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New insights on Natural Rubber microgel structure thanks to a new method for microaggregates extraction

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ABSTRACT

Size exclusion chromatography (SEC) columns pre-treated with a tetrabutylammonium bromide (TBABr) solution were used to develop a new method for extracting the microgel of Natural Rubber (NR). A solution of microaggregates smaller than 1 μm (Microgel$_{<1\mu}$) was obtained by collecting the corresponding elution volume after injecting the soluble fraction of the studied sample. The Microgel$_{<1\mu}$ solution was then characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM). Direct imaging of two populations of isolated microaggregates with different sizes and structures was carried out. Spherical microaggregates with a hydrodynamic diameter (d_h) of 500 nm were found to account for the majority of the isolated microaggregates. Larger microaggregates, with a d_h of 1000 nm, were also observed and may have been formed by aggregation of the former. An "apparent molecular density" parameter was used to compare their compactness: the larger microaggregates were found to be 66% denser than the smaller ones.

1. Introduction

Natural Rubber (NR) is made from the latex of *Hevea brasiliensis*, and accounts for 42% of global elastomer consumption [1]. Because of the outstanding mechanical properties of this bio-based material [2,3], composed of about 94% (w/w) *cis*-1,4-polyisoprene [4,5], NR is essential in the tire and anti-vibration industries. Some non-isoprene compounds [4], such as lipids (1.5–4% w/w) [5–8], proteins (1–3.5% w/w) [5,8–10], and minerals (0.2% w/w) [5,11] are assumed to be partly responsible for its superior mechanical properties [12–14], compared to synthetic rubbers [2,3]. In fact, these non-isoprene compounds are assumed to be involved in the interaction between *cis*-1,4-polyisoprene macromolecules, leading to the existence of a gel phase in NR. This gel phase is composed of an insoluble fraction, the "macrogel" [15,16], and of microaggregates dispersed in the soluble fraction, constituting the "microgel" [17,18]. To explain macrogel structure, Tanaka et al. [13,19] suggested some physical interactions between phospholipids linked to the α-end of the polyisoprene, and proteins at the ω-terminal end of the macromolecules. In a recent paper, Rolere et al. [20] showed that the amount of proteins in macrogel correlated with its crosslink density. Rippel et al. [18,21] highlighted the implication of calcium in the structuring of microaggregates, by ionic interactions between divalent cations (Ca^{2+}) and some carboxylate functional groups [22,23].

After NR dissolution in good solvents for polyisoprene, such as toluene or tetrahydrofuran (Fig. 1), the macrogel is easily extractable by centrifugation [23,24]. Consequently, several authors have considered that the gel phase of NR is only

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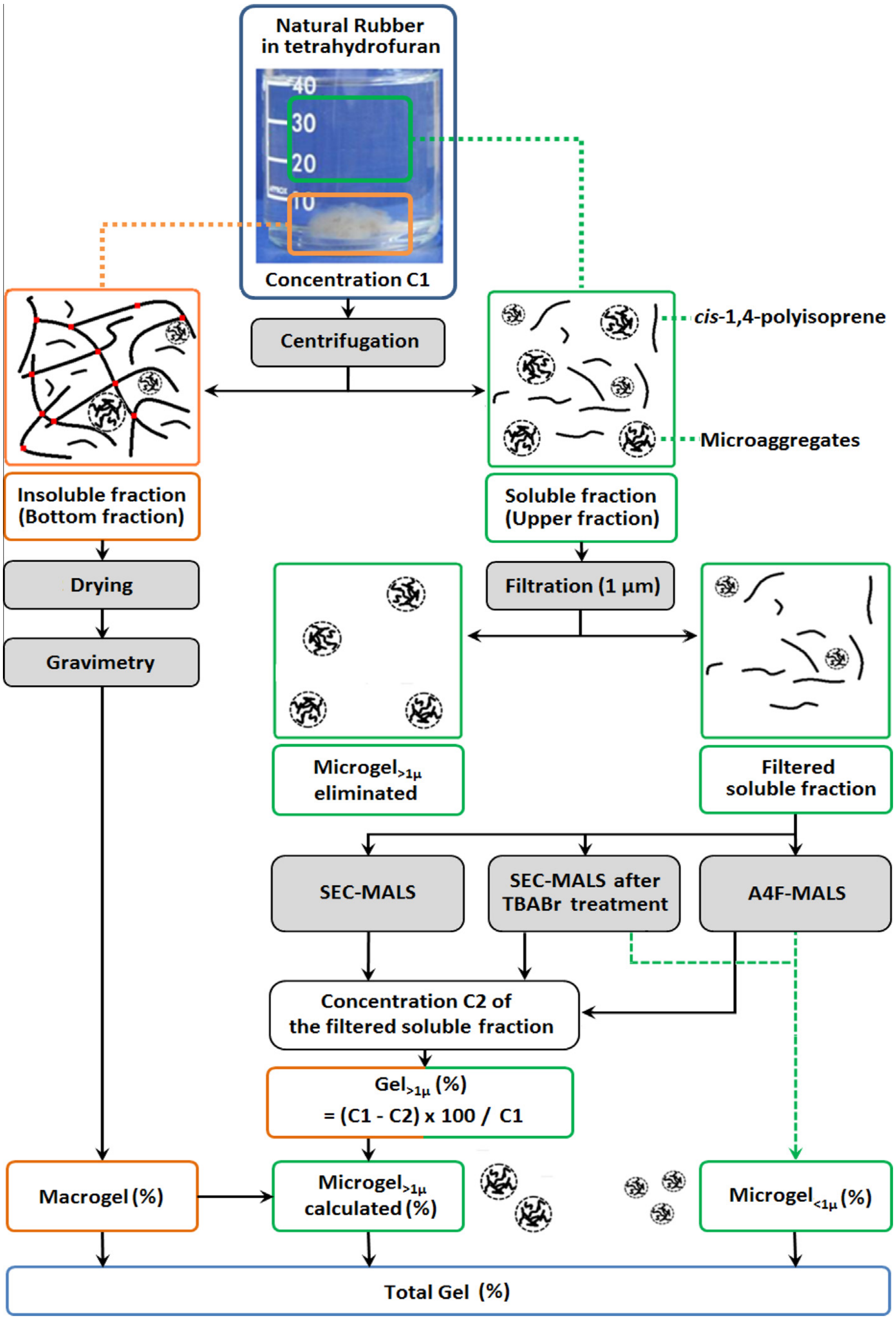

Fig. 1. Ways of quantifying the several fractions of gel present in Natural Rubber samples.

composed of the macrogel [13,19,25,26], neglecting the microgel. Studying the microgel of NR is far more difficult, as there is no extraction method enabling the characterization of isolated microaggregates. Nevertheless, filtration of the soluble fraction can be used to eliminate a proportion of the microaggregates, which are then quantified either directly by weighing the recovered microgel [23] or indirectly using size exclusion chromatography (SEC) [16,27]. However, the amount of microgel eliminated by filtration greatly depends on filter porosity: a usual filtration at 1 µm only eliminates microaggregates larger than 1 µm (Microgel$_{>1\mu}$; Fig. 1). Moreover, microaggregates trapped in the filter cannot be recovered for advanced investigations. For a long time, non-eliminated microaggregates (Microgel$_{<1\mu}$) were also neglected, because of the difficulty in studying them. Furthermore, abnormal elution of these microaggregates has been observed when injecting a filtered soluble fraction in SEC-MALS, leading to a probable overestimation of the structural parameters of the random coils