continuous medium (Newtonian or non-Newtonian fluid) such as: tomato puree, peanut butter, salad dressing (Rao, 1999; Saeseaw, Shiowatana, & Siripinyanond, 2005; Tadros, 2010). Considerable attention is given in the literature to the rheology of suspensions of particles in Newtonian fluids like starch granules in water (Bertolini, 2010; Rao, 1999). In contrast, even if the rheology of suspensions in non-Newtonian media is in the food engineering field, from a technological point of view, more important than its counterpart in Newtonian media, relatively few studies are conducted on the rheology of dilute or semi-dilute suspensions of solid particles in non-Newtonian food fluids. The rheology behaviour of suspension (spheres, fibres etc.) in pure viscoelastic fluids like polystyrene melt, PDMS are further reported (Larson, 1999). Addition of solid particles to food fluids does not simply change the magnitude of the viscosity, it can modify strongly the rheological properties of the fluid. However, external variables such as temperature and pressure can also influence the rheological behaviour (Doi & Edwards, 1994). Thus, knowledge of the rheological behaviour of this class of complex fluid is fundamental to understand the relationship between the food processing behaviour and relations between structure and property.

In food engineering, pseudo-plasticity or shear-thinning fluids as poly(ethylene oxide) (PEO) or carboxymethyl cellulose (CMC) are the most common type of time-independent non-Newtonian fluid (Chhabra, 2010). These fluids are characterized by an apparent viscosity (defined as the ratio between the shear stress σ and the shear rate $\dot{\gamma}$), which decreases with increasing shear rate. The rheological properties of polymer solutions are strongly related to the chemical formulation, the molecular weight and the concentration of the polymer and external variables such as temperature and pressure (Doi & Edwards, 1994). Poly(ethylene oxide) (PEO) is a polymer of ethylene oxide, flexible and non-ionic water-soluble used in many applications from industrial manufacturing to medicine (Phillips & Williams, 2000). The shear rheology of PEO solutions has been characterized by several authors. Effects of concentrations, molecular weights, salt and anionic surfactants on the viscoelastic character of PEO in aqueous solutions were commented by Lance-Gomez and Ward (1986). Carboxymethyl

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cellulose (CMC) is derived from cellulose, it is used as a viscosity modifier or thickener, and to stabilize emulsions in various food products including ice cream; it is known for its excellent water retaining capacity (Phillips & Williams, 2000). Moreover, it is the sodium salt of CMC (CH COONa) that promotes water solubility, which is not affected by the temperature of the water itself. The rheological properties of CMC solutions at high concentrations have both non-Newtonian and viscoelastic properties.

Food suspensions are complex materials whose rheological characteristics with respect to the nature of the solid particles as well as those of the fluid media often are determined using experimental modelling. Generally, the sizes of the particles are micrometric. Various food use microspheres of polyethylene (sizes from 10 μm to 1000 μm) as component: chewing gum base, cheese, etc. (Nussinovitch, 2010). To model, the simplest suspensions are composed of hard spheres in which the only interactions between particles are rigid repulsion that occur when particles come into contact. A widely appreciated example of a solid suspension is chocolate. Chocolate is a polydisperse suspension (sugar, cocoa and/or milk solids) in a Newtonian fluid (fat phase) (Afoakwa, Paterson, & Fowler, 2007). However, most foods are non-Newtonian fluids containing nonspherical particles, e.g. tomato or apple pulp, cassava paste etc. Thus, to understand more food fluid-solid particle interactions, it is advisable to use nonspherical particles like fibres.

Therefore, the purpose of this article is to study the changes in apparent viscosity of high molecular weight of PEO and CMC suspensions by adding micro-metric solid particles such as fibres or spheres. Steady shear flow tests were done to measure the steady-state viscosity of the suspension. Flow curves were reported for two PEO and CMC concentrations and various particle volume fraction ($0 \leq \Phi \leq 0.4$) and were fitted using a Cross model. For all experiments, the normalized steady shear viscosity, μ/μ_0, was modelled as function of particle volume fraction. Dynamic rheological measurements (upon verification of the linearity limit) were also performed to observe and explain more the influence of the particle concentrations on the rheological behaviour.

2. Materials and methods

2.1. Suspending fluids

Two different types of suspending fluids were used. Poly(ethylene oxide) (PEO) is used as shear-thinning fluid whereas sodium carboxymethyl cellulose (CMC) is, instead, used as viscoelastic carrier fluid. Both fluids have a density $\rho = 1000$ kg m^{-3} at C. PEO and CMC were provided by Sigma–Aldrich. POE has a nominal molecular weight M_w of 4×10^6 g mol^{-1} whereas CMC had $M_w \approx 7 \times 10^5$ g mol^{-1} with a degree of substitution of 0.80–0.95. The aqueous solutions of PEO and CMC were prepared by dissolving the appropriate amount of PEO and CMC in distilled water at room temperature. Sufficient time (>24 h) of continuous magnetic stirring was allowed to achieve complete homogenization. PEO concentrations were fixed in the range 1%–1.5% w/w whereas CMC concentrations were chosen in the range 1.5%–2.2% w/w.

2.2. Solid particles

Two types of glass bead microspheres purchased from Sigmund Lindner GmbH (Germany) were used as solid suspensions: A-type (size range: 0–50 μm) and B-type (size range: 40–70 μm). Carbon fibres were purchased from Zoltek (Panex 35, USA). The density of the glass beads was $\rho_s = 2448$ kg m^{-3} whereas for carbon fibres $\rho_f = 1810$ kg m^{-3}. Particle size distribution (PSD) of glass beads was determined using a laser scattering spectrometer Mastersizer S model MAM 5005 (Malvern Instruments Ltd., UK). The length and diameter of the fibre was constant $l_p = 100$ μm and $d_p = 7.2$ μm, respectively. Therefore the aspect ratio, i.e. length/diameter, was $r_p = 13.88$. Particle volume fraction, Φ, was varied between 0 and 0.4 for each polymer concentration.

2.3. Preparation of the suspensions

Preparation of the suspensions was done with care as homogeneous dispersion of non agglomerated particles is difficult to obtain especially for low solid concentrations. The solid particles were dried to remove moisture. The polymer solution and solid particles were then weighted and gently stirred (to avoid introducing air) in a beaker for 1 h at the desired proportion. Solutions of CMC and PEO were clear and colourless therefore transparent to light. Optical observation confirmed that the particles were well dispersed and did not form aggregates.

2.4. Rheological measurements

All the rheological measurements were performed on a rheometer (Carri Med, CSL2 100, TA Instruments, UK) using a 40 mm diameter parallel plate fixture with a gap $h = 600$ μm. The lower plate is equipped with a Peltier temperature control system; all tests were conducted at 20 °C with 3 repetitions. The samples were carefully loaded to the measuring plate of the rheometer using a spatula and then the measuring plate was raised at a very slow speed, in order to prevent the disruption of the solution structure. Moreover, it was checked that in all cases the time scale associated with sedimentation was much larger than the time scale of both sample preparation and experiment (10 min). For spherical particle, the settling time required to migrate 10% of the rheometer gap, h, under the influence of gravity, g (acting perpendicular to the gap) can be calculated from the Stokes law:

$$t_{settling} = \frac{0.45\mu_o h}{R^2 g(\rho_p - \rho)} \tag{1}$$

where g is the gravity, μ_0 is the dynamic viscosity of the suspending fluid, h is the gap, ρ_p and ρ are the particle density and fluid density, respectively.

For fibre particle, another settling time can be estimated from the settling vertical velocity (Happel & Brenner, 1965):

$$V_{settling} = \frac{d_p^2 g(\rho_p - \rho)}{16\mu_o}\left[2\ln(2r_p) - 1.614 - 0.355\ln(2r_p)^{-1} + O\left(\ln(2r_p)^{-2}\right)\right] \tag{2}$$

where d_p is the fibre diameter, r_p is the aspect ratio, g is the gravity, μ_0 is the dynamic viscosity of the suspending fluid, and ρ_p and ρ are the particle density and fluid density, respectively.

The flow curves were obtained by applying an increasing shear stress ramp at a constant stress rate of 0.05 Pa s^{-1}. Storage $G'(\omega)$ and loss $G''(\omega)$ moduli were measured at frequencies ranging from 0.1 to 10 Hz and, by applying a chosen stress value, allowing measurements within the linear viscoelastic region.

3. Results and discussion

3.1. Spherical particle size measurements

As, the De Brouckere mean diameter of the particles and the size distribution of the particles influence the flow behaviour