

Film Formation from Concentrated PDMS Emulsions

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Drying mechanisms and resulting structuring and distribution of surfactant were studied for concentrated, reactive emulsions of polydimethylsiloxane (PDMS) in water, using gravimetry, optical and infrared microscopy, and Attenuated Total Reflectance (ATR) in FTIR. The surfactant was a non ionic polyethoxylated fatty alcohol (C13E8). Drying was performed under various temperature and relative humidity conditions by casting the emulsion on glass. Upon drying elastomeric films were formed. The effects of various parameters were investigated, namely thickness of the cast layer, ageing of the emulsion, absence of the crosslinking catalyst, surfactant concentration, and presence of a CaCO₃ filler.

The emulsion dried in a pure normal mode, whatever the thickness of the deposited layer. Normal in the sense that water concentration gradients appeared in the direction normal to the surface, but not laterally. The drying process could be described as three successive fronts, roughly parallel to the surface, moving in a vertical direction, from top to bottom. The first front corresponded to the formation of a transparent, metastable, highly concentrated, non coalesced emulsion. The second front, closely following the first one, was a coalescence front. Coalescence destabilized the metastable transparent state and rejected water and surfactant mainly downwards. Underneath this coalescence front the emulsion was thus rediluted. This dilution was particularly clearly observed near the latex-substrate interface by ATR. The third front was associated to a partial or total phase inversion which restored the initial white colour to the system, by segregating the surfactant in domains separated from the crosslinked polymer.

The concentration profile of the surfactant in the film shortly after drying presented a depleted layer on top, a flat vertical line in the bulk and a strongly enriched layer in contact with the substrate. The vertical line corresponded in fact to an average over surfactant aggregates with a seemingly very high size polydispersity. **Drying and coalescence mechanisms had a major influence on the surfactant distribution. In the dry film, the distribution was unstable and, upon ageing, both film-air and film-substrate interfaces were progressively enriched with surfactant.**

Upon drying elastomeric films were formed, showing a vertical structuring depending on drying conditions and initial surfactant concentration. **Three layers were observed in the thickness: a top transparent, elastic skin, made of coalesced drops; an intermediate white, non cohesive layer; and a white, cohesive layer in contact with the substrate, containing separate surfactant domains as a dispersed phase. Structuring essentially depended on the local rate of water elimination, itself directly connected to the global drying rate.** This work is currently submitted to Langmuir.