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Distribution of Small Molecules in Latex Films. Correlation with Properties

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SUMMARY: The main results which can be found in the literature concerning the distribution of surfactants in latex films are briefly reviewed. Several parameters influence distributions, namely the nature of the systems, time, total amount of surfactant introduced in the latex, film formation conditions, mechanical story of the film. The interpretations are closely connected to film formation mechanisms, especially drying mechanisms. The effects of surfactants on adhesion properties of latex films were mainly studied through peel energy versus surfactant concentration data. There are three possible shapes for these curves, they can show a maximum, a minimum or a decrease to a plateau level. Qualitative interpretations of these shapes are proposed.

Introduction

Thin polymeric films almost always contain also small molecules. By thin films we mean some tens of micrometers and by small molecules we refer to molecular weights of a few tens to a few hundreds of g/mol. These small molecules can be very different in chemical nature. They can be residual monomers, oligomers or solvent, water, surfactants, stabilizers, plasticizers, tackifiers, rheology modifiers, ...Thin polymeric films are prepared in three main ways, namely from a melt, from a solution, and from a latex. Latices lead to latex films which tend to replace solvent borne films for obvious safety and ecological reasons. The practical applications of latex films have become numerous: paints, paper coatings, adhesives (especially pressure sensitive), carpet backing, floor polish, condoms and gloves, textiles and textile sizing, coatings for drug delivery and sustained/controlled release, reinforcing fiber coating, membranes (see 1 and references therein). In all these applications, the properties of latex films are strongly influenced by the presence, concentration and distribution of small molecules. In this paper, as a representative example, the case of one sort of small molecules, i.e. surfactants, and one kind of property, i.e. adhesion, will be briefly reviewed.

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Experimental

Several systems have been investigated. One system is defined by the nature of the polymer, of the surfactant and of the substrate on which the latex film is formed. Several of the classical polymers and copolymers synthesized in emulsion polymerization like acrylic, or acrylic/styrene copolymers, sometimes with acrylic or methacrylic acid, have been used. Less conventional water borne films like polyurethane(2) or crosslinked polydimethylsiloxane(3) were also studied. Representative examples of surfactants in the three main families were chosen, sodium dodecyl sulfate (SDS) or sodium dioctyl sulfosuccinate in the anionic family, hexadecyl pyridinium chloride or hexadecyl trimethylammonium bromide as cationic surfactants and polyethoxylated alkyls or phenol alkyls (NP) as non ionics. Glass, polymeric surfaces like polyethylene terephthalate or polyethylene, mercury, are examples of substrates.

Distribution of surfactants in films were studied by bulk and surface analytical methods. The analysis of the bulk was performed by photoacoustic spectroscopy (PAS)(4), infrared microscopy (IRM)(3), and nuclear magnetic resonance (NMR)(3) (in thick films by cutting samples out at various thickness'). Near the interfaces, attenuated total reflectance (ATR)(4, 5, 6) X-ray photoelectron spectroscopy (XPS)(7), secondary ion mass spectrometry (SIMS)(7) and contact angle measurements(8) were used.

Adhesion was measured by peel experiments at 180°, at various rates.

Results and discussion

It was demonstrated(4, 5) that many parameters influence the distribution of the surfactant in a latex film. The main parameters are: the nature of the system (i.e. nature of the polymer, of the surfactant and of the substrate), time (age of the film), total concentration of surfactant in the latex, film formation conditions (temperature and relative humidity), and even mechanical story of the film(9) (whether it was stressed and to what extend). The effect of time is illustrated in figure 1, in the case of ethoxylated nonyl phenol with 10 ethoxy groups (NP10) in poly(2-ethyl hexyl methacrylate) (P2EHMA). The surfactant concentration increases at both interfaces with time. Figure 2 shows different concentration profiles of surfactants in poly(2-ethyl hexyl methacrylate) latex films on glass. The interfaces can be either enriched, depleted, or show the same concentration as in the bulk. The shape of these profiles is qualitatively interpreted(6) in terms of desorption of the surfactant from the particle surface when particles come together in the film formation process and mobility of the surfactant in the still wet and then in the dry film.

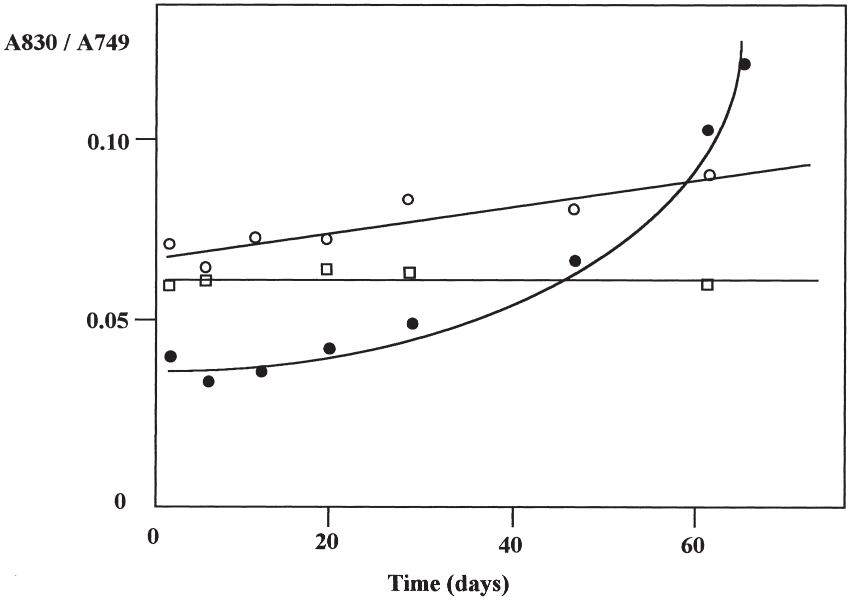


Fig. 1: Absorbance of an IR band characteristic of the surfactant (830 cm^{-1}) divided by the absorbance of a band characteristic of the polymer (749 cm^{-1}) versus time for P2EHMA latex films containing 6.5 wt % of NP10. The absorbance ratio is proportional to the surfactant concentration. ○ Film-glass interface (ATR results); ● film-air interface (ATR results); □ whole film (transmission results).

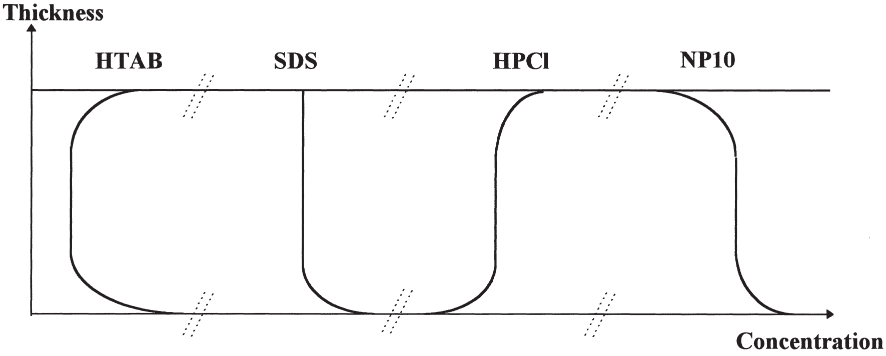


Fig. 2: Concentration profiles (qualitative shapes) of various surfactants in poly(2-ethyl hexyl methacrylate) latex films. Films aged 3 hours, dried at 23°C, 55 % relative humidity. HTAB = hexadecyl trimethylammonium bromide, SDS = sodium dodecyl sulfate, HPCl = hexadecyl pyridinium chloride, NP10 = polyethoxylated nonyl phenol with 10 ethoxy groups. Film-air interface on top. Film-substrate interface on bottom.

As far as adhesion is concerned, it was demonstrated[10, 11, 12)] that surfactants in latex films strongly influence adhesion but in a complex way. It was shown that peel energy versus surfactant concentration curves present either a maximum, or a minimum or a decrease to a plateau level (Fig. 3 & 4).

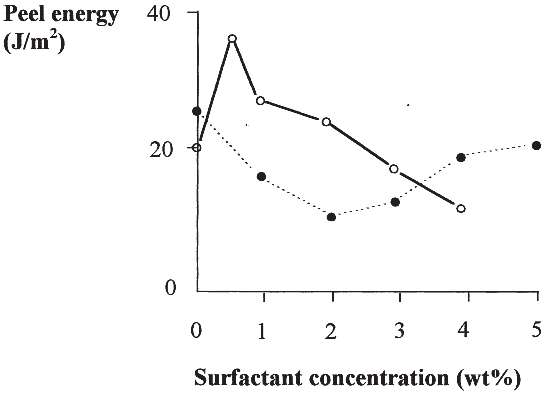


Fig. 3: Peel energy versus surfactant concentration for poly[methyl methacrylate-co-ethyl acrylate/hydrophilic polyester] on glass (see reference 12 for details). ○ SDS. ● NP30.

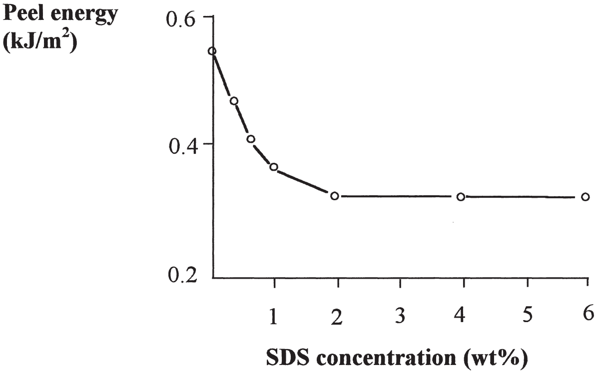
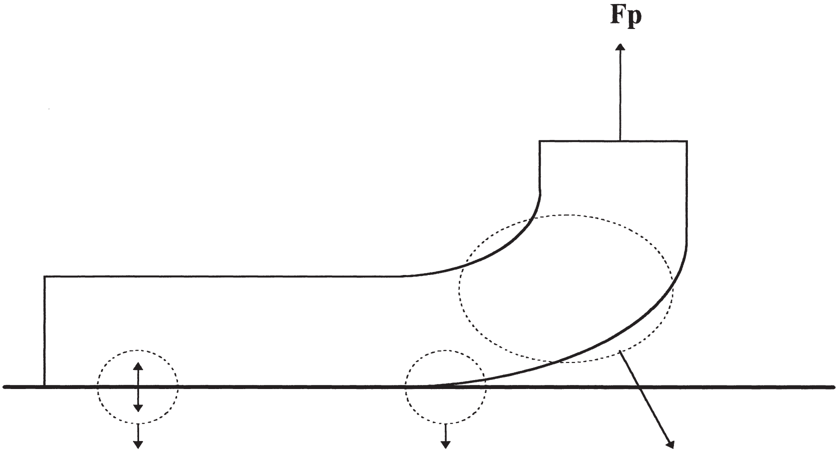


Fig. 4: Peel energy versus SDS concentration for poly(styrene-co-butyl acrylate-co-methacrylic acid) on glass (see reference 12 for details).

Surfactants influence adhesion of latex films through three effects (Fig. 5): modification of the interactions at the interface between the film and the substrate, modification of the dissipative processes associated with the crack propagation, and modification of the energy dissipated in the bulk of the film during peeling. Depending on the relative importance of these three effects along the concentration axis, the different curve shapes can be qualitatively understood.



	Interfacial interactions	Fracture propagation	Bulk dissipation
Length scale	1 nm	1 µm	10 µm
Effect on G	↑ (through W_A)	↓ (Weak Boundary Layer)	↑ (plasticizing) ↓ (antiplasticizing)

Fig. 5: Three different effects at different length scales for the influence of surfactants.

Conclusion

The distribution of the surfactant is a key factor. The mechanisms by which a given concentration profile is established in a latex film are insufficiently understood. Fast and precise methods to establish concentration profiles are still to be developed. Photoacoustic spectroscopy, confocal Raman microscopy, and NMR imaging are promising. Predictive quantitative models giving concentration profiles of surfactants in latex films seem no longer out of reach.

The qualitative interpretation of the shapes of the peel energy versus surfactant concentration curves should be confirmed by the use of simplified model systems (solution films). A deeper investigation of surfactant effects in adhesion of thin polymeric films could possibly help us to better understand the complex interplay between bulk and interfacial energy dissipations during peeling of such films.

A large research area on the effect of other kinds of small molecules on other properties of thin films is still open and will probably benefit from the above considerations.

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