Water Absorption in Acrylic Latex Films

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Synopsis

Water absorption in acrylic latex films was investigated. Films from post-stabilized latices exhibited low water uptake during a long-time immersion in water; this was caused by easier extraction of water soluble materials into water. The extraction of secondary emulsifiers was estimated by liquid chromatography; the structure of film surfaces was investigated by electron microscopy.

INTRODUCTION

Polymeric films from latices are formed by coalescence of discrete polymer particles; thus, they differ from those casted from solvent vehicles. Original particles do not lose their identity in the film,[1,2] and the resulting film usually contains various water soluble ingredients, which affect its water sensitivity. There are several factors, affecting the water absorption in latex films; some of them were studied in our previous works.[3–5] Water enters the polymer, in which it is soluble to a slight extent and diffuses into small pockets formed by salts and other water soluble materials. This penetration is driven by osmotic pressure, but is opposed by increasing hydrostatic pressure of the water cells produced in the film, this force being due to the resistance of the polymer to deformation. A strong decreasing of the water uptake of films during long-time immersion in water was reached by post-stabilization of initial latices by nonionic surfactants. This was ascribed to the premature flocculation of unstable particles during drying, resulting in a "spongy" film with high water absorption. This explanation is in good accordance with recent results of Okubo et al.[6] They found that in the post-stabilized latex the polymer particles can flow until close packing results in a homogeneous film. If the original emulsion is weakly unstable, polymer particles flocculate predominantly at the emulsion–air interface before close packing; this results in a skin film with a porous layer at the air side. One other factor, affecting the water absorption process, is the film aging, as shown in work of Anžur et al.[7,8] In this work the effect of post-stabilization, coalescing agents, and the film aging on the water absorption was studied.

EXPERIMENTAL

Materials

Butyl acrylate, acrylic acid (BASF), butyl methacrylate (Synthesia Semtín,

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USSR), Etoxon AF-5 ($C_9H_{19}C_6H_4(OCH_2CH_2)_5$-$OSO_3Na$) 30% act. matter (Spolchemie, USSR), ammonium persulfate and sodium metabisulfite (Lachema, USSR), Lutensol AP 9 and Lutensol AP 20 (ethoxylated nonyl phenols) (BASF), Texanol ($(CH_3)_2CHCH(OH)C(CH_3)_2CH_2OCOCH(CH_3)_2$) (Eastman Kodak Co.), distilled water. Initiators were pa grade; other materials, technical grade, were used.

Latex Preparation

The copolymer dispersion was produced by semicontinuous emulsion polymerization in a 2000-mL stainless steel reactor under nitrogen atmosphere. Polymerization temperature was 70°C, feeding time 3 h. Reactor charge: water 200 g, Etoxon AF-5 6.5 g, sodium metabisulfite 4 g. Emulsion feed: water 600 g, Etoxon AF-5 19.5 g, butyl methacrylate 632 g, butyl acrylate 152 g, acrylic acid 16 g, and ammonium persulfate 4 g.

Latex Properties and Modification

Solids = 48.1%, pH 2.05, particle size 0.17 μm—narrow distribution. Secondary emulsifiers were added as 25% water solutions; coalescing agents were added dropwise under good agitation.

Film Preparation and Water Absorption Estimation

The latices were casted onto silicone rubber plates and dried for 3 and 10 days at 23°C and 50 ± 7% relative humidity, and then additionally heated for 7 days at 60°C. The film thickness was 500 ± 50 μm. The samples 2 × 2 cm were immersed in water at 23°C, and the weight increase was periodically estimated by weighing. The amount of extracted material was not taken into account.

High-Performance Liquid Chromatography (HPLC)

HPLC was used to follow the extraction of secondary emulsifiers from the latex films into water. HPLC was carried out under isocratic conditions using a Varian 4100 chromatograph and a Varichrom UV-Vis variable wavelength detector, operating at 230 nm. The column dimensions were 250 × 2 mm i.d., particle size 10 μm, and temperature ambient. The flow rates were 0.25–0.75 mL/min. Separation of the nonionic surfactant into individual homologues (according to the number of oxyethylene groups), in order to compare the distribution of these homologues in film extracts and in a standard solution, was achieved on an adsorption column of silica gel, MicroPak SI 60 (Varian), using hexane–dioxane–methanol (60:30:10) as a mobile phase. Prior to chromatography, it was necessary to evaporate aqueous samples and to dissolve the residue in an organic solvent, e.g., dioxane–methanol (3:1) [Fig. 1(a),(b)].

The determination of the amount of extracted nonionic surfactant by separating it from the film extract as a single chromatographic peak was performed by reversed-phase chromatography on a C_{18}-bonded stationary phase. Aqueous

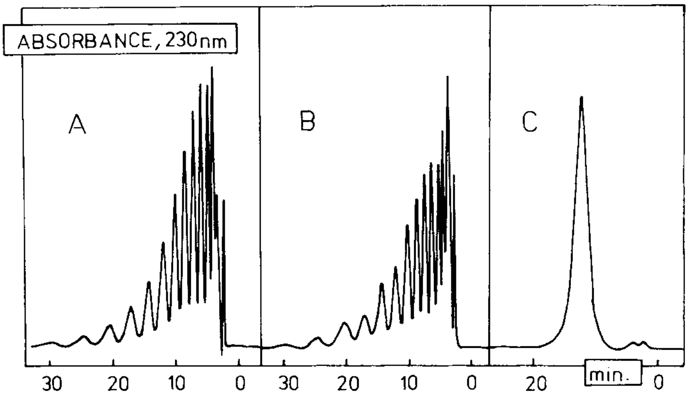

Fig. 1. High-performance liquid chromatography of Lutensol AP 9: (A) a standard separated by adsorption HPLC on silica gel (column MicroPak SI 60); (B) an extract from the latex film separated under the same conditions; (C) a standard separated by reversed-phase HPLC on a C_{18}-bonded phase (column MicroPak MCH). Absorbance, 230 nm.

samples were directly injected into a MicroPak MCH column (Varian) and eluted with methanol–water (85:15 or 80:20) [Fig. 1(c)].

For the chromatographic analysis the samples were taken in various time intervals from 50-mL water baths containing 3 g immersed acrylic films.

Film Surface Replicas

Film surface replicas were prepared by evaporating of 5% solution of poly(vinyl alcohol) casted onto the film surface. Negative replicas were shadowed by paladium and covered by carbon. PVA film was removed by warm water and the replicas were photographed by electron microscope Tesla BS 242 E.

RESULTS AND DISCUSSION

The dispersion prepared under the above-described conditions was weakly unstable. Its stability was improved by post-addition of nonionic emulsifiers (Table I). Post-addition of nonionic emulsifiers impeded also the water ab-

TABLE I
Mechanical Stability (High Speed Mixer, 3000 rpm) of Dispersions Modified by Secondary Emulsifiers

Secondary emulsifier wt %/polymer	Stability (min)	
	Lutensol AP 9	Lutensol AP 20
0	3–4	3–5
2	6–7	7–8
4	>30	>30
6	>30	>30
8	>30	>30
10	>30	>30

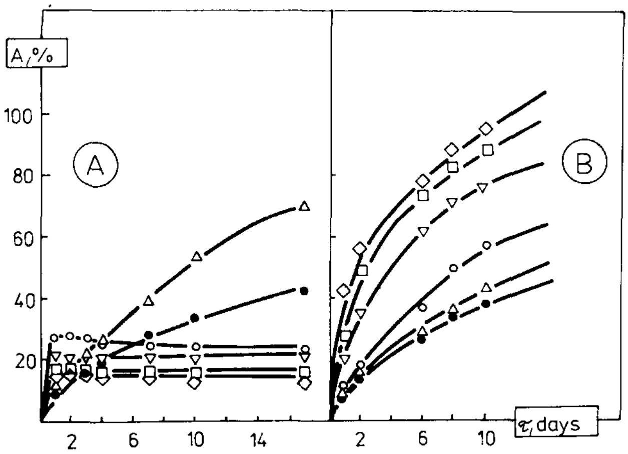

Fig. 2. Absorption of water in films casted from dispersion modified by Lutensol AP 9: (A) film aged 10 days at 23°C; (B) film aged 10 days at 23°C + 7 days at 60°C. Lutensol AP 9 (% polymer): (●) 0; (△) 2; (○) 4; (▽) 6; (□) 8; (◇) 10.

sorption in films, which were cast from these dispersions and dried at room temperature. Somewhat increased water uptake was found when dispersions contained 2–4 wt % of emulsifier (calculated on polymer), but the addition of higher amounts led to a decrease of the water uptake measured during a several days' immersion of films in water. In the light of previous works this phenomenon could be ascribed to a higher degree of regularity of the particle packing in the film. The water uptake, however, increased dramatically after additionally aging the film for 7 days at 60°C. This is shown in Figures 2 and 3. Similarly, also, coalescing agents increased the water absorption. The effect of the coalescing agent was very remarkable in the case of films prepared from weakly unstable dispersion and dried at room temperature (Fig. 4). When the coalescing

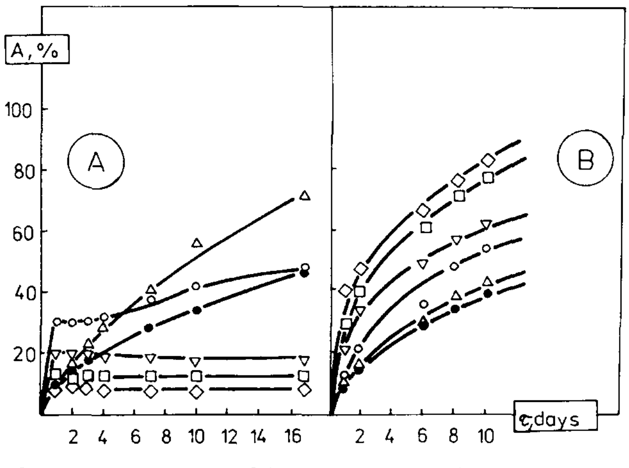

Fig. 3. Water absorption in films casted from dispersion modified by Lutensol AP 20. Aging conditions as in Figure 2 for Lutensol AP 9.

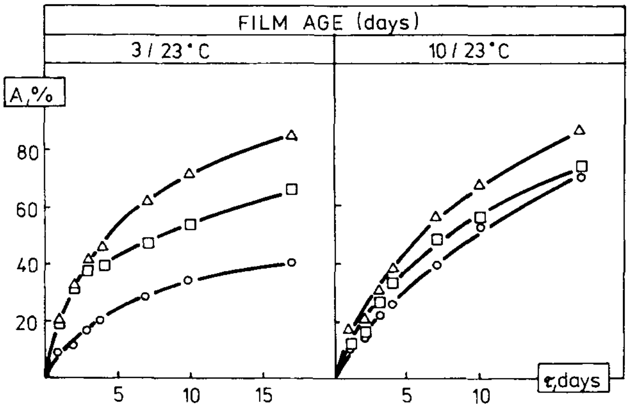

Fig. 4. Water absorption in films modified by 2 wt % polymer of Lutensol AP 9 in relation to the amount of coalescing agent and the film aging. Texanol (%): (○) 0; (□) 6; (△) 12.

agents were added to dispersions previously modified by greater amounts of secondary emulsifiers, their effect on the water absorption was greatest in heat-sealed films (Fig. 5). It may be concluded that the heat-sealed films absorb more water as a consequence of better coalescence of particles. The closed film structure hinders the extraction of emulsifier and other water-soluble components by water; this causes a greater water uptake due to osmotic pressure. This suggestion was confirmed by results obtained by liquid chromatography of water phase. Secondary emulsifiers were easily extracted from films dried at room temperature, but only a part of them was extractable from heat-sealed films. Figure 6 shows an increase of extracted material concentration during 17 days immersion in water. Some differences between the extraction rate of Lutensol AP 9 and Lutensol AP 20 are visible in this figure. The more ethoxylated emulsifier Lutensol AP 20 was extracted from the film aged at 23°C more easily than Lutensol AP 9. On the other hand, in comparison with Lutensol AP 9, Lutensol AP 20 was much more hardly extracted from the heat-sealed film. This

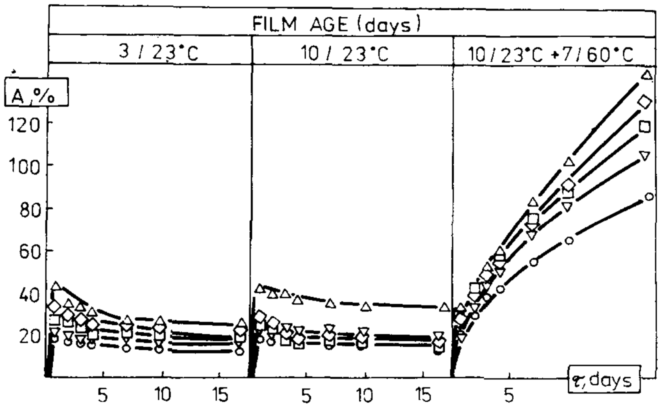

Fig. 5. Water absorption in films modified by 6 wt % polymer of Lutensol AP 9 in relation to the amount of coalescing agent and the film aging. Texanol (%): (○) 0; (▽) 3; (□) 6; (◇) 9; (△) 12.

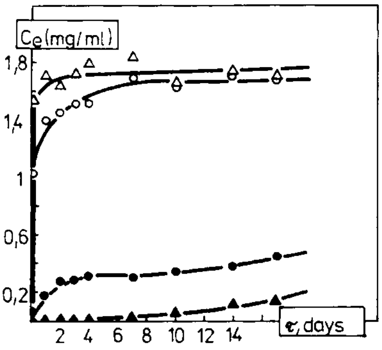

Fig. 6. Extraction of secondary emulsifiers from films modified by 10 wt % polymer of Lutensol AP 9 (○, ●) and Lutensol AP 20 (△, ▲), respectively, during immersion in water: (○△) film aged 10 days at 23°C; (●▲) film aged 10 days at 23°C + 7 days at 60°C.

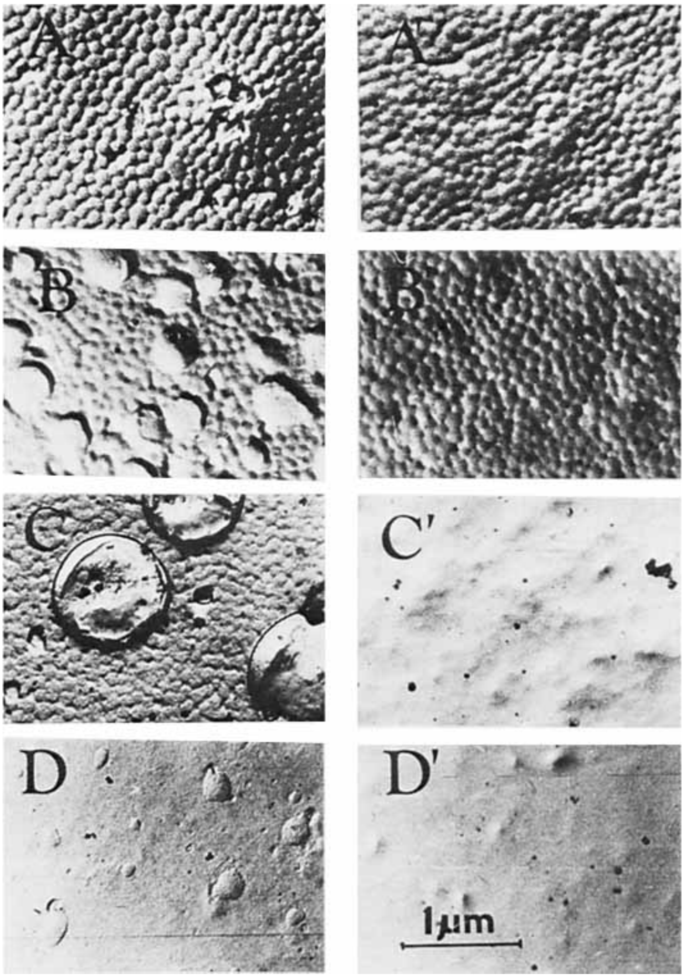

Fig. 7. Film surface replicas: (A–D) film casted from dispersion modified by 6 wt % polymer of Lutensol AP 20; (A′–D′) film casted from original dispersion. Film aging: (A,A′) 1 day at 23°C; (B,B′) 3 days at 23°C; (C,C′) 10 days at 23°C; (D,D′) 10 days at 23°C + 7 days at 60°C.

phenomenon was probably caused by differences in molecular weight, in polarity, and, consequently, in compatibility of the two emulsifiers with polymer. It was shown by Vanderhoff[2] that ethoxylated nonyl phenols with a low degree of ethoxylation may be dissolved in polymer particles while products with more than 15 ethylene oxide units are not compatible with polymer. We suppose that this is the reason of easy extraction of Lutensol AP 20 from films aged at ambient conditions, but very difficult extraction of this material from the heat-sealed film structure. No remarkable differences were found between distribution of ethoxylated homologues in the original and extracted material. These conclusions are also supported by electron-microscopic replicas of film surfaces (Fig. 7).

Post-added emulsifier Lutensol AP 20 is exuded onto film surface during drying and aging, forming pores and channels within the film. The original globular structure of the film surface remained visible even after 14 days aging at room temperature. This indicates that particles in the film are not well coalesced. On the other hand, film from original dispersion, i.e., without post-added ethoxylated nonyl phenols, did not exhibit the globular surface structure after 14 days, as did both films after heat sealing for 7 days at 60°C. From these results it can be concluded that the film formed from post-stabilized dispersions is "porous" to some extent; this enables a rapid extraction of water-soluble materials. Subsequent coalescence of particles during aging and/or heating results in closed film structure, causing an increase of water uptake in films during long-time immersion in water. These results are in good agreement with data of Anžur.[7,8]

CONCLUSIONS

Post-addition of secondary emulsifiers improves the latex stability and increases the initial speed of water absorption in the film. During long-period immersion of film in water, a rapid extraction of water-soluble materials proceeds, causing a low water uptake. Good coalescence of particles achieved by aging or heating of the film causes decreasing of initial rate of water absorption. During long-period immersion of film in water, however, a greater amount of water is absorbed in the film. This is caused by osmotic pressure produced by water soluble materials, which are hardly extractable from well-coalesced film. This phenomenon is very important from the practical point of view. The water sensitivity of films made of technical products is frequently tested, and it has to be borne in the mind that this property depends on the film treating before the testing.

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