



## Rapid Communication

## Wetting properties of cosmetic polymeric solutions on hair tresses

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## ABSTRACT

The objective of the present work is to investigate wetting of hair tresses with the solutions of two polyacrylate polymers broadly used in cosmetic products. Wetting properties of the neutralized Aculyn-22™ (A22) and Aculyn-33™ (A33) polymer solutions on dry hair tresses are studied. Wetting behaviour on the dry undamaged hair tresses is drastically different between the two polymers and, in a first approximation, not directly linked with their bulk rheology. In the case of A22 the droplet spreads and remains on the tress after spreading for at least half an hour, during which it slowly evaporates and possibly penetrates inside the hair. For A33 fast penetration of the droplet inside the hair tress is observed when the advancing contact angle reaches a critical value of about 60°. It can be attributed to the so-called Cassie–Wenzel wetting transition, in which the liquid starts to penetrate inside the hair array.

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Interactions between hair and water occur frequently not only in shower during application of the hair care products such as shampoos, conditioners or hair colourants, but also in contact with the atmospheric moisture. Water can absorb and diffuse into hair making it wet. As a result, the wetted strands stick to each other and form several clumps due to cohesive forces caused by water bridges [1]. Hair wettability, and how hair care products affect its wetting properties, is of considerable interest in cosmetic science [2,3].

The majority of research presented in the literature concentrate on interaction of a single hair fibre (dry or wet) with various liquids [2,4–5]; however, wetting of dry hair tresses with polymer solutions is largely unexplored up to now. This attracts significant interest from the industry, particularly for treatments which are applied on dry hair, e.g., for hair colouring products, hair styling products, leave-on conditioners and serums. There is a trend to minimize the use of harsh surfactant in such systems; cosmetic polymers with a pronounced affinity to interfaces, like Aculyn™ 22 and Aculyn™ 33 solutions, are such alternatives. These polymers are used in the production of shampoos, bath foams, foaming facial cleansers, hair styling gels, liquid soaps, lotions, moisturizing creams and hair colourants [6].

Below wetting of dry hair tresses by polymer solutions of Aculyn™ 22 (A22) and Aculyn™ 33 (A33) is investigated. A22 is a hydrophobically-modified anionic alkali soluble polymeric emulsion, and A33 is an anionic alkali soluble, lightly crosslinked emulsion of the ethyl acrylate and methacrylic acid. General structures of the polymers are presented in

Refs. [7,8]. Aqueous solutions of the polymers in the concentration range 1.0–1.5% w/w were prepared by diluting and neutralizing the stock polymer emulsions with a 2% ammonia solution in ultra-pure water produced by Millipore Q, and further buffered with ascorbic and citric acids (0.2% w/w each). Sodium chloride (NaCl) was added to the solutions in the range 0–1.5 M, and isopropyl alcohol (i-propanol, iPr-OH) was used at 0 or 1.67 M (10% w/w) concentration. Sodium dodecyl sulphate surfactant (SDS) was used at the concentration 5 mM. The above compositions have been chosen to represent typical systems used in the cosmetic applications where the polymers are utilized, for example in hair colourant applications. In our researches presented below and in Refs. [9,10] the following procedures were used by Procter & Gamble Co. to produce cosmetics formulations with A22 and A33. Rheology and surface tension measurements were conducted as described in Refs. [9,10].

Blended human hair tresses (brown, Caucasian origin) were supplied by International Hair Importers, arranged into flat tresses of 12 cm length, width 2.5 cm and approximately 3 mm thickness. The average weight of the hair tress was 2 g and the average number of hair fibres in the tress was 4000. For wetting measurements, the tresses were secured in a special custom made frame to provide as much hair alignment as possible. Frame allows fixing bunch of hair in a way which enables measurement of contact angle on hair. The surface of hair tress was as flat as possible. Example of hair arrangement is presented in Fig. 1.

The thickness of the tress was sufficient to avoid contact of the investigated liquid with the frame material. There was some expected variation in the arrangement of individual hair fibres on the frame in the course of repeated experiments, leading to a considerable standard

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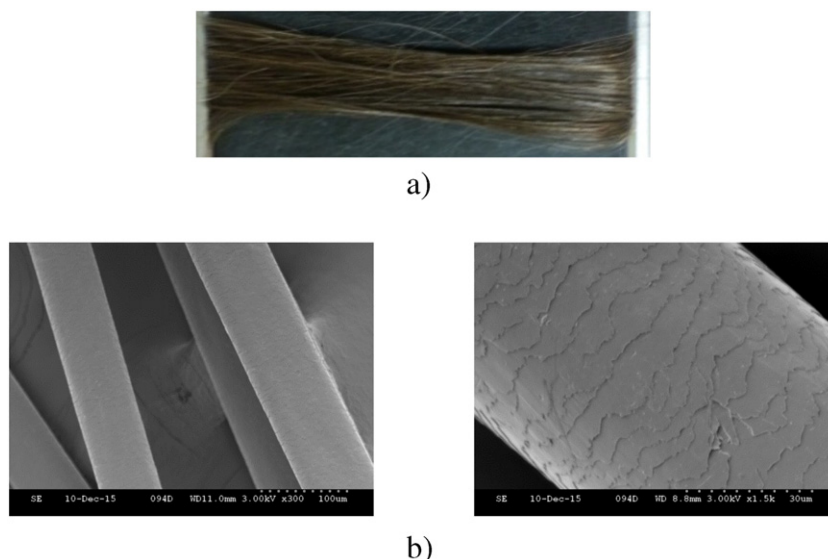


Fig. 1. a) Example of hair tress used for contact angle measurements. b) SEM images of hair fibres.

error of measurements. The porosity of tress of hair was estimated as  $\sim 0.43$  and the distance between the fibres was  $\sim 17.4 \mu\text{m}$ .

Each hair tress was washed by a neutral shampoo, rinsed 3 times in distilled water and dried naturally. Measurements of the apparent contact angle were performed on dry hair tresses using the drop shape analysing software DSA 3, KRUSS. This software provides the contact angles  $\theta$ , the droplet volume  $V$ , and the droplet base diameter  $DB$ , all as a function of time  $t$ . The movies were recorded with a constant speed of 5 fps. The recorded process time below is defined as the time during which the droplet remains on the hair tress. During this time various parallel processes (spreading, penetration, and evaporation) occur. The initial contact angle was measured immediately after a droplet was placed on the support material. The final (advancing) contact angle is the contact angle after spreading stops, when the  $DB$  reaches a constant value. All measurements were made at  $20^\circ\text{C}$  and 40% relative humidity. Teflonated silicon wafers (Teflon below) were selected as a reference support material for the contact angle measurements, as the initial contact angle on Teflon and hair tresses (both hydrophobic) is similar. It was demonstrated in Ref. [11] that there is no influence of the droplet volume on the contact angle measurement. In present experiments, the droplet volume was  $2\text{--}3 \mu\text{l}$  for each measurement. However, different droplet volumes resulted in different base diameters, but the differences were compensated in the equipment software by converting the base diameter into the equivalent volume.

In the case of measurements on Teflon, reproducibility was very good, and the relative standard error was around 2–3%. When measuring on hair tresses, at least 10 repeated measurements were performed, however, the error was still in the range of 10–20% due to variations in the tress arrangement on the frame, as mentioned above.

Rheological and surface properties of the solutions under investigation are shown in Table 1. Data presented in Table 1 show that both polymers reduce surface tension, and the surface tension of the A33 solutions is lower than that of the A22 solutions. Both A22 and A33 solutions demonstrate well pronounced shear thinning behaviour. Viscosity is presented at shear rate  $12 \text{ s}^{-1}$  because this particular shear rate is of industrial interest. Viscosity decreases considerably with increase in the salt concentration, and remains always higher for the A22 solutions of comparable concentration vs. the A33 solutions. It was found that both bulk and surface viscoelasticity of the polymer mixtures depend rather smoothly on the content of A22, and no synergetic effects were observed. Therefore, it can be concluded that there is little interactions between the two polymers in solution within the studied concentration range.

Table 1 presents comparison of the wetting properties: the initial contact angle, the final contact angle (contact angle after spreading), the spreading time and the process time for the investigated solutions.

Initial contact angle of water on Teflon is around  $110^\circ$ , and on hair is around  $100^\circ$ . It confirms the expected hydrophobic nature of the

Table 1

Comparison of bulk viscosity, surface tension and wetting properties of investigated solutions on hair tresses.

Solution	Surface tension <sup>1</sup> , mN/m	Bulk viscosity at $12 \text{ s}^{-1}$ , mPa s	Initial contact angle, deg	Spreading time, s	Final contact angle, deg	Process time, s
Water		1	100	5–10	90	–
A22 1% 0.3 M NaCl	$42 \pm 1$	$550 \pm 10$	100	10–20	80	2000
A22 1% 0.3 M NaCl 10% ipr-OH	$36 \pm 1$	$400 \pm 7$	80	1–4	60	2400
A22 1% 0.3 M NaCl 5 mM SDS	$35 \pm 1$	$510 \pm 15$	90	40–50	50	2000
A22 1% 1.3 M NaCl	$38 \pm 1$	$100 \pm 5$	100	10–20	80	2000
A22 1% 1.3 M NaCl 10% ipr-OH	$32 \pm 1$	$40 \pm 5$	0	Immediate penetration		
A33 1% 0 M NaCl	$30 \pm 1$	$100 \pm 10$	100	5–25	60	200
A33 1% 0 M NaCl 10% ipr-OH	$33 \pm 1$	$100 \pm 10$	90	1–5	30	10
A33 1% 0 M NaCl 5 mM SDS	$32 \pm 1$	$108 \pm 10$	90	1–5	30	10
A33 1.5% 0 M NaCl	$27 \pm 1$	$500 \pm 50$	100	10–30	60	100
A33 1.5% 0 M NaCl 10% ipr-OH	$30 \pm 1$	$500 \pm 50$	90	2–3	50	60
A33 1.5% 0 M NaCl 5 mM SDS	$35 \pm 1$	$560 \pm 10$	80	1–8	25	70
A22:A33 = 1:1	–	$90 \pm 10$	100	25–80	65	180
A22:A33 = 1:3	–	$40 \pm 10$	100	10–40	50	140
A22:A33 = 3:1	–	$400 \pm 15$	100	40–50	60	2000

<sup>1</sup> Ref. [10].

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