Experimental report

05/08/2019

Proposal: 9-11-1875 **Council:** 4/2018

Title: Influence of Plasticiser Functionality on Surfactant Segregation in Poly-Vinyl Alcohol Films and Links to Matrix Free Volume Properties

Research area: Materials

This proposal is a new proposal

Main proposer: Richard THOMPSON

Experimental team: Ophelie SQUILLACE
Rebecca FONG

Local contacts: Philipp GUTFREUND

Samples: Polyvinylalcohol (PVA)
propylene glycol (H or D6)
ethylene glycol (H, or D4)

Instrument	Requested days	Allocated days	From	To
FIGARO	3	3	07/09/2018	10/09/2018
D17	3	0		

Abstract:

Plasticised PVA film is widely used in packaging for detergents (unit dose) and foods. We wish to understand the interplay between plasticisers, polymers (PVA) and materials contacting the films such as surfactants. This will provide data to test new models to guide the design of future industrial formulations. We propose to build on our original studies on glycerol plasticised films with ethylene glycol and propylene glycol, enabling parameterisation of the influences of molecular weight, surface tension and hydrophobicity. Specular NR will be used to quantify the surface segregation of each plasticiser in PVA film with and without the influence of a non-ionic surfactant. The influence of these new plasticisers on surfactant segregation is a non-trivial problem. By studying this process for these systems we anticipate being able to parameterise and predict molecular migration in complex polymer films for many additional types of formulation.

Effect of plasticiser functionality on surfactant and plasticiser segregation

Rebecca Fong, Ophelie Squillace, Philipp Gutfreund & Richard Thompson

Analysing the free volume properties of poly(vinyl alcohol) films has revealed that glycerol and propylene glycol have substantially different plasticising behaviours. This could have a profound effect on additive mobility in PVA films, and thus on the segregation behaviour of surfactants, as well as the plasticisers. In order to assess the effect of plasticiser functionality on surfactant segregation, ethylene glycol, propylene glycol and glycerol were incorporated into PVA films at different loadings, and the vertical concentration profile of plasticiser and the surfactant $C_{12}E_5$ in the film was measured using neutron reflectivity. Samples were prepared by spin casting from aqueous solution, yielding films approximately 60 nm thick.

In contrast to glycerol, propylene glycol is enriched on the surface of the PVA film, in the absence of any other additives. Extensive loss of ethylene glycol (EG) and propylene glycol (PG) from films (in the absence of surfactant) was identified (Fig. 1), although this was particularly significant for ethylene glycol, which has a lower enthalpy of vaporisation. Despite the loss of plasticiser from the film, the incorporation of these additives are still capable of impacting the distribution of surfactant established during the spin coating process.

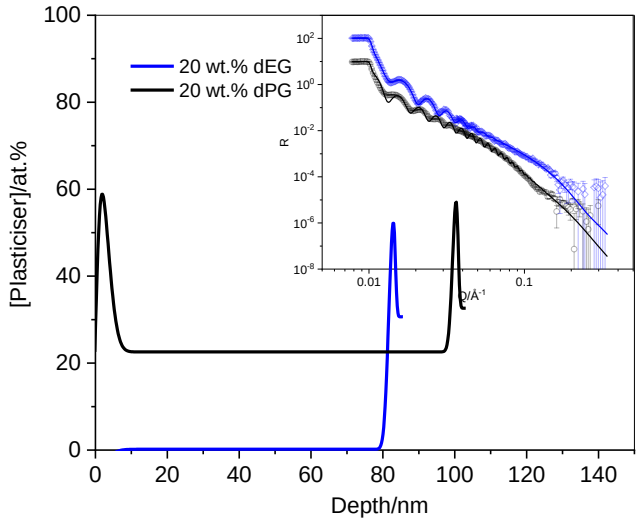

Figure 1. Distribution of EG and PG in spin-cast PVA films in the absence of any surfactant.

The distribution of EG in the presence of 10 % $C_{12}E_5$ is shown in Figure 2. It can be seen that EG is not always completely lost from the films and is thus this loss is likely to occur over time, not just during the spin coating.

As seen previously for glycerol, both ethylene glycol and propylene glycol increases the surface excess of the non-ionic surfactant. However, results are complicated by varying film thickness, and likely loss of plasticiser to different extents.

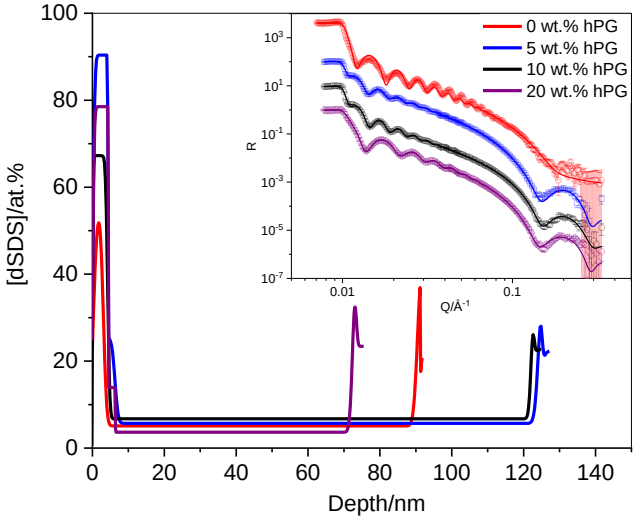

Figure 2; Effect of propylene glycol concentration on dSDS distribution

Figure 2 shows the effect of SDS on EG distribution. The SLD of the bulk film layers is consistent with each plasticiser loading, and similar to that of pure PVA, suggesting the loss of the majority of the plasticiser from the film. Although there are differences in the surface region of the film, this is affected by total film thickness, which is itself related to concentration of plasticiser in initial solution.

The effect of each plasticiser on the segregation of dSDS is summarised in Table 1, where z* denotes the surfactant surface excess, and *f* represents the fraction of the total surfactant segregated to the surface. It can be seen that increasing the concentration of each plasticiser causes a significant increase in SDS segregation. Although there is little difference in the effect of EG and PG on enhancement of surfactant segregation, it is clear that glycerol has a greater effect on the SDS distribution.

Plasticiser loading/ wt.%	**Ethylene glycol**		**Propylene glycol**		**Glycerol**	
	z*/ nm	*f*	z*/ nm	*f*	z*/ nm	*f*
0	1.3	0.25	1.3	0.25	1.3	0.25
5	4.45	0.30	4.41	0.36	6.52	0.5
10	3.56	0.58	3.53	0.25	8.51	0.49
20	4.07	0.55	4.10	0.59	2.52	0.81