

Films from styrene–butyl acrylate lattices using maleic or succinic surfactants: mechanical properties, water rebound and grafting of the surfactants

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Abstract

A series of anionic and zwitterionic maleic surfactants have been synthesized and engaged in styrene–butyl acrylate emulsion polymerization. Some non-reactive succinic analogs have been synthesized in order to perform their comparison with the maleic surfactants in polymerization experiments.

Films from the obtained lattices were cast, and their mechanical properties and the water rebound were tested. The results of water rebound demonstrate significant difference between the films prepared with maleic or succinic surfactants. Water rebound of the films after 34 days in the case of succinic surfactants was found to be between 51 and 95%, while for maleic surfactants it is only 25–40% of the initial weight of samples, which is a significant improvement.

Mechanical properties do not present essential difference, but a clear tendency has been observed in the three cases investigated—the films prepared using maleic surfactants are less resistant to the deformation and they are more extended at the rupture of the samples.

Both series of results could be explained assuming heterogeneous inclusions of non-reactive surfactant (succinic derivatives) having an ionomer character. Both the results of water rebound and mechanical properties can be considered as an indirect proof of grafting of maleic surfactant on the polymer. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive surfactants; Maleates; Emulsion polymerization

1. Introduction

Film forming polymers used in many industries (paints, paper coatings, adhesives, etc.) are produced in excess in water by emulsion polymerization for environmental reasons [1–4]. These polymerization processes, generally performed through radical mechanism, need the use of surfactants to stabilize and control the size of the particles to be coalesced, for producing continuous films. These surfactants are the source of some drawbacks because they are not strongly anchored to the surface of the particles, and then they can migrate into the serum, which may cause flocculation in some circumstances (freeze, shear stress, etc.). They can also migrate towards the surface of the film, causing lack of adhesion upon the substrate, or concentrate in hydrophilic domains by phase separation within the film, which then becomes water sensitive upon exposure to humidity.

One of the best ways to avoid these drawbacks is to use reactive surfactants, able to participate in the radical processes so that they will remain attached to the particles, hopefully, at the surface. In order to achieve such a property, they can be used as initiators (inisurfs), transfer agents (transurfs) or comonomers (surfmers).

Previous studies [5,6], in which different surfmers were tested and screened to demonstrate the best compromise between the overall reactivity, identified the maleic function as a potentially very interesting group for being incorporated in a surfmer. Surface active monomer alkyl sulfopropyl maleate has been reported by Tauer et al. [7] to produce lattices whose sera contains a lower surfactant concentration, indicating that the surfactant was chemically anchored to the particles.

In our research we have used non-ionic maleates [8], anionic maleates [9] and also cationic and zwitterionic maleates [10,11]. In both cases monodisperse particles with a size value depending on the structure of the surfactant have been obtained upon emulsion polymerization of

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styrene. Recently, Montoya Goñi et al. [12] have reported studies on the same polymerization using a maleate function located at different positions, and have compared them with corresponding non-reactive succinate compounds. Stable lattices were produced in both cases with a rather high attachment to the particle surface as judged by the high surface tension of the sera. In the case of maleates, the chemical incorporation in the polymer occurred rather early in the polymerization process.

A series of maleate, as well as, succinate surfactants have been used in our laboratory to produce core–shell lattices of polystyrene (core)–poly (styrene-co-butyl acrylate) [9,13,14]. In this paper, we report about mechanical properties and behavior in the presence of water, of films produced with these lattices obtained using hemiester or hemiamide of maleic acid, or also zwitterionic maleic derivatives.

2. Experimental part

2.1. Materials

All experiments were performed with deionized water. Styrene and butyl acrylate (Aldrich) were distilled under vacuum and stored at -20°C . All the other materials, from Aldrich–maleic anhydride, succinic anhydride, 1-hexadecanol, 1-hexadecylamine, 2-(*N,N*-diethylamino) ethyl chloride hydrochloride, 1,3-propane sulfone, 4-dimethylaminopyridine, potassium hydrocarbonate, sodium dodecyl sulfate and solvents (heptane, 1,4-dioxane, methanol, ethanol, ethyl ether, acetone, 2-butanone, dimethylformamide, ethyl acetate, chloroform), or from Acros–sodium hydroxide, potassium persulfate, were used as received.

2.2. Synthesis of surfactants

2.2.1. Hexadecylester of maleic acid (**HE16**) [8]

Maleic anhydride (49.03 g; 0.50 mol) and 1-hexadecanol (121.22 g; 0.50 mol) were stirred in a melted state at 80°C for 1 h. Heptane (150 ml) was added to the homogenous reaction mixture and stirred for 15 min at 80°C . The solution was left at room temperature for 3 h, then at 15°C for two more hours, with stirring from time to time.

The precipitate formed was collected and recrystallized from heptane (150 ml). White bright crystals of monohexadecylmaleate (151.52 g; 89%) were obtained with m.p. $71\text{--}72^{\circ}\text{C}$. ^1H NMR (Bruker AC, 250 MHz, CDCl_3 , δ , ppm): 0.88 (t, 3H, CH_3); 1.26 (m, 26H, $(\text{CH}_2)_{13}$); 1.72 (m, 2H, $\beta\text{-CH}_2$); 4.28 (t, 2H, $\alpha\text{-CH}_2$); 6.35–6.50 (q, 2H, $-\text{CH}=\text{CH}-$, $I^3_{cis} = 13$ Hz).

2.2.2. Hexadecyl ester of succinic acid (**HES16**)

Succinic anhydride (25.02 g; 0.25 mol) and 1-hexadecanol (60.85 g; 0.25 mol) in 1,4-dioxane (75 ml) were stirred at 80°C for 15 h. The solution was left at room temperature to crystallize. The precipitate formed was collected, dried and recrystallized from ethanol. White bright crystals of

monohexadecylsuccinate (64.37 g; 75%) were obtained with m.p. $62\text{--}63^{\circ}\text{C}$. ^1H NMR (CDCl_3 , δ , ppm): 0.88 (t, 3H, CH_3); 1.26 (m, 26H, $(\text{CH}_2)_{13}$); 1.62 (m, 2H, $\beta\text{-CH}_2$); 2.62–2.68 (m, 4H, $2(\text{CH}_2\text{-CO})$); 4.09 (t, 2H, $\alpha\text{-CH}_2$).

2.2.3. Hexadecylamide of maleic acid (**HA16**)

Maleic anhydride (49.03 g; 0.50 mol) and catalyst-4-dimethylaminopyridine (DMAP, 0.30 g) were dissolved in chloroform (300 ml) at 60°C . A solution of 1-hexadecylamine (120.73 g; 0.50 mol) in chloroform (100 ml) was slowly added. The reaction mixture was stirred at 60°C for 100 min. The solution was left at room temperature to crystallize. The precipitate formed was collected and without drying recrystallized from ethanol (200 ml). White crystals of monohexadecylamide (152.83 g; 90%) were obtained with m.p. $100\text{--}101.5^{\circ}\text{C}$. ^1H NMR (DMSO, δ , ppm): 0.86 (t, 3H, CH_3); 1.25 (m, 26H, $(\text{CH}_2)_{13}$); 1.48 (m, 2H, $\beta\text{-CH}_2$); 3.17 (q, 2H, $\alpha\text{-CH}_2$); 6.18–6.44 (q, 2H, $-\text{CH}=\text{CH}-$, $I^3_{cis} = 5$ Hz).

2.2.4. Hexadecylamide of succinic acid (**HAS16**)

Succinic anhydride (10.00 g; 0.10 mol), catalyst-4-dimethylaminopyridine (DMAP, 0.10 g) and 1-hexadecylamine (24.15 g; 0.10 mol) were dissolved in 1,4-dioxane (400 ml) and stirred at 80°C for 16 h. The reaction mixture was left at room temperature to crystallize. The precipitate formed was collected, and without drying recrystallized from ethanol (100 ml). White crystals of monohexadecylamide succinate (26.81 g; 79%) were obtained with m.p. $94\text{--}95^{\circ}\text{C}$. ^1H NMR (DMFA, δ , ppm): 0.88 (t, 3H, CH_3); 1.29 (m, 26H, $(\text{CH}_2)_{13}$); 1.47 (m, 2H, $\beta\text{-CH}_2$); 2.39–2.55 (m, 4H, $2(\text{CH}_2\text{-CO})$); 3.13 (q, 2H, $\alpha\text{-CH}_2$); 7.42 (s, 1H, H–N).

2.2.5. 2-[*N,N*-diethyl-*N*-(3-sulfopropyl)ammonio] ethyl hexadecyl maleate (**ZW16**)

Monohexadecyl maleate (20.43 g, 0.06 mol), 2-(*N,N*-diethylamino)ethyl chloride, hydrochloride (10.32 g, 0.06 mol) and potassium hydrocarbonate (15.03 g, 0.15 mol) in acetone (200 ml) were stirred at room temperature for 18 h, then at 60°C for 24 h. Reaction mixture was washed with hot acetone (50°C , 2×50 ml). The joint filtrate was evaporated in vacuum until no liquid is left. The residue was dissolved in a small amount of dimethylformamide (DMFA, 10 ml); 1,3-propane sulfone (7.33 g, 0.06 mol) was added and the reaction mixture was stirred at 95°C for 24 h.

Ethyl acetate (240 ml) was added and the reaction mixture was stirred at 70°C for 30 min. After 18 h at room temperature, ethyl acetate solution was decanted from the residue and the last one treated with hot acetone (300 ml). The product obtained was dissolved in methanol (100 ml) and the solution was treated with charcoal and silica. Dry diethyl ether (400 ml) was added drop by drop to yellow methanol solution. The precipitate was collected in an inert atmosphere and dried in vacuum.

Table 1

Used amounts (in grams) of components for seed-feed polymerization experiments; mixture of styrene (Sty) and butyl acrylate (BA) = 1/1 (in mass)

SF ^a	Latex	Seed					Feed				
		Water	PS seed latex ^b	SF	NaOH ^c	Sty/BA	Water	KPS	SF	NaOH	Sty/BA
HE16	G1	75	50	0.15	0.022	2	94	0.15	0.60	0.088	12
HES16	G2	75	50	0.15	0.022	2	78	0.15	0.60	0.088	12
HA16	F4	70	50	0.19	0.0275	2	80	0.30	0.56	0.0825	12
HAS16	F6	75	50	0.19	0.0275	2	75	0.30	0.56	0.0825	12
ZW16	E16	75	50	0.31	0.0275	2	70	0.30	0.93	0.0825	12
ZWS16	E17	75	50	0.31	0.0275	2	70	0.30	0.93	0.0825	12
SDS	H1a	75	50	0.16	0.0275	2	70	0.30	0.48	0.0825	12

^a Total amount of surfactant in all cases is 2.20 mmol.^b Solids content of seed latex (7.35–9.63%).^c Total amount of NaOH in all cases is 2.75 mmol.

2.2.6. 2-(*N,N*-diethyl-*N*-(3-sulfopropyl)ammonio)ethyl hexadecyl succinate (**ZWS16**)

The above substance was obtained in a similar way. In this case succinic anhydride was used instead of maleic and the quaternarization time with 1,3-propane sultone being prolonged to 48 h at 80°C. The treatment of the obtained product was simplified in this case by just washing with 2-butanone and filtering. White crystals of the product **ZWS16** were obtained (17.6 g, 66%). Calc., %: N: 2.49; S: 5.71. C₂₉H₅₅NO₇S. Found, %: N: 2.30; S: 5.54.

The ¹H NMR spectra of synthesized surfactants have been published previously [9,13].

2.3. Emulsion polymerization

2.3.1. Preparation of polystyrene (PS) latex

The polymerization is performed under nitrogen at 70°C with mechanical stirring at 250 turns/min. 995 g of deionized water, 1.5 g of anionic surfactant sodium dodecyl sulfate (SDS) and 1 g of sodium hydrogen carbonate (NaHCO₃) were introduced in a 1000 ml polymerization reactor and left for degassing by nitrogen for approximately 1 h at 70°C. Then 100 g of distilled styrene were added. The emulsion polymerization was started by the addition of 0.75 g of initiator-potassium persulfate (K₂S₂O₈) dissolved

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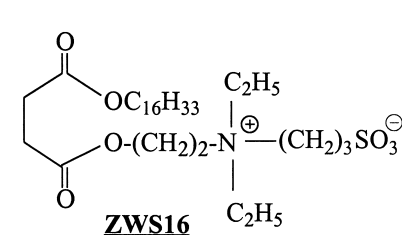
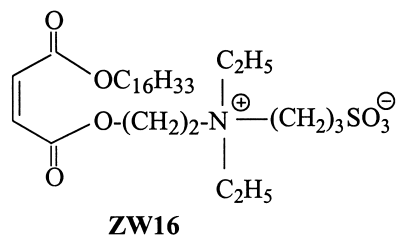
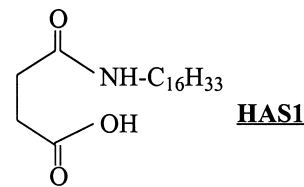
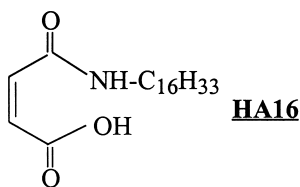
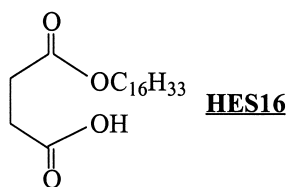
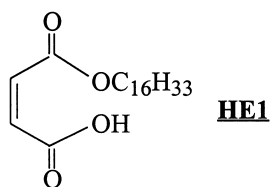


Table 2
Characteristics of lattices used for film formation

Latex	SF	<i>n</i> SF (mmol)	<i>n</i> NaOH (mmol)	SC ^a (%)	<i>T_g</i> (°C)	<i>T_{test}</i> (°C) (<i>T_{test}</i> / <i>T_g</i> = 1.9)
Anionic lattices						
H1a	SDS	2.20	2.75	8.99	24	–
G1	HE16	2.20	2.75	7.29	15	28
G2	HES16	2.20	2.75	8.03	13	24
F4	HA16	2.20	2.75	8.28	19	35
F6	HAS16	2.20	2.75	8.10	16	30
Zwitterionic lattices						
E16	ZW16	2.20	2.75	8.85	17	31.5
E17	ZWS16	2.20	2.75	9.92	13	24

^a Solids content.

in 5 g of water. The process was completed after 20 h, then the particle size and final conversion were determined.

Before using in seed-feed polymerization the seed latex was washed in ionic exchange resins.

2.3.2. Seed-feed polymerization

2.3.2.1. Surfactants HE16, HES16, HA16 and HAS16. A small amount of surfactant (0.15–0.19 g, i.e. 18–20% from the amount calculated for polymerization) and NaOH (0.022–0.0275 g) were dissolved in 75 g of deionized water at 70°C and introduced in a 250 ml reactor together with 50 g of PS seed latex. After degassing by nitrogen for 20 min, 2 g of distilled monomer (styrene/butyl acrylate = 1/1) was added and the latex was left for approximately 3 h at room temperature, with a stirring rate of 160 turns/min.

The solution of surfactant (0.56–0.60 g) and NaOH (0.0825–0.088 g) in water (75–94 g) was prepared and degassed for 30 min. Then the temperature in the reactor was raised up to 70°C and the rate of stirring up to 220 turns/min. The polymerization process starts in nitrogen atmosphere at 70°C by the addition of initiator KPS (0.15 g dissolved in 2.5 g of water). At the same moment, addition of the prepared solution of surfactant (with a rate 15–18 ml/h) and 12 g of monomer (with a rate 3 ml/h) was begun. In 4 h addition was completed. During the fifth hour of polymerization, another portion of KPS (0.15 g) was introduced. Polymerization was left for completion for 15 h, giving totally 20 h of polymerization. The particle size and conversion measurements were performed.

The detailed amounts of surfactants and other components used in each experiment are given in Table 1.

2.3.2.2. Surfactants ZW16 and ZWS16. A small amount of surfactant (0.31 g, i.e. 25% from the amount calculated for polymerization) and sodium hydroxide (0.0275 g) were dissolved in 75 g of deionized water at 70°C and introduced in a 250 ml reactor together with 50 g of washed PS seed latex (solid content 8.86%). After degassing by nitrogen for 20 min, 2 g of distilled monomer (styrene/butyl

acrylate = 1/1) was added and the latex was left for approximately 3 h at room temperature, with a stirring rate of 160 turns/min.

The solution of surfactant (0.93 g) and sodium hydroxide (0.0825 g) in water (70 g) was prepared and degassed for 30 min. Then the temperature in the reactor was raised up to 70°C and the rate of stirring up to 220 turns/min. The polymerization process begins in nitrogen atmosphere at 70°C by the addition of the initiator KPS (0.15 g dissolved in 2.5 g of water). At the same moment addition of the prepared solution of surfactant (with a rate 14.1 ml/h) and 12 g of monomer (with a rate 2.4 ml/h) was started. After 5 h addition was finished. During the fifth hour of polymerization, another portion of KPS (0.15 dissolved in 2.5 g of water) was introduced. Polymerization was left for completion for 15 h, giving totally 20 h of polymerization. The particle size and conversion measurements were performed.

2.4. Glass transition temperature measurements

The glass transition temperatures (*T_g*) of polymers were determined by differential scanning calorimeter (DSC, TA Instruments). Heating rate for all samples was 5°C/min. *T_g* was taken at the midpoint of the inflection during the second scan.

2.5. Film casting

20 ml of latex was placed on the special Teflon plate (6 × 5 cm²) and left in the thermostat at 33°C with a relative humidity 75% for four weeks to evaporate the water. Then several samples (type H3) from formed films were cut and mechanical and water absorption tests performed. Two or three samples for each measurement were used, and the result calculated as a medium value.

2.6. Measurements of mechanical resistance

Tests of mechanical resistance were carried out at different temperatures, in order to keep a constant ratio *T_g*/*T_{test}*. Mechanical tensile curves represent elongation of the film

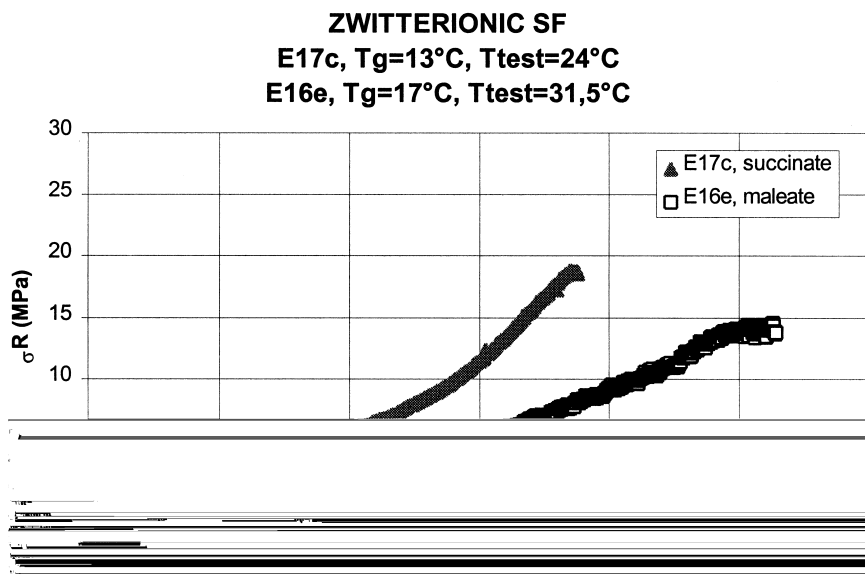


Fig. 1. Traction curve for polymers containing zwitterionic surfactants.

sample depending on the mechanical force applied. Tensile tests were carried out in the thermostated cell. Samples (type H3) were $4 \times 17 \text{ mm}^2$ in size and their average thickness was 0.3–0.6 mm. Traction speed used was 50 mm/min.

2.7. Water rebound measurements

For the water absorption measurements the samples of films were weighted, then completely immersed in water and the difference of weight was measured for wiped samples twice a week for 34 days. The temperature during

these 34 days was kept at 25°C. From the following ratio the amount of absorbed water was calculated:

$$\frac{(\text{weight in time } t - \text{initial weight}) \times 100\%}{\text{weight in time } t} \quad (1)$$

3. Results and discussion

Polymer films were formed from the synthesized lattices and their mechanical properties and water rebound were

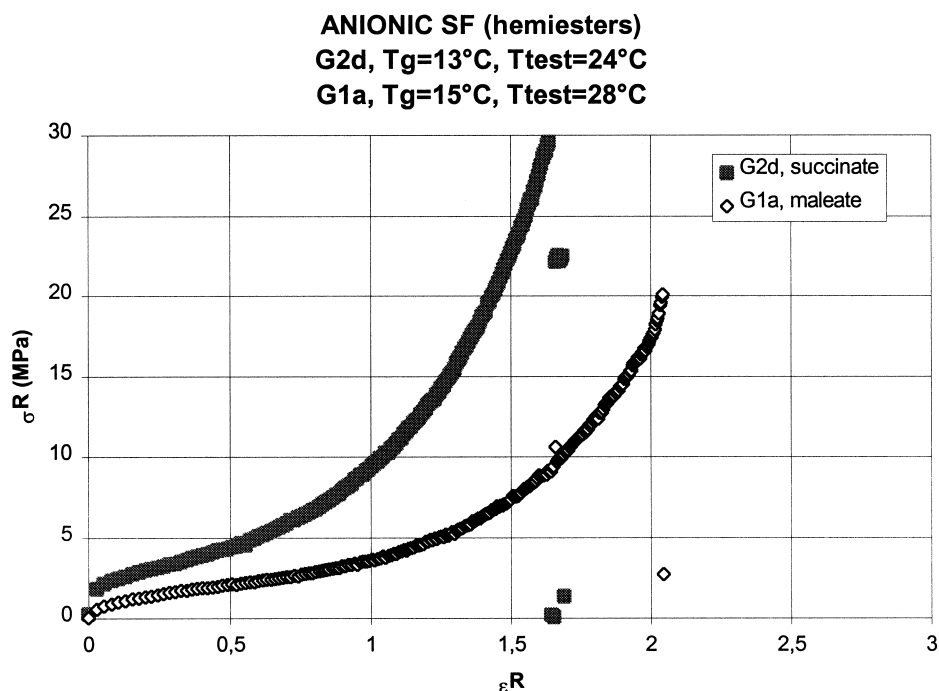


Fig. 2. Traction curve for polymers containing anionic surfactants (hemiesters).

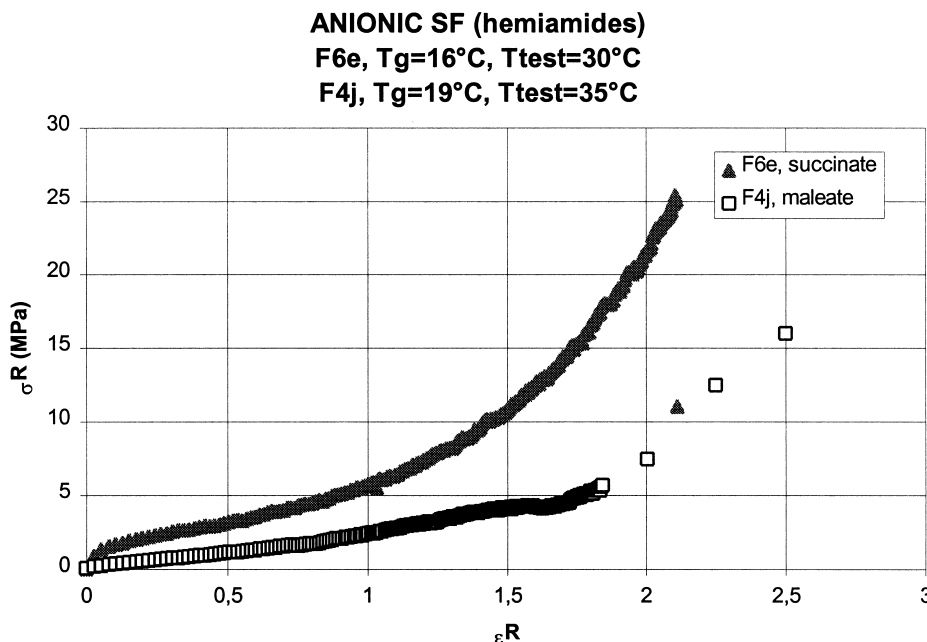


Fig. 3. Traction curve for polymers containing anionic surfactants (hemiamides).

studied. Characteristics of the used lattices are presented in Table 2.

There are two main phenomena during the filmification process: water evaporation and deformation of polymer particles. If the filmification temperature is too high the particle deformation is faster than water evaporation, causing formation of bubbles in the polymer film. On the contrary, when the filmification temperature is too low (lower or close to the glass transition temperature (T_g)), the particles need more time to coalesce. The best solution is to perform the film formation at a temperature 10–20°C higher than the T_g of the polymer.

Therefore, the choice of the filmification temperature in our case was determined by glass transition temperature values for investigated polymers, which are between 13 and 24°C. The films were cast at 32°C, which is 8–19°C higher than T_g of the synthesized polymers.

3.1. Mechanical resistance

Because the polymers have different glass transition temperatures, the traction tests were carried out at different temperatures, in order to keep constant the ratio T_{test}/T_g . Then the effect of T_g on the film properties is minimized, and different materials can be compared safely.

During the test, where the polymer samples are deformed homogeneously, the movement of the traction machine and the force applied are measured. The nominal constraint (σ , MPa) and the nominal elongation (ϵ) are dependent on the initial length (L_0) and the initial section (S_0).

These nominal values are correct only in the case of small deformations, where the initial section of the sample is considered to be constant during measurement. Actually,

during the tensile test the initial section of polymer sample changes very significantly. This variation is taken into account, when rational constraint (σ_R) and real deformation (ϵ_R) are calculated according the following equations:

$$\sigma_R = F/S, \quad (2)$$

$$\epsilon_R = \ln(1 + \epsilon) = \ln \lambda, \quad (3)$$

where σ_R is the rational constraint in MPa, F the force applied, S the section during the deformation, ϵ_R the real deformation and ϵ is the nominal deformation.

Three pairs of styrene/butyl acrylate copolymers have been investigated, in each pair one has been prepared with a reactive surfactant, while the other, using its non-reactive analog. Experimental curves of traction are shown in Figs. 1–3, where σ_R has been presented as a function of ϵ_R . For each polymer three to five samples were tested, but only the average curve is presented. The experimental accuracy is 0.5 MPa, which means that all the curves of the same polymer are located within the interval $\sigma_R \pm 0.5$ MPa.

Within the three groups of reactive–non-reactive surfactants the results demonstrate a substantial difference between the two types of materials: polymers prepared with non-reactive surfactant are more resistant to mechanical traction forces. The same effect has been observed in all the three cases—for two groups of anionic surfactants (hemiesters and hemiamides) and for zwitterionic surfactants. As the same amount of surfactant (2.20 mmol) and sodium hydroxide (2.75 mmol) was used for all the polymerizations, the difference is the representation of the influence of surfactant on the polymer properties. The experimental values of σ_R (characterizes the resistance of

Table 3
Characterization of films at the rupture (accuracy: ± 0.5 MPa)

Latex	SF	Sample	M_w (g/mol)	T_g ($^{\circ}\text{C}$)	σ_R at $\epsilon_R = 1.0$	ϵ_R max	σ_R max (MPa)
Hemiesters							
G1	HE16	G1a	402 698	15	3.61	2.04	20.09
G2	HES16	G2d	357 677	13	9.45	1.64	29.57
Hemiamides							
F4	HA16	F4j	558 470	19	2.42	2.64	5.79
F6	HAS16	F6e	392 050	16	5.79	2.11	25.12
Zwitterionics							
E16	ZW16	E16e	388 752	17	2.90	2.64	13.75
E17	ZWS16	E17c	337 310	13	5.70	1.88	18.55

the material to the deformation) at $\epsilon_R = 1$ are higher for the polymers containing non-reactive surfactants (Table 3).

On the contrary, the elongation values ϵ_R at rupture are smaller in the case of succinic surfactants, and this means that polymers prepared using non-reactive surfactants are less deformable than those prepared with maleic surfactants.

Results could be explained assuming ionomer type inclusions in the case of non-reactive surfactant: possibly there are some domains, where the surfactant is concentrated due to the phase separation taking place during the coalescence process. Such domains might be responsible for faster material breaking, forming heterogeneities in the polymer. On the contrary, reactive surfactant can be incorporated into the polymer during the polymerization process; then the material, being more homogeneous, is able to support the traction forces by more elongation.

The different behavior of the two class of materials could be an indirect proof of the incorporation of the reactive surfactant in the polymer.

The comparison of three different maleic surfactants

(Fig. 4) shows that the film prepared with hemiester **HE16** is more resistant to deformation and less deformable than the films with the zwitterionic surfactant **ZW16** or hemiamide **HA16**. On this basis it seems that the order of reactivity of these maleic surfactants is **HA16** > **ZW16** > **HE16**. This consideration agrees well with the results of conductimetric titration of surface charges in the case of lattices prepared with hemiesters or hemiamides [9], 34–61% of hemiester and 54–68% of hemiamide were titrated onto the surface of the polymer particles.

3.2. Water absorption tests

Water rebound was studied for all polymers. The polymer film prepared with SDS has been used as a reference. The samples of films with the same surface ($4 \times 17 \text{ mm}^2$) and weight between 0.11 and 0.16 g were completely immersed in water for 34 days at the room temperature (25°C). Wiped samples were weighted from time to time and the difference between initial weight calculated. Three samples of each

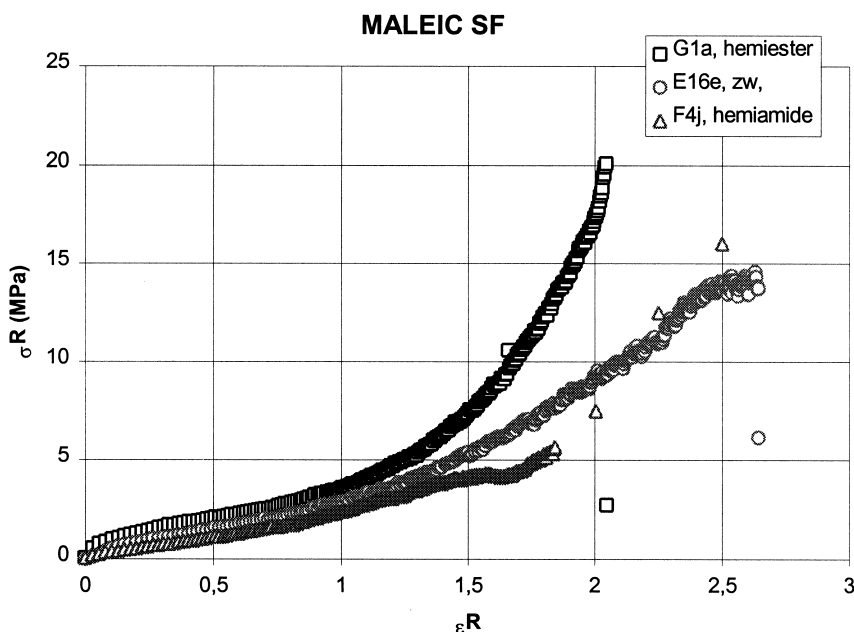


Fig. 4. Comparison of the traction curves corresponding to maleic surfactants.

Table 4
Water rebound of polymer films in 34 days, in %

Days	SDS	Esters		Amides		Zwitterionic SF	
		G1	G2 (succ)	F4	F6 (succ)	E16	E17 (succ)
1	22	9	7	3	8	6	16
9	37	24	25	12	43	20	36
16	42	32	34	18	68	27	44
27	45	37	45	22	88	32	50
34	49	40	55	25	95	35	51

polymer were used and the average value of water rebound was used as the final value.

The results of water absorption show the same tendency for three pairs of reactive–non-reactive surfactants. In the case of films made with non-reactive surfactant, water absorption is higher than for the reactive one (Table 4, Fig. 5). Generally, water rebound is twice more intensive for the polymers containing succinic surfactants than for maleic surfactant. For example, after 34 days the polymer E17 (prepared using non-reactive succinic surfactant **ZWS16**) had absorbed 51% (of its weight) of water, while for polymer E16 (with reactive maleic surfactant **ZW16**) the figure is only 35% (Fig. 6).

The results obtained could be explained as well by the ionomer type domains of non-reactive surfactant in the polymer, which may cause higher water absorption. On the contrary, results for the reactive surfactant used allow us to consider, that maleic surfactant has been actually copolymerized into the polymer.

Only in one case (E17, **ZWS16**) the equilibrium of water adsorption was reached and the law of Fick then can be applied to calculate the diffusion constant of water through the polymer film. In all the other cases it seems that 34 days is too short a time to absorb the maximum amount of water. It is not quite sure that the final value for the maleic surfactant is very different from that of the succinic product. However, we can say that in these 34 days the rate of water rebound has been measured, and was found to be

twice as large for polymers with succinic surfactants (Fig. 6).

Most of the models developed for describing kinetics of water diffusion in the materials are based on the law of Fick, where the hypothesis about the proportionality of water mass transfer throughout the unity of surface and the concentration gradient of water at this surface is used. The general form of this law is as follows [15]:

$$\frac{\delta C}{\delta t} = \text{div}(D \overrightarrow{\text{grad}} C), \quad (4)$$

where C is the concentration of water, t the time and D the diffusion coefficient.

In case of films, when their thickness is much more smaller than surface, the diffusion coefficient can be calculated using the following equation:

$$\frac{M_t}{M_m} = \frac{1}{h} \left(\frac{D_x t}{\pi} \right)^{\frac{1}{2}}, \quad (5)$$

where D_x is the diffusion coefficient in mm^2/s , M_t the water content in time t , M_m the water content at the equilibrium, h the thickness of film in mm and t the time in s.

Upon plotting M_t versus $t^{0.5}$ the initial slope of the linear curve allows to obtain the component M_t^2/t .

From the data about the E17 film, containing the non-reactive surfactant **ZWS16**, the value of water diffusion coefficient was found to be $0.38 \times 10^{-4} \text{ mm}^2/\text{s}$. The calculated value is close to that of polystyrene cited in the literature $-0.14 \times 10^{-4} \text{ mm}^2/\text{s}$ [16].

The comparison of the reactive surfactants between them indicates that hemiamides absorb the smallest amount of water. One can consider that from the three types of reactive surfactants investigated the hemiamide is the best incorporated into the polymer, i.e. this polymer contains the smallest amount of non-reacted surfactant, which is responsible for water rebound. This fits well with the results of traction tests, hence, the three surfactants can be classified according to their incorporation (copolymerization) level into the polymer: hemiamide **HA16** > zwitterionic SF **ZW16** > hemiester **HE16**.

3.3. Grafting of surfactants

In order to find some other proof of maleate incorporation into the polymer an additional experiment was carried out. The polymer G1 (surfactant **HE16**) was washed by hot methanol for 20 h to extract the oligomers with small molecular weight or non-reacted surfactant. The extracted product was analyzed by ^1H NMR and GPC.

The molecular mass of extracted product was found to be around 700 g/mol, but ^1H NMR did not detect any surfactant or oligomer. The spectrum corresponds to just fatty alcohol, which could be formed upon the hydrolysis of the surfactant. Normally, the surfactant **HE16** is soluble in methanol, so this result shows that there is no residual surfactant which could be desorbed during the extraction with methanol, and

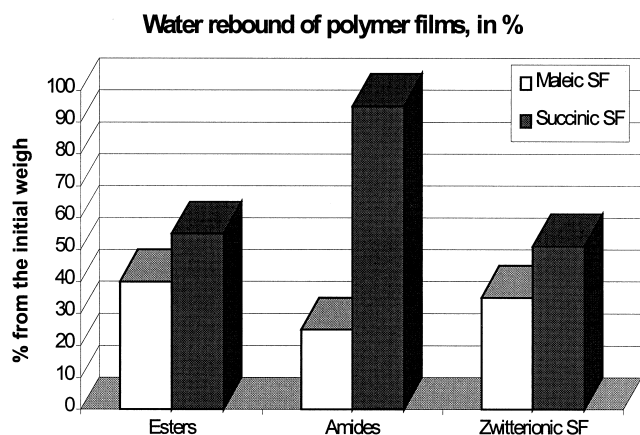


Fig. 5. Water rebound of polymer films after 34 days.

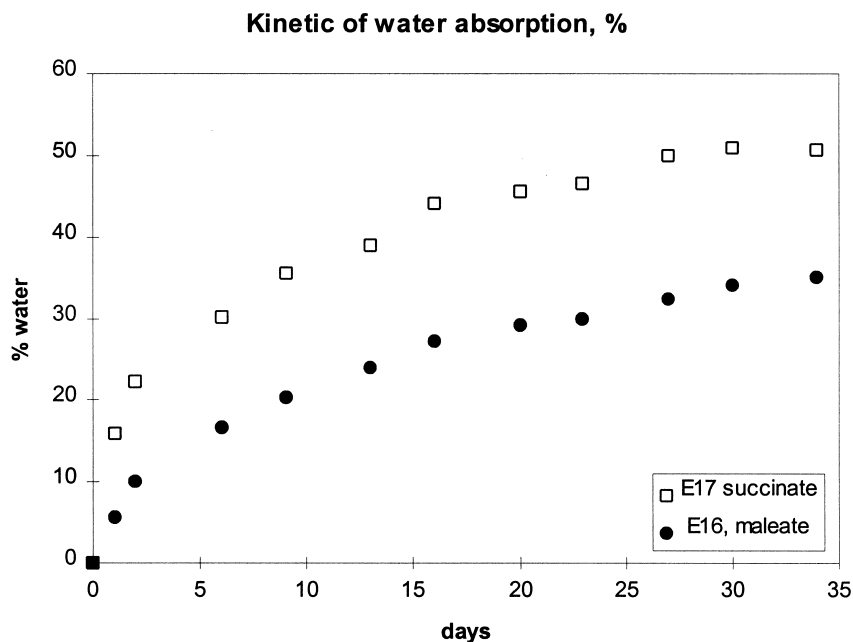


Fig. 6. Kinetics of water absorption of the polymer films containing zwitterionic surfactants **ZW16** (E16) and **ZWS16** (E17).

it means, that the surfactant is incorporated (copolymerized) in the polymer.

4. Conclusion

Two series of experiments—mechanical properties and water rebound of polymers—have shown coherent results. Water rebound is twice intensive for polymers prepared with non-reactive surfactant. It is evident from the results, that maleic surfactants used as stabilizers cause increasing hydrophobicity of films.

The films prepared with maleic surfactants are less resistant to the deformation and more deformable in comparison with polymers containing the succinic surfactants.

Both phenomena could be explained by heterogeneous inclusions of non-reactive surfactant throughout the polymer. These hydrophilic domains make the polymer more fragile and facilitate the pumping of water into the film.

From the fact, that all the results distinguish rather well the maleic and succinic surfactants, one could consider, that there are such lesser number of domains in the polymer in case of reactive surfactant: which is incorporated in the polymer in a homogenous way, most probably copolymerized. If so, the results of film experiments are at least one indirect proof for this complicate and interesting question, concerning incorporation of reactive surfactant in the polymer.

Another indication that the maleic surfactant is incorporated in the polymer, is, for instance in the case of **HE16**, that it cannot be extracted by methanol. Other techniques tried (^1H NMR of lattices in the water, ^1H NMR of polymers) to determine the presence or the absence of a double

bond, which might be associated with the non-reacted surfactant, are not capable of answering the question of surfactant grafting.

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