Influence of Emulsifiers on Film Formation from Cellulose Acetate Latexes. Modeling Approach to the Fate of Emulsifiers in Highly Plasticized Films. II

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Synopsis

Experimental results on the redistribution of sodium dodecyl sulfate in cellulose acetate membranes produced from latexes (Part I) are interpreted in terms of a framework involving both thermodynamic (affinity of the components, composition) and kinetic (plasticizer evaporation rate) parameters. Two situations were examined, corresponding to liquid–liquid and liquid–solid phase separation. The proposed model better accounts for the observed phenomena than more classical views about the fate of emulsifiers.

INTRODUCTION

The use of aqueous dispersions for coating or film casting is advantageous, since it circumvents problems inherent in organic solutions, in particular air pollution and solvent toxicity. However, latex systems may quite often be stabilized by one or several emulsifiers. In some circumstances, the presence of these emulsifiers can be a serious drawback, since they subsist in the dry films and can therefore dramatically modify their characteristics.

The first paper of this two-part series[1] was concerned with phase separation phenomena in cellulose acetate (CA) membranes prepared from latexes containing sodium dodecyl sulfate (SDS). Above a certain concentration, SDS was shown to alter the structure, as well as the mechanical and permeation properties of CA films, due to redistribution of this surfactant into small islets during the film-forming process. This phenomenon was found more pronounced for cast than for sprayed films. The aim of this second paper is to examine the mechanisms underlying demixing phenomena and to develop a modeling approach to film formation from plasticized CA dispersions. Our approach is then used to interpret a few experimental results.

From Part I, the following features of SDS behavior inside latex CA membranes were found.

1. SDS is forced into small islets when its concentration by weight of CA exceeds 0.5% (see Figs. 1–5 of Part I).

2. Shape, size, and number of islets are very much influenced by the amount of SDS, the initial concentration of plasticizer in the latex and the drying conditions, and thickness of films (Figs. 1, 2, 3 and 5 of Part I).

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3. Plasticizer properties sharply affect intensity of the phase separation process (Figs. 1 and 2 of Part I).

4. Islets form the internal phase of the films and are thus surrounded by the CA matrix; these islets can be much larger than the spaces between the particles.

5. Cast membranes undergoing phase separation are asymmetric (Fig. 8 of Part I).

6. In contrast to cast films, SDS islets cannot be seen (under a light microscope) inside membranes obtained by spraying; mechanical and permeation testing results further suggest basic differences between both kinds of films (Figs. 9–13 of Part I).

A satisfactory modeling approach to film formation should account for all the above observations.

MODELING CONSIDERATIONS

Model Characteristics

Figure 1 is a schematic view of a possible mechanism of film formation, as it appears to take place following the works of Jäckel,[2] Wheeler et al.,[3] and Talen and Hover.[4] According to this approach, latex films never become truly homogeneous (by forming a true solution in the thermodynamic sense) but two phases permanently coexist during the drying, a polymeric and an
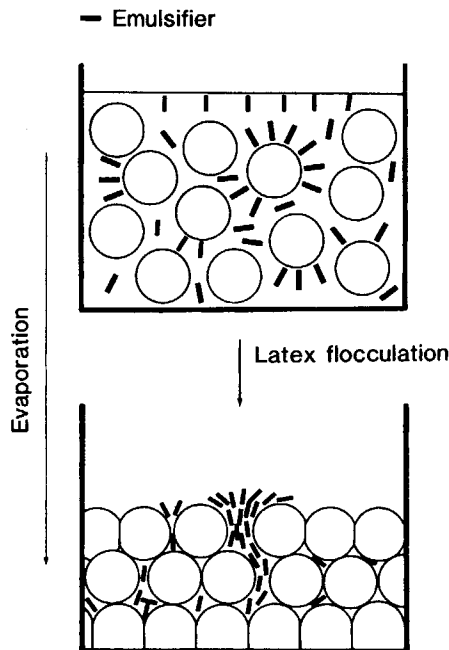

Fig. 1. Schematic representation of film formation from latexes as usually described: (top) aqueous dispersion; (bottom) formation of an emulsifier interstitial phase and exudation toward film surface.
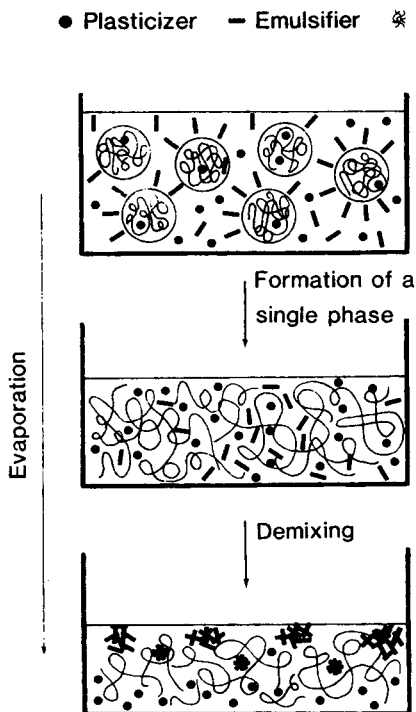
● Plasticizer   ━ Emulsifier   ✷ Polymer

Fig. 2. Proposed representation of film formation from highly plasticized latex systems: (top) aqueous dispersion; (middle) homogeneous system; (bottom) asymmetric film with emulsifier domains.

interstitial one, the latter containing water and surfactant. The effect of the presence of a plasticizer or of residual water is not taken into consideration.

In our opinion, Figure 1 may correctly describe film formation from an unplasticized latex, but it is certainly not adequate for dispersed systems that require a high plasticizer load, such as CA latexes. For instance, the previous approach can hardly explain the appearance of surfactant islets which are much larger than the latex particles. The same conclusion holds when we have to account for the impact of the SDS content, or that of the nature and amount of plasticizer.

Figure 2 matches our observations much better. The steps generating islets with a high emulsifier content are summarized as follows.

1. The casting blend is initially a two-phase system. The polymeric particles contain water, plasticizer, and traces of emulsifier. The aqueous phase contains some plasticizer and the major part of the emulsifier.

2. During water evaporation, we observe a redistribution of the plasticizer and the emulsifier. After coalescence of the particles, the system polymer/emulsifier/plasticizer/water becomes a single phase. The emulsifier is distributed almost homogeneously.

3. Following evaporation of part of the plasticizer, the quaternary system (polymer, emulsifier, plasticizer, and residual water) becomes thermodynamically unstable. Its separation into two phases results in a lower Gibbs free energy. Two kinds of demixing are possible in theory, which may occur

simultaneously: a liquid–liquid phase separation with nucleation and growth of the phase enriched in surfactant, and a crystallization of the emulsifier.

Predictive Capabilities of the Proposed Model

From our model, one can establish a set of relationships between the growth of the emulsifier phase and the following parameters:
—the drying duration corresponding to evaporation of most of the water and plasticizer,
—the temperature,
—the amount of plasticizer incorporated in the latex,
—the boiling point of the plasticizer or more exactly its partial vapor pressure in the casting or spraying liquid,
—the solubility of the emulsifier in the plasticizer.
These points, although interrelated, will be discussed separately.

Prolonged drying duration favors formation of large islets. This is obvious when one compares the structure of cast and sprayed films (see Part I). In contrast to casting blends, the plasticizer evaporates very quickly from sprayed liquids. Thus, the emulsifier cannot redistribute over a large distance. Hence, the domains arising from phase separation remain very small, and sprayed membranes containing 2% SDS or more appear visually as uniformly white after contact with water and drying. These structure differences are also reflected by the mechanical and permeation properties of both kinds of films (see Part I, Figs. 10–13). Large islets like those encountered in cast films result in a strong decrease in tensile strength and a sharp rise in permeability. In contrast, tiny islets apparently do not have a great effect on any of these parameters.

One could expect a relatively low drying temperature to have an effect somewhat similar to that of prolonged drying. Figure 3, which corresponds to films plasticized with ethylene glycol monoacetate (320% by weight of CA) and dried at room temperature, shows that this is indeed what is happening. Very large SDS crystals are seen at the surface of films. Membranes washed
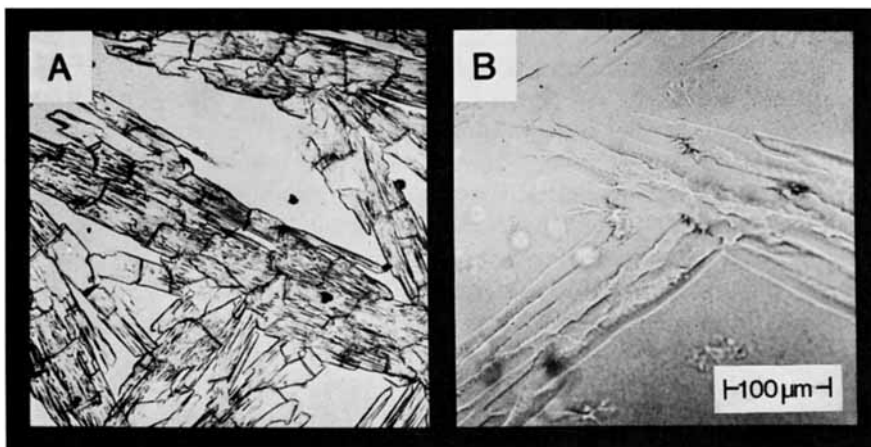

Fig. 3. Optical micrographs showing recrystallization of sodium dodecyl sulfate. Films were dried at room temperature and contained ethylene glycol monoacetate as a plasticizer. Sodium dodecyl sulfate content: 3.5%. (A) Initial aspect of the films; (B) aspect after contact with water.
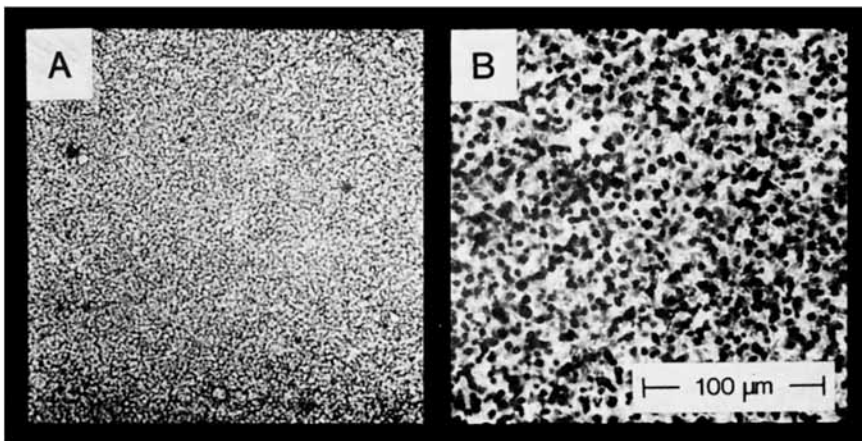
Fig. 4.   Optical micrographs of films plasticized with ethyl lactate and washed with water. Sodium dodecyl sulfate content: 3.75%. Initial plasticizer loading: (A) 160% of cellulose acetate weight; (B) 320% of cellulose acetate weight.

with water exhibit "fingerprints" resulting from the dissolution of SDS, but, in contrast with Figure 2 of Part I, no islets are visible. This is because the exudation of SDS toward the film surface is much more pronounced at 20°C, due to very slow evaporation of the plasticizer.

The amount of plasticizer added to the latex has considerable influence on the islet size and structure (see Fig. 3 of Part I). A high proportion of plasticizer favors large islets, because both the drying duration and the diffusion coefficient of the surfactant within the film are enhanced. Inversely, incorporation of a very volatile plasticizer such as ethyl lactate seems to prevent the growth of nucleation sites and islets apparently retain a roughly spherical shape (Fig. 4).

A last important point is the solubility of the surfactant in the plasticizer, or more exactly in plasticizer containing some water. Table I supplies some information about the miscibility of various plasticizer/water systems and about the solubility of SDS in these plasticizers. This table shows that only plasticizers able to dissolve SDS, either in the absence or in the presence of water, give rise to films displaying islet formation. Therefore, the degree of hydrophobicity of the plasticizer seems to play a prominent role. Plasticizers that are poorly miscible with water and that do not solubilize SDS, such as dimethyl phthalate or diethyl succinate, do not allow formation of an homogeneous quaternary mixture at a given stage of the drying. An interstitial water phase probably subsists throughout the course of evaporation. Actually, emulsions of dimethyl phthalate, diethyl or dimethyl succinate [composition: 40% plasticizer, 0.2% Arlacel 80 (Atlas), 0.2% Tween 80 (Atlas), 59.6% water] were incorporated in CA latexes (plasticizer 160% of CA weight, 7.7% CA in the casting liquid) prior to casting. The resulting membranes were brittle and weak even for a SDS content as low as 0.5%. Under the microscope at low magnification, a network of ribs was apparent that corresponded to segregation of SDS, as attested by autoradiography.[5]

TABLE I

Solubilities of Water and of Sodium Dodecyl Sulfate in Various Plasticizers in Regard to Islet Formatior

Plasticizer	Solubility of water in plasticizer at 22°C (% w/w)	Solubility of sodium dodecyl sulfate in plasticizer[a]			Presence o islets of well-define shape in dry films
		Room temp.	ca. 80°C	With 5–10% water added (room temp.)	
Diacetin[b]	∞	−	+	+	Yes
Diethyl succinate	2.1	−	−	[c]	No
Diethyl tartrate	∞	+	+	+	Yes
Dimethyl phthalate	1.8	−	−	[c]	No
Dimethyl succinate	4.0	−	−	[c]	No
Ethyl diglycol acetate	∞	−	[d]	+	Yes
Ethyl lactate	∞	+	+	+	Yes
Ethylene glycol monoacetate[b]	∞	−	+	+	Yes
2-Phenoxyethanol	11.0	−	+	+	Yes
Triacetin	3.0	−	−	[c]	No
Triethyl citrate	3.6	−	+	[c]	No
Triethyl phosphate	∞	+	+	+	Yes
Trimethyl phosphate	∞	+	+	+	Yes

[a] + = 2 g SDS or more dissolves in 100 mL plasticizer; − = less than 2 g SDS dissolves in 100 n plasticizer.

[b] Technical grade chemicals.

[c] SDS dissolves in the added water which itself is not miscible with the plasticizer phase.

[d] Coloration.

It is worth emphasizing that films cast from solutions of CA and SDS in triethyl phosphate or ethylene glycol monoacetate also undergo phase separation. This is also verified for other polymers such as ethyl cellulose. Thus, this similarity to latex films confirms the validity of our approach (more precisely the assumption of homogeneity at a given stage of drying) applied to highly plasticized latex systems.

Further Thermodynamic Considerations

Deeper insight into phase separation phenomena within films containing emulsifiers can be gained from Flory–Huggins theory[6] and by considering what type of demixing occurs.

Liquid–Liquid Phase Separation

In this case, the emulsifier (subscript 2) can be a low-molecular-weight liquid, an amorphous polymer or perhaps less frequently a low-molecular-weight solid or a crystalline polymer. The plasticizer (subscript 1) acts as a solvent for the emulsifier and for the polymer (subscript 3), water being neglected. The emulsifier does not separate out as a pure crystalline solid, but phase separation yields two liquid phases, both containing some emulsifier. The ternary mixture plasticizer/emulsifier/polymer can be characterized by three Flory–Huggins interaction parameters, i.e., χ_{12}, the plasticizer–emul-

sifier interaction parameter, χ_{13}, the plasticizer–polymer interaction parameter, and χ_{23}, the emulsifier–polymer interaction parameter. By neglecting water, the study of phase separation phenomena in latex films becomes analogous to that of phase equilibria in ternary systems. The Gibbs free energy of mixing, ΔG_M, is

$$\Delta G_M/RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \chi_{12} n_1 \phi_2 + \chi_{13} n_1 \phi_3 + \chi_{23} n_2 \phi_3 \quad (1)$$

where n_i and ϕ_i are the number of moles and the volume fraction of component i, respectively.[6] R is the gas constant and T is the absolute temperature. By differentiating eq. (1), three equations can be written for the chemical potential of the components that could be solved to determine the composition of the coexisting phases,[6] if values of the interaction parameters are known. Depending on the molecular weight of the emulsifier and the interaction parameters, the actual phase diagrams may be classified as either of the type solvent (1)/nonsolvent (2)/polymer (3) or of the type solvent (1)/polymer (2)/polymer (3).[7-11] Here however, the subject of concern is the appearance of a phase enriched in emulsifier, independently of whether phase separation is the result of a reduced entropy of mixing (as is usually the case for pairs of polymers[12,13]) or a large value of χ_{23} (as would be expected when the emulsifier is a low-molecular-weight compound).

Flory–Huggins theory is only approximate; a more elaborated approach such as the Flory–Prigogine–Patterson theory[14-16] would put forward the role of packing and spatial interpenetration of the components.

Liquid–Solid Phase Separation

The following rationale applies to emulsifiers in the solid crystalline state at the temperature at which the films are dried.

We consider here again ternary systems of the type plasticizer/emulsifier/polymer. The emulsifier is characterized by a melting point, T_f, and a heat of fusion, ΔH_2^F. The plasticizer acts as a solvent both for the emulsifier and the polymer.

The relative activity a_2^S of a component in the solid state compared to that of the supercooled component at temperature T is given by[17]

$$\ln a_2^S = \ln p_2^S/p_2^0 = \frac{-\Delta H_2^F}{R}\left(\frac{T_f - T}{TT_f}\right) \quad (2)$$

where p_2^S and p_2^0 are the vapor pressure of the solid and of the supercooled liquid, respectively.

For a saturated solution in equilibrium with a solid component, the partial vapor pressure of the solute is equal to the vapor pressure of the solid. Therefore, the solubility of the solid (volume fraction ϕ_2) can be obtained from

$$\ln a_2^S = \ln \phi_2 + 1 - \phi_2 - x_2\phi_1 - \frac{x_2}{x_3}\phi_3 + (x_2\chi_{12}\phi_1 + \chi_{23}\phi_3)(\phi_1 + \phi_3)$$

$$- x_2\chi_{13}\phi_1\phi_3 \quad (3)$$

where x_2 and x_3 are the ratios of the molar volumes V_2/V_1 and V_3/V_1, respectively.

Equations (2) and (3) show that the solubility of the solid emulsifier is strongly influenced by the difference between its melting point T_f and the temperature T of the mixture, which in our case corresponds to the film drying temperature. In other words, choice of an emulsifier with a high melting point increases the risk of recrystallization inside the films. Hence, the behavior of the system should change in the vicinity of the melting point T_f. Above T_f, only liquid–liquid phase separation can occur.

EXPERIMENTAL OBSERVATIONS

The following observations bring some support to the previous thermodynamic considerations.

1. For an identical SDS content, intensity of phase separation can be very different depending on the plasticizer (see Figs. 1 and 2 of Part I). Similarly, films plasticized by the same additive but containing different emulsifiers (e.g., SDS and sodium dioctyl sulfosuccinate, see point 3) exhibit different structures. Thus, relevant physicochemical properties of plasticizer, emulsifier, and polymer (such as boiling point, melting point, molecular weight, and cohesive energy density), together with a single interaction parameter, do not unambiguously determine the membrane structure. At least three binary systems (polymer/plasticizer, polymer/emulsifier, and emulsifier/plasticizer) should be studied in order to characterize a latex film. This point is ignored in the literature which only considers the casting of organic solutions. For those films indeed, the mechanical strength is usually assumed to be related mainly to polymer–solvent affinity.[18]

2. Different batches of films were prepared from a latex stabilized with 3.75% hexadecanol and 1.9% SDS. The plasticizer was unvariably ethylene glycol monoacetate (320% of CA weight), but the drying temperature was varied. Figure 5 shows that drying at 20°C resulted in films with large dark domains. In contrast, films dried at 60°C (melting point of hexadecanol = 50°C) displayed a much denser alternance of clear and dark spots which likely indicate a very fine separation of phases. Membranes processed at 20°C were wavy and could be torn easily. On the contrary, films produced at 60°C were planar and resistant. Furthermore, bulk crystals, melting at around 50°C, were seen under a polarization microscope inside films dried at 20 and 37°C. These differences suggest a relation between film structure and physicochemical properties of the emulsifier. Use of an emulsifier which is solid at the processing temperature (e.g., hexadecanol at 37°C) is usually associated with recrystallization phenomena. Large islets are observed in this situation. In contrast, choice of a liquid emulsifier (e.g., hexadecanol at 60°C) seems to result in nucleation of a very large number of tiny droplets which do not considerably impair film strength.

3. Films cast from latexes containing 3.75% dioctyl sulfosuccinate (but no SDS), an emulsifier of soft waxy consistency, did not display islet formation, whatever plasticizer was used. Diacetin, diethyl tartrate, ethylene glycol monoacetate, triethyl, and trimethyl phosphate were tried. After exposure to water, films plasticized with diacetin and triethyl phosphate were somewhat
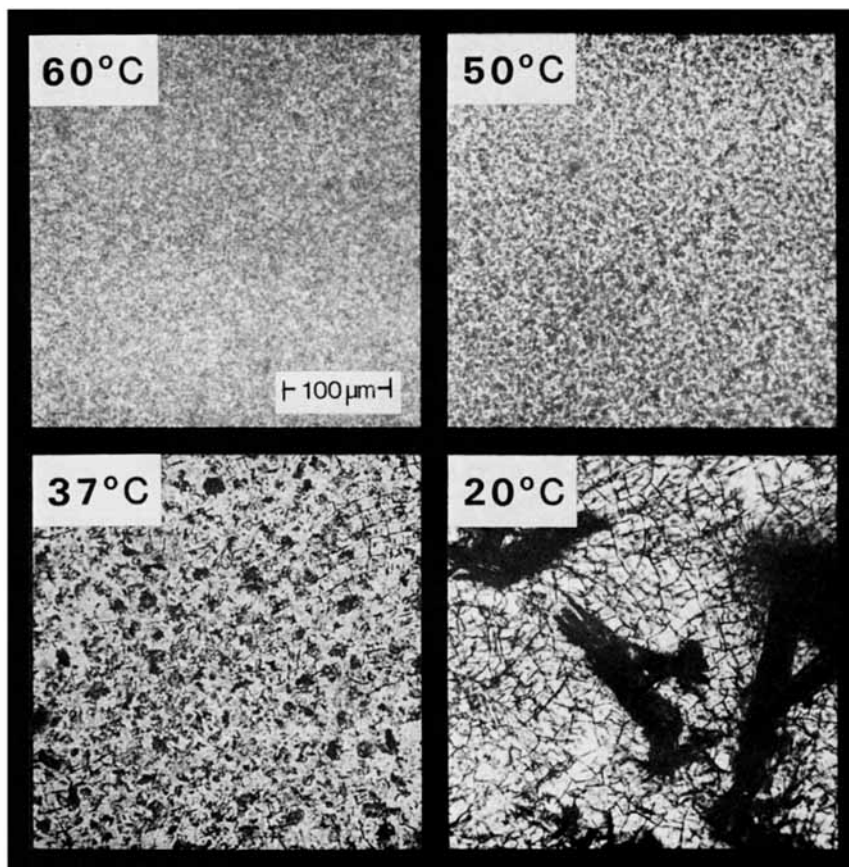
Fig. 5. Optical micrographs of films containing hexadecanol and dried at various temperatures.

hazy while the others remained transparent. Since dioctyl sulfosuccinate is probably only associated with liquid–liquid phase separation phenomena, it is again tempting to conclude that the selection of a liquid or waxy emulsifier is preferable, since it prevents islets formation and film cracking.

CONCLUSIONS

We have developed a framework to account for phase separation phenomena in CA membranes produced from highly plasticized latex systems. We find that the nature of the emulsifiers entering the composition of a latex system cannot be ignored when one attempts to prepare membranes, nor is the choice of the plasticizer irrelevant. In this respect, selection of a liquid emulsifier, which can only result in liquid–liquid demixing and not in crystallization, would be preferable.

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