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Stability of Aqueous Polymeric Dispersions for Ultra-Thin Coating of Bi-Axially Oriented Polyethylene Terephthalate Films

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Abstract: The stability of polyacrylate and polyester based aqueous dispersions designed for ultrathin coating of extruded plastic films, especially bi-axially oriented polyethylene terephthalate (BOPET), was studied. Also, the effect of the gemini surfactant based defoaming/wetting agent on the properties of the dispersions was examined. The addition of the defoaming/wetting agent resulted in reducing the surface free tension of the polyacrylate and polyester dispersion by 15% and 20%, respectively and the initial foam height by 60% and 15%, respectively. At the same time, the agent addition did not compromise the temperature and pH stability of the dispersions. Such modified dispersion can be utilized for ultrathin coating of plastic film used for packaging, to improve their processability, printability, and metallization.

Keywords: ultra-thin films; coating; polymeric dispersion; water based

1. Introduction

Plastics have long ago become common packaging materials. They are used to protect products like food, pharmaceuticals, medical products, cosmetics, electronics, and many others [1]. Namely in the food manufacturing process, packaging of the product is one of the most important steps, as it maintains the quality of food for storage, transportation, and end use [2]. A single-layer plastic material is usually not capable of fulfilling all the requirements of all the processes in the manufacturing chain, thus multilayer flexible films are produced, mainly by in-line coating, lamination, coextrusion, etc. [3].

Coated plastic films provide many advantages over the standard material—e.g., resistance against high temperatures—which in turn allows their usage in the pasteurization and sterilization processes. Moreover, a coating can improve antibacterial and barrier properties (oxygen and vapor transmission rates), lower the coefficient of friction, allow metallization of the film, etc. Another reason for coating the substrate is bringing its surface free energy closer to the surface tension of printing inks (reprographic, flexographic, photosensitive, ...), improving adhesion for lamination or making the surface antistatic. Recently, many different chemical compositions have been used for coating extruded plastic films. The film forming compound of such composition (polymeric dispersion) is usually polyester, polyurethane, or polyacrylate resin and the dispersed phase is often chemically and/or sterically stabilized. The thin film coating process can be substituted with corona treatment, to increase the substrate surface free energy. Such an approach is demanding though, because of high initial cost and process complications (possible electric interference with other equipment in the production line and the maintenance cost). Besides, corona treated polymer surfaces are known to suffer from so called "aging" of the treatment, a gradual reversal of the surface properties towards those of the untreated

surface. Aging is known to be accelerated by elevated temperature and moisture and occurs with most plasma treatment processes [4–10].

The coating process of typical polymeric foils (polyethylene, polypropylene, and even polyethylene terephthalate) also meets with difficulties such as poor wetting of the substrate with the dispersion (when the surface tension of the dispersion is relatively high with respect to the surface free energy of the substrate to be coated). The dispersions themselves can perform well, however in industrial conditions (gravure cylinder coating at high rate) their foaming can be a problem, as it can compromise the surface properties of the final thin film on a substrate. Various additives can be used to overcome such problems, though they should not compromise the properties of the initial dispersion, namely its stability. This article gives information on modifying the properties of polymer dispersions that can be used for ultra-thin coating of biaxially-oriented films and the effect of the additive on the properties of the dispersions. Promoted adhesion of the substrate can significantly improve the performance of further conversion steps (metallization, SiO_x, and AlO_x coating) and lamination with other materials as BOPP, PE, aluminium foil, etc. and help in formulation of new advanced packaging materials [1,11]. Namely in the case of BOPET, it is almost impossible to perform metallization of the foil without proper pre-treatment with a suitable thin film.

2. Materials and Methods

2.1. Solution Preparation

Co-polyester polymer aqueous dispersion Eastek™ 1200 (Eastman, Kingsport, TN, USA), referred to as Co-PES further in the text, and acrylic polymer aqueous dispersion PRIMAL™ AC-261 (Dow, Midland, MI, USA), referred to as ACR further in the text, were examined in the means of particle size (z-average) temperature and pH dependence, zeta potential temperature and pH dependence, surface free tension (SFT), foam forming, and stability. The testing solution was prepared by mixing the concentrated polymeric dispersion with deionized water so that the total solid content was approximately 6 wt.%, followed by homogenization with Teflon® coated magnetic stirrer (VWR International, Randor, PA, USA) for 15 min. Fresh solution was prepared prior to each measurement to avoid gel formation. Modified testing solutions were prepared by adding given amount of the defoaming/wetting agent (2,4,7,9-tetramethyl-4,7-decanediol) (Air Products, Allentown, PA, USA), designated as Agent 1 further in the text, followed by homogenization with a Teflon® coated magnetic stirrer for 5 min.

2.2. Surface Tension Measurement

The critical aggregation concentration (CAC) and critical micellar concentration (CMC), of the gemini surfactant in polymeric dispersion were determined from equilibrium surface tension measurements as a function of surfactant concentration at 25 °C. The surface tension of the solutions was measured by the Wilhelmy plate method with the K100MK3 automatic tensiometer (Krüss GmbH, Hamburg, Germany), with the platinum plate at 25 °C. The tensiometer sample chamber was connected to the thermostat (Termostat CC-308B Pilot Huber, Offenburg, Germany), to maintain the desired temperature. Where appropriate (surface tension dynamics), the solution was stirred prior to each measurement for 30 s with a clean glass rod and the measurement itself was initiated within the 30 s period starting from the point when the stirring had finished. For each solution, at least three separate measurements were performed.

2.3. Particle Size and Zeta Potential Measurement

The z-average (mean hydrodynamic diameter), zeta potential, and their temperature and pH dependencies were measured by dynamic light scattering method (DLS) with the Zetasizer Nano ZS (Malvern Instruments, Malvern, UK), coupled with the MPT-2 automatic titrator (Malvern Instruments, Malvern, UK). The scattered light was observed at a 173° angle. The disposable folded capillary cell

(Malvern Instruments, Malvern, UK) was used for the z-average and zeta potential measurement. Each presented value is the average of five measurements with different samples.

2.4. Foam Forming

The formation of foam was measured with polymeric dispersions prepared according to the Section 2.1, modified with 0–0.517 wt.% of Agent 1. Then, 50 mL of modified solution was transferred into the 250 mL graduated cylinder covered with Parafilm M® (Bemis Company, Inc., Oshkosh, WI, USA), the cylinder was agitated with both hands for 30 s and the height of the generated foam was recorded in time intervals 0, 5, and 30 min.

2.5. Thin Film Coating

The BOPET polymeric substrates (FATRA) with the thickness of 50 and 12 μm were used for the laboratory and industrial scale testing, respectively. The coating of the BOPET polymeric substrates with Co-PES and ACR dispersions was performed with an adjustable Baker Film applicator 3525 (Elcometer Ltd., Manchester, UK) on the laboratory scale and also in the industrial scale in a professional production line with a gravure coating cyllinder (Brückner Group GmbH, Siegsdorf, Germany) at the cooperating company (Fatra A. S., Napajedla, Czech Republic). In the laboratory scale, the substrates were pre-treated with low temperature plasma, prior to dispersion coating. The treatment was performed in the commercial Diener PICO plasma apparatus (Diener electronic, Ebhausen, Germany), with capacitive radiofrequency coupling at the frequency 13.56 MHz and pressure 0.4 mbar. The following procedure was utilized: The substrates were placed inside the plasma chamber, then the vacuum pump was activated and after 5 min the chamber was purged with pure air at 10 sccm for another 5 min to minimze the effect of contaminants possibly present in the chamber. Subsequently, while the air flow was adjusted to 10 sccm, the glow discharge was initiated. The forward power was set to 100 W and the reflected power was kept under 10%. In the industrial process, the pre-treatment was performed with the corona discharge unit built directly in the production line.

2.6. Thin Film Characterization

The surface of coated and uncoated substrates were analyzed with a scanning electron microscope (SEM) Phenom Pro (Phenom-World B.V., Eidhoven, The Netherlands) in the environmental mode (Phenom-World). The surface free energy of the coated and uncoated substrates was determined with the non-toxic testing inks (Arcotest GmbH, Moensheim, Germany).

3. Results and Discussion

3.1. Surface Tension of Pure and Modified Dispersions

Surface tension of pure ACR and Co-PES dispersions was measured. The data in Figure 1 suggest a similar trend for both pure dispersions—decent drop of the surface tension value over the 180 s period. Pure ACR and Co-PES dispersion start at approx. 44 mN/m and 52 mN/m, respectively. Very similar data were obtained for solutions aged for 24 h at 40 °C. From the SFT point of view, both dispersions remain stable enough over the typical processing period (preparation of dispersion—short-term storage—coating), even at elevated temperatures.

In order to improve wetting properties, the ACR and Co-PES dispersions were modified with the Agent 1. The dependencies of surface tension versus surface active agent concentration show two breaks—at approx. 0.14 wt.% and 0.40 wt.%—which were attributed to the critical aggregation concentration and critical micellar concentration, respectively, of Agent 1 (Figures 2 and 3). The trend of curves seems to be unaffected by the chemical nature of dispersions and Agent 1 is highly efficient already at low concentrations. The addition of 0.14 wt.% provides reduction of SFT value by 15% and 20% for ACR and Co-PES dispersion, respectively, which is favorable for the thin-film coating process.

The Agent 1 (as a representative of gemini surfactants) contains two hydrophilic and hydrophobic part within one single molecule, thus its surface active properties (efficiency and effectivity) are remarkably better than would be with their single hydrophilic/hydrophobic analogues [12–14].

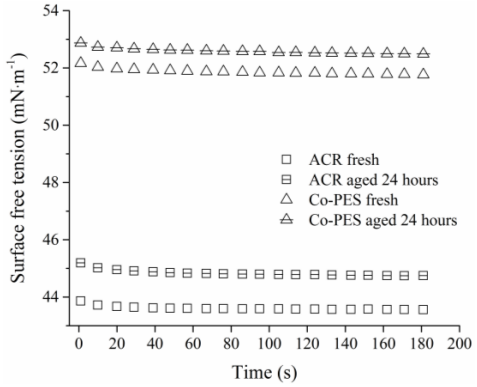


Figure 1. Surface tension time dependence of ACR and Co-PES dispersions; fresh and aged for 24 h at 40 °C.

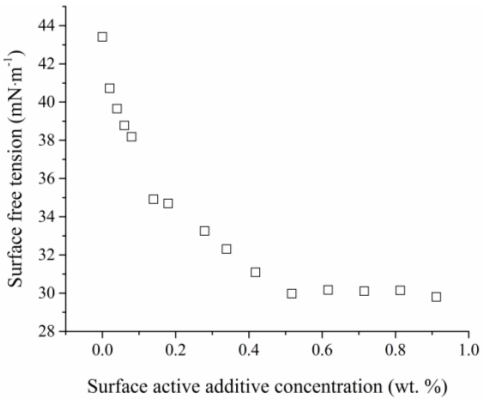


Figure 2. Surface tension of ACR dispersion vs. surface active additive (Agent 1) concentration.

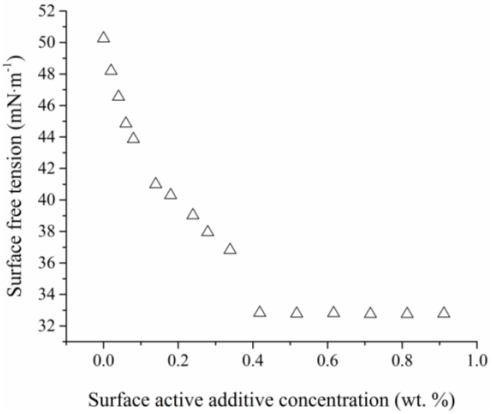


Figure 3. Surface tension of Co-PES dispersion vs. surface active additive (Agent 1) concentration.

3.2. Particle Size and Zeta Potential of Pure Dispersions

The measurement with pure dispersions at the temperature 25 °C revealed the z-average value of (144 ± 4) nm and zeta potential value of (−20.0 ± 0.6) mV for the ACR dispersion. With the Co-PES the values were (15.0 ± 0.1) nm and (−39.0 ± 1.0) mV, respectively. These numbers (namely the

zeta-potential value) correspond with the practical experience, where the Co-PES dispersion remains rather stable during storage and ultra-thin film coating, while the ACR dispersion shows the tendency towards gelation of the stock solution with prolonged storage and/or exposure to elevated temperatures in the coating process. In the Figure 4, the z-average temperature dependence of both systems is shown. The Co-PES dispersion exhibits similar stability in the observed temperature range (except the fluctuations in the interval from 10 to 20 °C), as the ACR dispersion.

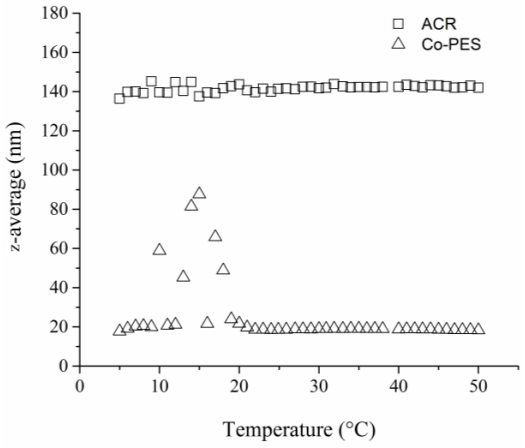


Figure 4. z-average temperature dependence of ACR dispersion (**squares**) and Co-PES dispersion (**triangles**).

The zeta potential temperature and pH dependencies of both systems are shown in the Figures 5 and 6, respectively. As can be seen, the zeta potential drops continuously with increasing temperature for the ACR dispersion, though for the Co-PES dispersion it reaches a plateau at about 30 °C. The total change of zeta potential is about 12–15 mV in the interval 5–50 °C in both systems, though the absolute value for the Co-PES dispersion stays above −30 mV at 50 °C (stable) while for the ACR dispersion, it approaches −15 mV at 50 °C. The ACR dispersion is less stable at elevated temperatures and this should be considered in the coating process setup (for example additional cooling of the stock container, if the excess dispersion from the gravure cylinder refluxes there). From the pH point of view, on the other hand, the ACR dispersion keeps its zeta potential value down to pH 7 and then increases slowly (IEP about pH 4) whereas the Co-PES dispersion exhibits abrupt change already at pH 8 and the IEP is approached around pH 7.

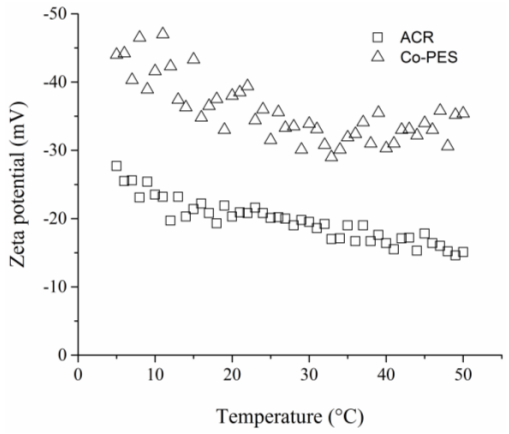


Figure 5. Zeta potential temperature dependence of ACR dispersion (**squares**) and Co-PES dispersion (**triangles**).

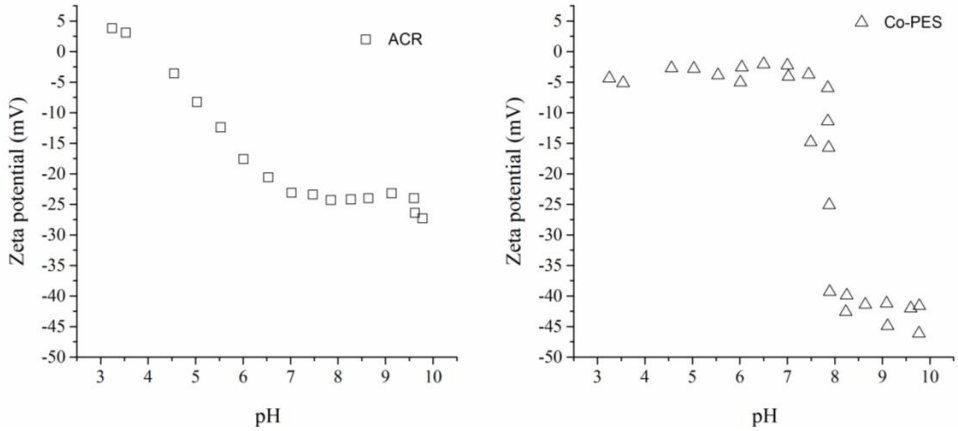


Figure 6. Zeta potential pH dependence of ACR dispersion (**squares**) and Co-PES dispersion (**triangles**).

3.3. Particle Size and Zeta Potential of Modified Dispersions

The concentration and chemical structure of used defoaming/wetting agent can have a significant influence on particle size and its distribution, viscosity, dispersion stability, or film formation. Therefore, the particle size and zeta potential measurements were performed. Based on the SFT measurements of polymeric dispersions with various concentrations of surface active additive, the optimal concentration of Agent 1 was selected for the ACR and Co-PES dispersions modification, as described in the Section 3.1. Based on those measurements, the optimal concentration was defined as 0.14 wt.% of the Agent 1. Then, the same dependencies as for pure dispersions were measured. The z-average temperature dependence (Figure 7) is similar to that of pure dispersions, except that there are no fluctuations at low temperatures, suggesting that the stability of the system could even be improved by modification with the surface active agent.

From the zeta potential point of view, the situation is different, as in Figure 8. The zeta potential values of the ACR and Co-PES dispersions drop almost to zero at temperatures approaching 40 °C. The ACR dispersion keeps the −10 mV value by the temperature of about 30 °C, while with the Co-PES dispersion a rapid drop of zeta potential does not occur until about 37 °C. These observations should be kept in mind when designing an industrial process involving such dispersions with defoaming/wetting agent and proper measures should be applied (e.g., cooling the stock dispersion, as mentioned above). The pH stability at 25 °C, on the other hand, remains almost unchanged, Figure 9.

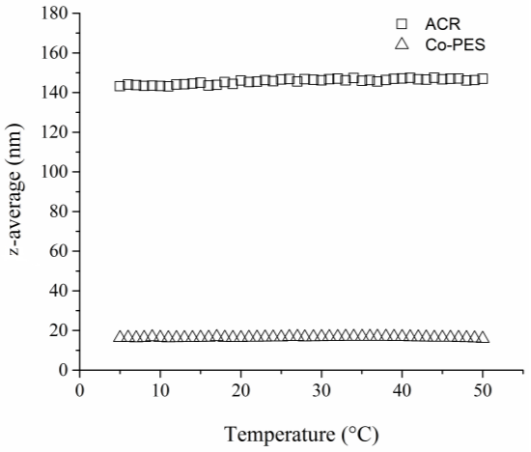


Figure 7. z-average temperature dependence of modified ACR dispersion (**squares**) and Co-PES dispersion (**triangles**).

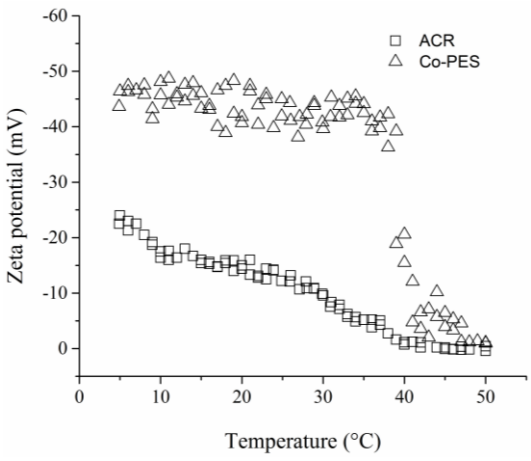


Figure 8. Zeta potential temperature dependence of modified ACR dispersion (**squares**) and Co-PES dispersion (**triangles**).

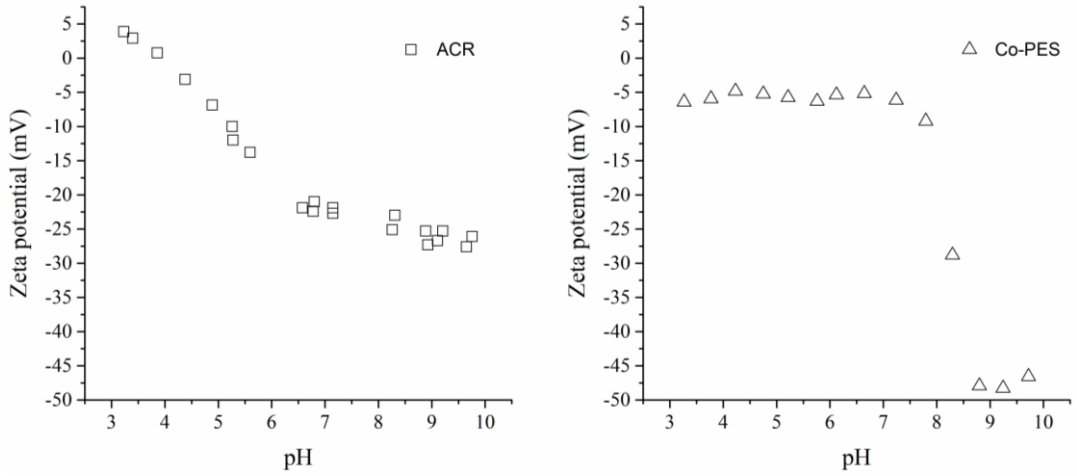


Figure 9. Zeta potential pH dependence of modified ACR dispersion (**squares**) and Co-PES dispersion (**triangles**).

3.4. Foam Forming

Foaming of both polymeric dispersions was determined as a function of defoaming/wetting agent concentration and time. The results for ACR dispersion (Figure 10a) show higher value of the foam height of pure ACR dispersion, compared to pure Co-PES dispersion (Figure 10b). The foaminess of ACR is 2.6 times higher than for Co-PES. The foam height of pure ACR dispersion was around (108.0 ± 4.0) mm. The first addition of Agent 1 caused lowering of foam height to (40.0 ± 0.5) mm, i.e., more than 60%. As can be seen in the Figure 10a, the foaming of ACR decreases markedly between 0.02 and 0.08 wt.% concentration of the Agent 1 (close to the CAC value). When the concentration of Agent 1 is close to the CMC, the foam height reaches a plateau.

Similar results were observed for Co-PES, Figure 10b. The foam height of pure Co-PES dispersion was around (41.0 ± 3.0) mm. The first addition of Agent 1 caused lowering of foam height to (35.0 ± 0.1) mm, i.e., about 15%. When the concentration of Agent 1 exceeded the Agent 1 CAC (0.14 wt.%), again the plateau was reached.

These results indicate that Agent 1 can work as defoamer for both ACR and Co-PES dispersions, though the direct impact will be more profound in the acrylic dispersion.

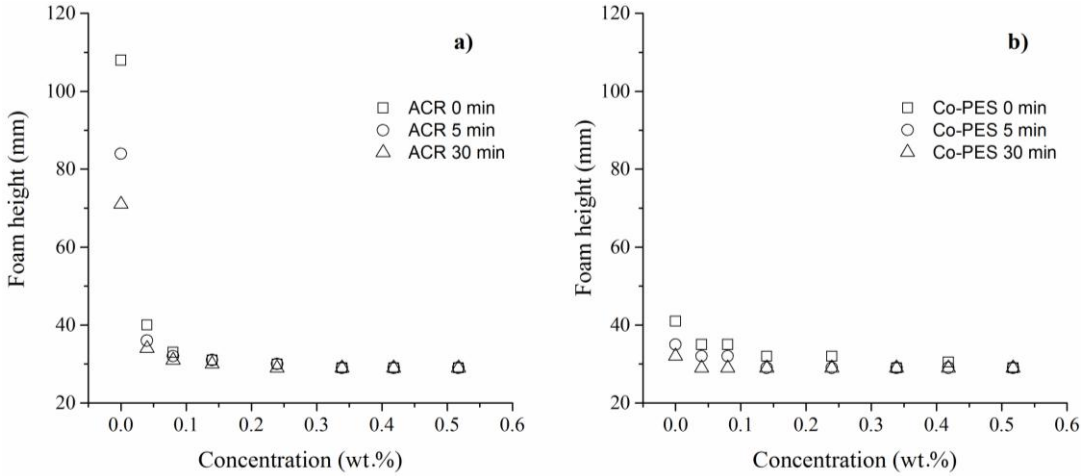
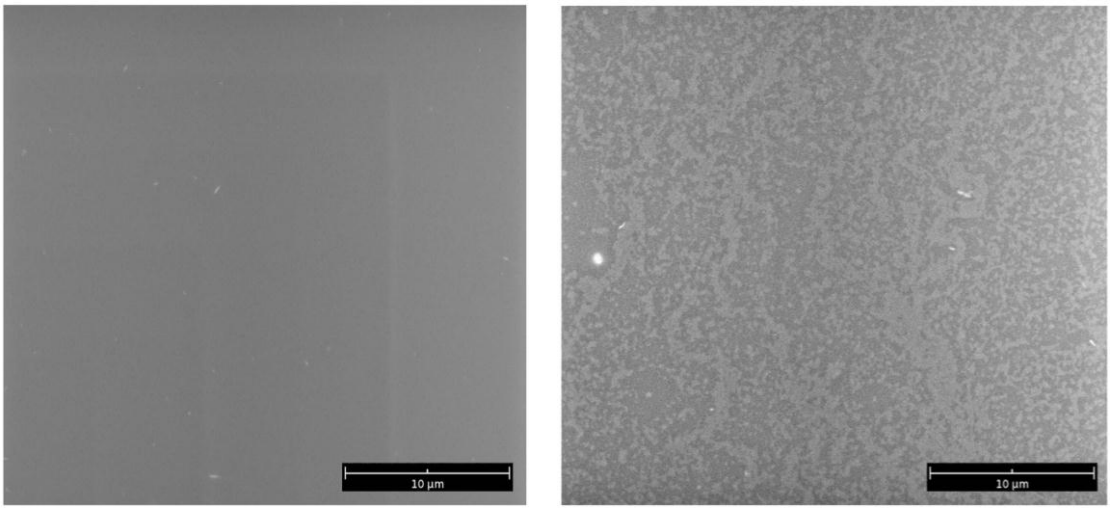


Figure 10. Foam height time dependence of the ACR dispersion (**a**), and Co-PES dispersion (**b**) with different concentrations of the Agent 1.

3.5. Thin Film Coating and Characterization

The coating in the laboratory scale was performed solely for the purpose of determination whether the dispersions will wet the substrate and thus would be suitable for the industrial process. Figure 11 displays the surface of virgin and ACR dispersion coated substrates. As can be seen, the manual coating provides a relatively thick (up to 10 microns) layer. In the case of the industrial process, the layer is so thin (partly because of the thin liquid layer deposited with the gravure cyllinder and also due to the biaxial stretching—the dispersion is deposited before the transverse direction orientation takes place), it can hardly be analyzed with any other method than surface tension measurement (either inks or sessile drop method). Testing the substrate with ink revealed the surface free energy of approx. 42, 40, and 62 $mJ \cdot m^{-2}$ for virgin BOPET, ACR coated BOPET, and Co-PES coated BOPET, respectively.



(**a**) (**b**)

Figure 11. SEM images of the virgin (**a**) and laboratory ACR coated (**b**) substrates.

4. Conclusions

The effect of the gemini surfactant based defoaming/wetting agent on the properties of aqueous acrylic and polyester dispersions was studied. The dispersions were examined from the perspective of surface tension, particle size, zeta-potential, and foaming. Pure ACR and Co-PES dispersion were

found to have the SFT about 44 mN/m and 52 mN/m, respectively and kept this value relatively well when aged for 24 h at both 25 °C and 40 °C. The addition of 0.14 wt.% of Agent 1 reduces the SFT value by 15% and 20% for ACR and Co-PES dispersion, respectively, which is favorable for the thin-film coating process. Taking the above-mentioned into account, the modified dispersions will provide better wetting of a substrate without the need for its surface treatment and will withstand short-term storing even at mildly elevated temperatures. On the other hand, according to the data obtained from the z-average and zeta-potential measurements, prolonged storage and/or exposure to elevated temperatures in the coating process can possibly bring problems with gelation in the case of ACR dispersion. The Co-PES dispersion is expected to perform better in such conditions. Besides better wetting, the addition of the Agent 1 is defoaming the dispersions significantly, though its effect is more obvious in the ACR dispersion than in the Co-PES dispersion (initial foam reduction 60% and 15%, respectively). Such modified dispersion can be utilized for Co-PES ultrathin coating of plastic film (especially BOPET) used for packaging, to improve their processability, printability, metallization, and barrier properties.

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Author Contributions: Petr Smolka conceived and designed the experiments and wrote the paper; Lenka Musilová performed the experiments and performed data evaluation; Aleš Mráček performed data evaluation and literature research; Tomáš Sedláček contributed the materials and analytical apparatus.

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