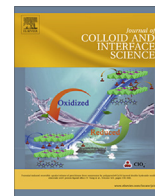




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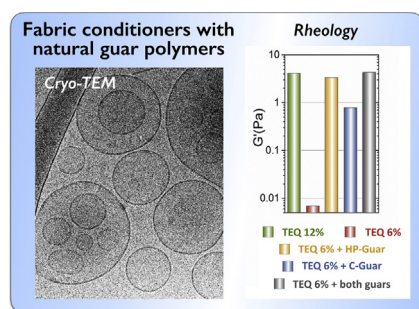
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Regular Article

Design of eco-friendly fabric softeners: Structure, rheology and interaction with cellulose nanocrystals

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GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Concentrated fabric softeners are water-based formulations containing around 10–15 wt% of double tailed esterquat surfactants primarily synthesized from palm oil. In recent patents, it was shown that a significant part of the surfactant contained in today's formulations can be reduced by *circa* 50% and replaced by natural guar polymers without detrimental effects on the deposition and softening performances. We presently study the structure and rheology of these softener formulations and identify the mechanisms at the origin of these effects.

Experiments: The polymer additives used are guar gum polysaccharides, one cationic and one modified through addition of hydroxypropyl groups. Formulations with and without guar polymers are investigated using optical and cryo-transmission electron microscopy, small-angle light and X-ray scattering and finally rheology. Similar techniques are applied to study the phase behavior of softener and cellulose nanocrystals considered here as a model for cotton.

Findings: The esterquat surfactants are shown to assemble into micron-sized vesicles in the dilute and concentrated regimes. In the former, guar addition in small amounts does not impair the vesicular structure and stability. In the concentrated regime, cationic guars induce a local crowding associated to depletion interactions and leads to the formation of a local lamellar order. In rheology, adjusting the polymer concentration at 1/10th that of the surfactant is sufficient to offset the decrease of the elastic property associated with the surfactant reduction. In conclusion, we have shown that through an appropriate choice of natural additives it is possible to lower the concentration of surfactants in fabric conditioners by about half, a result that could represent a significant breakthrough in current home care formulations.

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1. Introduction

Concentrated fabric softeners are water-based formulations containing around 10–15 wt% of double tailed surfactants, primarily synthesized from palm oil derivatives. These laundry products are used since the 1960's to make cotton fabrics soft, fresh smelling and wrinkle free. For the last decade, efforts have been made to develop conditioners based on natural and less aquatic materials [1]. The first step towards more eco-friendly formulations has been taken with the replacement of dialkyldimethylammonium surfactants by esterquats. Esterquats are quaternary ammonium compounds having two (C(16)–C(18)) fatty acid chains with two weak ester linkages. The inclusion of ester linkages has significantly improved the biodegradation kinetics of these materials, lowering the environmental exposure [2]. The second step for the development of eco-friendly products is modern and concerns the reduction of the surfactant concentration used in house and personal care formulations. In this work we explore this possibility to lessen the surfactant content in fabric softeners while preserving the initial deposition and softening performances.

Although softeners were used for decades [3], there is still a lack of consensus pertaining to the active deposition on cotton fibers as well as on the softening mechanism. It has been shown that the surfactants used in conditioners are self-assembled into micron size vesicles [4–6]. In general it is assumed that the softening effect is due to the formation of a lubricating surfactant layer on the fibers [7–9]. Recent studies have correlated fabric frictional characteristics with smoothness and softness [10], while others have put forward that the friction between the human skin and fabrics has a more prominent role [11]. Following Igarashi et al. the softening effect would come from the reduction of H-bonding between the bound water molecules and the cotton fibers [12,13]. Crutzen has suggested that hydrophobic interactions derived from the long alkyl chains of cationic surfactants are the primary driving force for adsorption [14], whereas Kumar et al. proposed that the deposition process is electrostatically driven and that intact vesicles adsorb on cotton or viscose fibers [5,15]. The deposition of vesicular structures (including uni/multilamellar and multivesicular vesicles) on solid substrates results in the formation of a so-called supported vesicular layer (SVLs) [8,16]. Understanding the SVL formation is also important for conditioner and active delivery applications. In fabric softeners, surfactant vesicles act as vehicles for driving water insoluble molecules (e.g. fragrances) on cotton [17]. In a recent paper, we have shown that in contact with cellulose nanocrystals, vesicles maintain their shape, in agreement with the work by Kumar and coworkers [5] and are strongly associated to the surfactant membrane *via* electrostatic forces [6]. To produce the next conditioner generation, it is essential to understand the intrinsic processes pertaining to the deposition and softening mechanism, as well as being able to control them through a solid physicochemistry approach.

Recently the Solvay application laboratories have filed a series of patents that describe the benefits of adding minute amounts of polysaccharides to actual formulations in order to improve their softening and fragrance delivery performances [18,19]. Natural hydrocolloid polymers such as cationic guar gum (C-Guar) and a hydroxypropyl guar (HP-Guar) extracted from the seeds of *Cyamopsis tetragolobus* plant were considered as additives for this application. In these patents, it is reported that towels treated with different formulations, including additive-free benchmark were evaluated from independent panellists in double-blinded tests. The softness of the treated towels was rated in a scale of 1 to 5, wherein 1 represents the lowest softness and 5 represents the highest. According to this survey, esterquat formulations modified with the C-Guar and HP-Guar polymers received the highest

ranking for the softening performance, 4.4 against 4.0 for the additive-free benchmark. At the same time the surfactant concentration could be reduced by about half, from 10.5 wt% to 4–6 wt%.

In this work, we investigate the effects of cationic and hydroxypropyl guar polymers focusing on the structural and rheological properties of novel conditioner formulations. The dispersions are investigated using a combination of techniques including optical and cryo-transmission electron microscopy, small-angle X-ray scattering and rheology. It is found that at low concentration, the polymers do not alter the local structure of the cationic esterquat vesicles, whereas at higher concentrations the phase and rheological behaviors are modified. By adjusting the polymer concentration at around 1/10 that of the surfactant, it is possible to offset the decrease of the elastic property associated with the surfactant reduction. The deposition on model cotton fibers is simulated following the interaction of vesicles and polymers with cellulose nanocrystals [20–23]. Cellulose nanocrystals are here used as a stand-in for cotton to facilitate the assessment of the interactions in bulk phases. We finally show that the physicochemical study of conditioners in the dilute and concentrated regimes, combined with the testing of their deposition and softening performances are useful to help guide the development of novel and environmentally friendly softeners.

2. Experimental section

2.1. Materials and sample preparation

2.1.1. Materials

The esterquat surfactant ethanaminium, 2-hydroxyN,N-bis(2-hydroxyethyl)-N-methyl-esters with saturated and unsaturated C16–18 aliphatic chains, abbreviated TEQ in the following was provided by Solvay®. For TEQ, the gel-to-fluid transition related to the long-range order of the surfactant molecules in the membrane is found at $T_M = 60^\circ\text{C}$ [6]. The counterions associated to the quaternized amines are methyl sulfate anions. The polysaccharide polymers are a cationic guar gum (C-Guar, molecular weight $2 \times 10^6 \text{ g mol}^{-1}$) and a hydroxypropyl guar gum (HP-Guar, molecular weight $0.5 \times 10^6 \text{ g mol}^{-1}$), both synthesized by Solvay® (Scheme 1). Guar is a natural polymer extracted from the seeds of *Cyamopsis tetragolobus* plant. HP-Guar is widely used in oil and gas recovery, paints, cosmetics and biology [24] as a thickening and lubricant agent [25,26]. Cationic guar is known for its conditioning properties, notably on hair [27–29]. They were obtained by introducing positively charged trimethylamino(2-hydroxy)propyl into the backbone.

Cellulose nanocrystals (CNC) was prepared according to earlier reports using catalytic and selective oxidation [30]. Briefly, cotton linters provided by Buckeye Cellulose Corporation were hydrolyzed according to the method described by Revol et al. treating the cellulosic substrate with 65% (w/v) sulfuric acid at 63°C during 30 min [30]. The suspensions were washed by repeated centrifugations, dialyzed against distilled water until neutrality and sonicated for 4 min with a Branson B-12 sonifier equipped with a 3 mm microtip. The suspensions were then filtered through $8 \mu\text{m}$ and then $1 \mu\text{m}$ cellulose nitrate membranes (Whatman). At the end of the process, a 2 wt% aqueous stock suspensions was obtained. The resulting nanoparticles are in the form of laths and have a length of $180 \pm 30 \text{ nm}$, a width of $17 \pm 4 \text{ nm}$ and a height of 7 nm. These values were confirmed by Cryo-TEM (see Supplementary Fig. S1). Using light scattering, the CNC dispersion prepared at pH 4.5 and at a concentration of 0.1 wt% displays a single relaxation mode in the autocorrelation function. $g^{(2)}(t)$ is decreased rapidly above delay times around $10^3 \mu\text{s}$, indicating that

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