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SUMMARY OF THE THESIS

STUDY OF THE THIN FILMS OBTAINED BY LAYER BY LAYER DEPOSITION

SCIENTIFIC COORDINATOR

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Key words: hydrophobically modified polyelectrolytes; layer-by-layer electrostatic self-assembling; polyelectrolyte-surfactant complexes; umectability; rugosity; morphology; contact angle; thin films; hydrophobic architectures.

Introduction

The hydrophobically modified polymers have aroused the scientific interest in the last two decades due to their reassembling with the biological systems, and also for their self-associative behavior in aqueous solution. These macromolecular compounds have a hydrophilic chain on which are grafted hydrophobic groups. In aqueous solution these polymers present hydrophobic microdomains or form so called “local micelles” by the intramolecular aggregation of the neighbour hydrophobic chains.

Hydrophobically modified polyacrylates (HMPA) represent a peculiar class of polyelectrolytes. Their particular behavior owns to the electrostatic repulsions of the carboxylate groups and to the interactions of hydrophobic grafts which self-associate forming micellar aggregates. To avoid water, the hydrophobic groups associate forming intra and inter-molecular bonds and these interactions depend on concentration. Stronger associations appear if the alkyl chain is longer and the polymers become harder soluble in water. HMPA are often utilized as dispersing agents, viscosifiers, emulsifiers **[1-4]**. HMPA have applications in chemical industry, biochemistry, medicine, being used in paintings, cosmetic, pharmaceuticals, in oil recovery, drug delivery, etc. [**5-7].**

The purpose of this doctoral thesis is to obtain hydrophobic thin films by using hydrophobically modified polyelectrolytes. The following objectives are considered:

- **Obtaining and characterization of hydrophobically modified sodium polyacrylates** by grafting the poly(acrylic acid) (PAA) with amines having 10-18 carbon atoms;
- **Obtaining of thin films** using the layer-by-layer electrostatic self-assembling;
- **Glass hydrophobization** with the aid of hydrophilic polyelectrolytes;
- **Obtaining and characterization of the architectures** that use as raw material the polymer-surfactant complexes;
- **Influence of inorganic electrolyte, pH and aging time** upon the umectability of films of polyelectrolyte and polyelectrolyte-surfactant complexes;

The thesis contains three parts and seven chapters. The first part presents theoretical aspects regarding the polymers, surfactants, hydrophobically modified polyacrylates, multilayers of polyelectrolytes or polyelectrolytes-surfactants, and information about the hydrophobic surfaces. The aim and objectives of the thesis are also mentioned in the first chapter. In the second part the experimental methods used to characterize the polyelectrolyte solutions and the obtained films are described.

The third part contains the original contributions of the thesis and has three chapters. Chapter 4 describes the synthesis and characterization of hydrophobically modified polyacrylates, and the layer-by-layer electrostatic deposition method.

Chapter 5 contains the study of hydrophobically modified polyelectrolytes films by using DLS, contact angle (CA), AFM, SEM, FT-IR, ellipsometry, refractometry, XPS.

Chapter 6 presents the study of the films of complexes between hydrophobically modified polyelectrolytes and cationic surfactants. The experimental data were obtained by measurements of electrical conductivity, surface tension, Zeta potential, contact angle, AFM, SEM, FT-IR, ellipsometry, refractometry, XPS.

Experimental results and discussions

4.1. The synthesis of hydrophobically modified polyacrylates

For this thesis we have also prepared hydrophobically modified cesium polyacrylates and their counterparts in acid and cesium form. The amidation of PAA was done at 60^{o}C using 1-methyl 2-pyrrolidone (NMP) in the presence of N,N`-dicyclohexylcarbodiimide (DCC) [7]. Hydrophobically modified PAA was neutralized and precipitated in NaOH (40%), CsOH (40%) or with ethyl ether. The obtained polymers were purified by dialysis and recovered by lyophilization.

FT-IR and NMR results have demonstrated that the amidation of PAA was successfully accomplished. Moreover, ^{1}H-NMR spectroscopy allowed the calculation of the grafting degrees calculated that were approximately equal to 3 % (mol).

4.2. Preparation of LbL films

The method of thin films deposition was published in **Applied Surface Science 371 (2016) 519-529.**

The films of hydrophobically modified polyelectrolytes were obtained by using the LbL self-assembling technique. The procedure of LbL self-assembling is presented in **Figure 1**. To obtain the positively charged substrate, the glass plates are initially washed and immersed in aqueous solition of 5x10^{-2}M PEI for 20 minutes. After that, they were washed with distilled water for three times, one minute each time. Then, the substrate is immersed in 10^{-2} M PACnNa for 20 minutes, and the negatively charged external layer is deposited, and the same sequence of washing is done. Next, the plate is immersing in 10^{-2} M PDADMAC for 20 minutes, followed by the washing sequence. The depositing steps are repeated as many times is neccessary to obtain the desired number of bilayers. There was no drying procedure of the film between the depositing steps, except for the last deposited one. The drying procedure consists in exposing the films in dessicator.

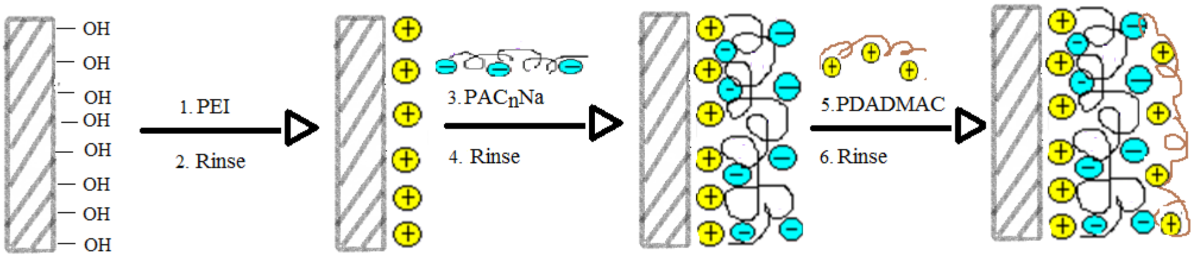


Figure 1. Schematical presentation of LbL self-assembling of thin films of PAC_nNa/PDADMAC.

The depositing procedure for the films that contain polyelectrolyte-surfactant complexes is similar with that for polyelectrolytes, with the difference that the solution of anionic polyelectrolyte is replaced with the negatively charged complexes of PAC_nNa-C_xTAB.

5. Study of polyelectrolyte films

Althongh the polyelectrolyte films were intensely studied, those of hydrophobically modified polyacrylates are not investigated yet. To fill the gap this chapter presents the umectability results of the films made from hydrophobically modified polyelectrolytes, freshly prepared and naturally aged. The results are published in **Applied Surface Science 371 (2016) 519-529** and in **Applied Surface Science 412 (2017) 489–496**.

The surface morphology as well as the wetting properties of the LbL films can be controlled by the chemical composition of the system and by the number of deposited bilayers. To this aim, hydrophobically modified polyelectrolytes with alkyl chains of 10-18 carbon atoms were LbL assembled on a glass support, alternatively with polydialyldimethylammonium chloride. It is important note that we obtained hydrophobic films by using hydrophilic solutions of polyelectrolytes grafted with alkyl chains. By increasing the alkyl chain of the polyelectrolyte from 10 to 18 carbon atoms the water contact angle increases and implicitly, the surface umectability diminishes. The amount of adsorbed species at the surface and the film's morpghology can be controlled by adjusting the number of bilayers, as observed in **Figure** 2. At the same time, the external layer of PDADMAC increases the contact angle (see **Figure 3**).

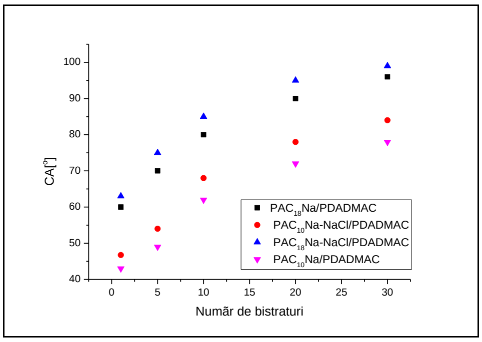
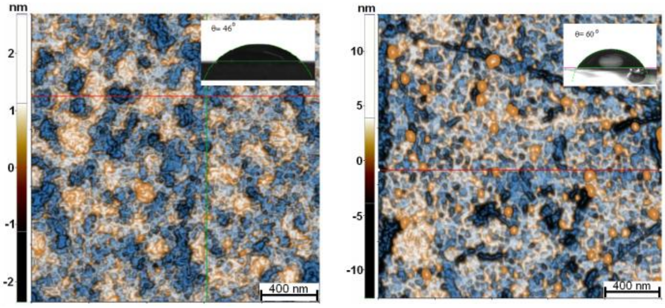


Figure 2. Variation of contact angle with the number of bilayers of the PAC$_n$Na/PDADMAC films, in presence or absence of 0,01M NaCl.



(a) (b)

Figure 3. AFM images for a layer of PAC$_{10}$Na (a) and a bilayer of PAC$_{10}$Na/PDADMAC (b), in presence of 0,01M NaCl.

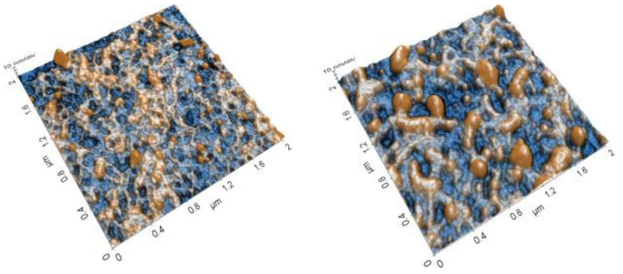
The addition of inorganic electrolyte into the system improves the contact angle and decreases the thickness and rugosity of the film.

Table 1. Influence of aging time upon the water contact angle of (PAC$_n$Na/PDADMAC)$_5$ films

Curr. No.	Aging time (Months)	PAC$_{10}$Na/PDADMAC	PAC$_{18}$Na/PDADMAC
		CA (˚)	CA (˚)
1	0	54,2	75,4
2	2	65,9	99,3
3	12	72,6	103,1
4	36	73,5	105,0

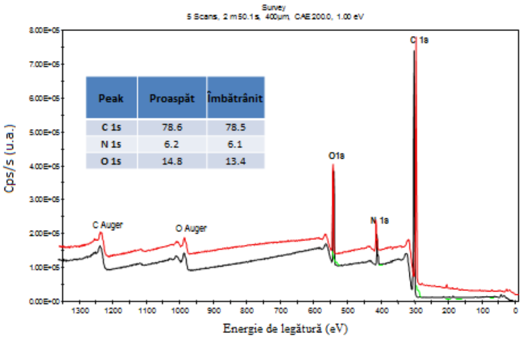
The aging time determines the increase of surface hydrophoby. The data in Table 1 show that the contact angle increases abruptly in the first 12 months of the aging process, while in the following 24 reaches a plateau. We can conclude that the morphological changes of the film occur in the first year of storage in optimal conditions. After this period the variations are extremely small.

The AFM data (**Figure 4**) demonstrate that the aged films are more coarse as they are dehydrated in time, with the formation of empty spaces. Herein, air bubbles can be confined and thus the surfaces become more hydrophobic.



(a) (b)

Figure 4. AFM 3-D image of $(PAC_{10}Na/PDADMAC)_1$ (RMS=2,42 nm) (a) and of $(PAC_{18}Na/PDADMAC)_1$ (RMS=4,25 nm) (b) films, aged for 12 months. Subscript 1 indicates the number of bilayers.



Peak	Proaspăt	Îmbătrânit
C 1s	78.6	78.5
N 1s	6.2	6.1
O 1s	14.8	13.4

Figure 5. XPS spectra for the $(PAC_{18}Na/PDADMAC)_{20}$ film, freshly prepared (red line) and aged for 12 months (black line).

XPS analysis (**Figure 6**) demonstrated that the films do not modify their composition in time. Both the aged and freshly prepared films present aproximatively the same atomic percentage. These values are presented in the table inside the figure. For example, the percent of Cl1s, O1s, N1s does not change significantly (the variations are much under the detection limit of the instrument, which is of 3%), and confirms the supposition that these multilayers are stable in time.

By this procedure we have obtained hydrophobic surfaces using cheap and environmentally friendly materials. At the same time, the investigated HMPA are the key toward a new class of compunds useful for obtain surfaces with self-cleaning properties.

6. Study of the films made from polymer-surfactant complexes

This chapter investigates the umectability of the films made from complexes of hydrophobically modified polyelectrolytes and cationic surfactants. It was done both on freshly prepared and naturally aged films. The results were published in **Applied Surface Science 371 (2016) 519-529** and in **Applied Surface Science 412 (2017) 489–496.**

We wanted to demonstrate that the films morphology and wetting properties can be controlled by the chemical composition of the system. To this aim, we prepared polymer-surfactant complexes. The hydrophobically modified polyelectrolytes with alkyl chains of 10-18 carbon atoms were complexed with alkyltrimethylammonium bromide. Then, they were alternatively assembled on glass, with polydialyldimethylammonium chloride. The contact angle measurements showed that the polymer-surfactant architectures are more hydrophobic than those with hydrophobically modified polyelectrolytes. The increase of the surfactant alkyl chain enhances the hydrophoby of the film made by polymer-surfactant complex.

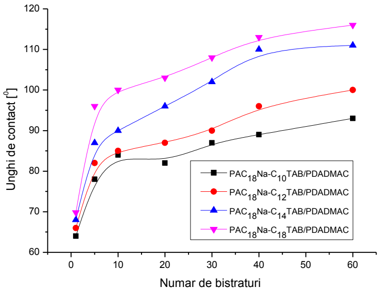
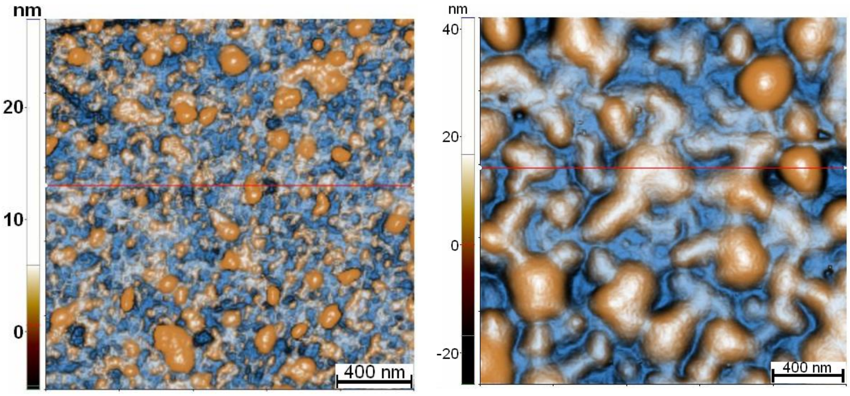


Figure 6. The water contact angle for the films of PAC$_{18}$Na-C$_x$TAB/PDADMAC at different number of bilayers.



a) b)

Figure 7. 2-D AFM images of the films of (a) (PAC$_{18}$Na-C$_{18}$TAB/PDADMAC)$_1$ (RMS=14.39 nm) and (b) (PAC$_{18}$Na-C$_{18}$TAB/PDADMAC)$_5$ (RMS=51.22 nm); Subscipts 1 and 5 refer to the number of bilayers.

The umectability data presented in **Figure 6** indicate an abrupt rise of the contact angle at 5 bilayers of PAC$_{18}$Na-C$_x$TAB/PDADMAC, which can be correlated with the surface morphology obtained by AFM investigation. **Figure 7** presents morphological changes from 1 to 5 bilayers of PAC$_{18}$Na-C$_{18}$TAB/PDADMAC based on AFM images at (2x2) nm^2 scale. The RMS value demonstrates that the surfactant alkyl chain plays an important role in the surface morphology. By increasing the number of bilayers from 1 to 5, RMS increases from 14,39 nm for one bilayer of (PAC$_{18}$Na-C$_{10}$TAB/PDADMAC)$_1$ (**Figure 7a**) to 51.22 nm for (PAC$_{18}$Na-C$_{18}$TAB/PDADMAC)$_5$ (**Figure 7b**). This deposition of multilayers leads to the formation of irregular structures with high rugosity and air bubbles can be captured in the empty spaces created, enhancing the hydrophobic character of the films. It is important to mention that Buron and coauthors [8-9] described a similar worm-shaped morphology for 5 bilayers of poly(dimethylammoniummethylmethacrylate chloride)/ polyacrylic acid. The increase of rugosity enhances the contact angle, as demonstrated by the results presented in **Figure 6**.

It is important to mention that the aging time leads to more hydrophobic surfaces. Moreover, for the aged films of PAC$_{18}$Na-C$_{18}$TAB/PDADMAC with 5 bilayers, one obtains a contact angle identical with that for 60 bilayers of PAC$_{18}$Na-C$_{18}$TAB/PDADMAC freshly prepared. A significant increase of rugosity together with a thickness decrease appears at 1 and 5 bilayers. By rising the number of bilayers, the surface morphology and the contact angle do not modify significantly.

XPS analysis showed that the films do not modify their composition in time, while FTIR measurements demonstrated their dehydration.

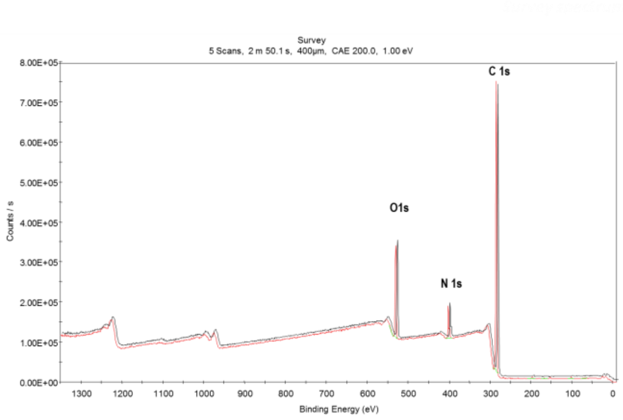


Figure 8. XPS spectra for the films of (PAC_{18}-C_{18}TAB-NaCl/PDADMAC$)_{20}$ (freshly prepared- red line, aged- black line).

With the aid of XPS method one could identify the atomic species both in the freshly prepared film and in the aged one. **Figure 9** illustrates the XPS spectra which indicate the presence of the chemical elements. The XPS spectra were deconvoluted and the relative concentration of the elements (at.%) was determined for C2p, Na1s, Si2p, N1s, Cl1s, Br3d ,’’as-received state’’. The data obtained for the fresh and aged film show that aging time does not affect their chemical composition. FT-IR measurements provided additional data about the films.

Figure 9 presents the FT-IR spectra for the aged films of PAC_{18}-C_{18}TAB-NaCl/PDADMAC with 20 bilayers. The characteristic bands attributed to the methylenes in the alkyl chain and to the carboxyl, hydroxyl and amide groups are present both in the fresh and aged films of (PAC_{18}-C_{18}TAB-NaCl/PDADMAC$)_{20}$. The spectral bands are not shifted by aging. These data demostrate that no compositional change occurs by aging, except for the loss of free water.

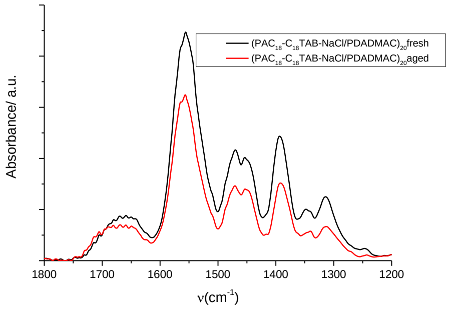


Figure 9. FT-IR spectra (1200-1800 cm^{-1} region) for fresh (black line) and aged (red line) films of (PAC$_{18}$-C$_{18}$TAB-NaCl/PDADMAC)$_{20}$.

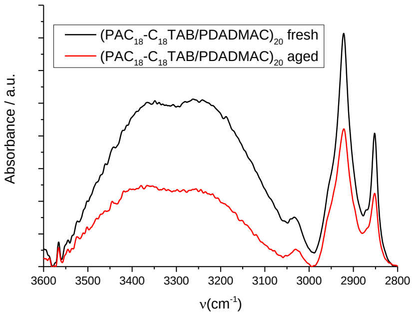


Figure 10. FT-IR spectra (3600-2800 cm^{-1} region) for fresh (black line) and aged (red line) films of (PAC$_{18}$-C$_{18}$TAB-NaCl/PDADMAC)$_{20}$.

Figure 10 presents the FT-IR spectra of (PAC$_{18}$-C$_{18}$TAB-NaCl/PDADMAC)$_{20}$ films, freshly prepared and aged for 12 months. One observes a large band at 3300 cm^{-1} (peak 1) which is specific to OH groups and covers the characteristic bands of NH units. The vibrational bands characteristic to CH$_2$ and CH$_3$ groups are present at 2875 and respectively at 2958 cm^{-1} (peak 2).

The semi-qantitative evaluation of the water content during film's aging was obtained by the ratio between the intensities of characteristic stretching vibrations, the first harmonic bending and the first overtone bending of water and the vibrations of organic skeleton, used as invariant [10]. The integrals of peak 1 or 2 allow calculating this ratio. The water content determined as above decreased for aged films, as compared with the fresh ones. Thus, it has been obtained a water loss of 55.68% for the aged films. This phenomenon owns to films dehydration, as formerly demonstrated [11-12].

The aged films are coarser, due to dehydration in time that creates empty spaces where the air bubbles are captured. In this way, more hydrophobic surfaces are obtained.

This procedure of obtaining hydrophobic films starting from polyelectrolyte-surfactant complexes is important because it uses cheap and environmentally friendly materials. Within this chapter it was demonstrated that the natural aging of films made from complexes between HMPA and cationic surfactants with long alkyl chains is beneficial for the obtaining of more hydrophobic materials. This aging process is the key toward the diminution of materials consumption and at the same time, it offers solutions for long-term coatings.

General Conclusions

- Hydrophobically modified polyelectrolytes with alkyl chains of 10-18 carbon atoms have been prepared.
- Thin films of sodium polyacrylate and of hydrophobically modified sodium polyacrylate were deposited on glass by layer-by-layer self-assembling, based on electrostatic interactions with polydialyldimethylammonium chloride;
- The wettability data have demonstrates that the length of the alkyl chain (R) of the hydrophobically modified polyelectrolyte determines the morphology of the films. The increase in R from 10 to 18 carbon atoms leads to a decrease in wettability
- Films with outer layer of cationic polyelectrolyte are more rough and have a higher contact angle;
- The film morphology and the amount of adsorbed species on the surface can be controlled by adjusting the number of bilayers containing both polyacrylate films and polymer-surfactant complexes;
- The presence of inorganic electrolyte (0.01M NaCl) in the system decrease the film wettability, thickness and roughness for all the studied architectures;
- The wettability tests have shown that the films of polymer-surfactant complexes are more hydrophobic than those without surfactant;
- The higher the hydrophobic surfactant, the greater the contact angle,
- By natural aging , the films are more hydrophobic for both polyelectrolyte and PS complexes
- The aged films dehydrated, which was been proved by FT-IR measurement;
- XPS analysis has shown that films composition does not change by aging;
- The obtaining of hydrophobic films using simple or hydrophobic polyacrylates and PS complexes is important because they are environmental friendly and inexpensive materials;
- The films have self-cleaning properties and are used in coating as well as windows cars.

Original Contributions

The studies made in this doctoral thesis are original, because architectures formed both of hydrophobically modified polyelectrolytes and their complexes with cationic surfactants such as alkyltrimethylamonium bromide have been obtained for the first time;

Although the polyelectrolytes used are hydrophilic, they led to a decrease in the wettability of glass. The increase in the alkyl chain of PMH results in an increase in contact angle.

Hydrophobic multilayers are obtained by increasing the number of electrostatically deposited layers, addition of inorganic electrolyte, pH modification.

The films obtain with polymer-surfactant complexes have higher contact angle than those without surfactant, resulting in more hydrophobic surfactant.

The effect of natural aging on wettability of newly created architectures by LbL deposition is another original aspect of this doctoral thesis. The aging is useful method that reduces material consumption and provides suitable solution for the long-term coating.

These materials are the key to a new class of materials used to produce self-cleaning and antiseptic surface with applications in medicine, civil engineering and artworks.

Dissemination of the research results

The results presented in this doctoral thesis were the subject of two papers published in international ISI journals. Great parts of the data obtained in the period of doctoral studies have been presented at national and international scientific events, totally 4 oral communications and 28 poster presentations.

List of published papers related to the thesis topic

1. Surface hydrophobization by electrostatic deposition of hydrophobically modified poly(acrylates) and their complexes with surfactants, I.C. Gîfu, M.E. Maxim, A. Iovescu, E.L. Simion, L. Aricov, M. Anastasescu, C. Munteanu, D.-F. Anghel, *Applied Surface Science* 371 (2016) 519-529, **FI:3,387**.

2. Natural aging of multilayer films containing hydrophobically modified poly(acrylate)s or their complexes with surfactants, I.C. Gîfu, M.E. Maxim, A. Iovescu, L. Aricov, E.L. Simion, M. Anastasescu, C. Munteanu, D.-F. Anghel, *Applied Surface Science* 412 (2017) 489-496, **FI:3,387**.

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12. N. Landhari, J. Hemmerlé, Y. Haikel, J.C. Voegel, P. Schaaf, V. Ball, Stability of embossed PEI-(PSS-PDADMAC)20 multilayer films versus storage time and versus a change in ionic strength, *Appl. Surf. Sci.* 255 (2008) 1988-1995.