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.

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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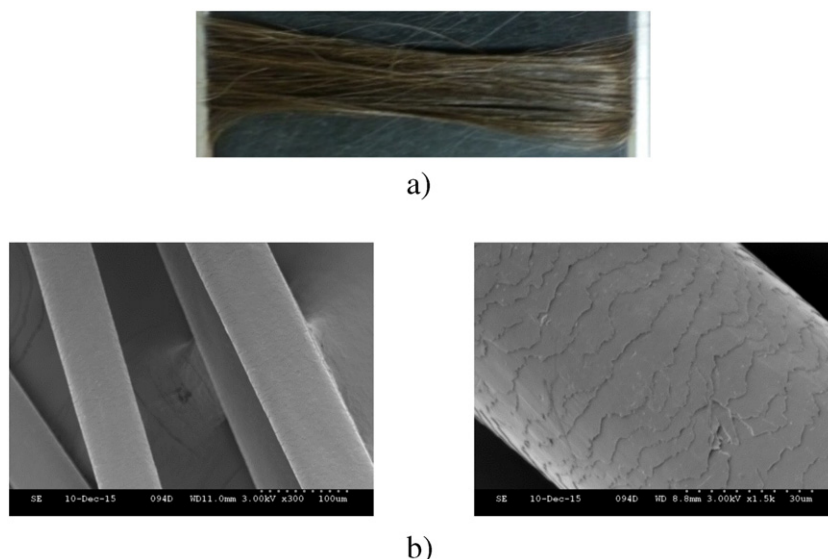   E-mail address: V.M.Starov@lboro.ac.uk (V. Starov).

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 ~0.43 and the distance between the fibres was ~17.4 μm.

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 $θ$, 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 °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 2–3 μl 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 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°, and on hair is around 100°. 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[1], mN/m	Bulk viscosity at 12 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 ± 1	550 ± 10	100	10–20	80	2000
A22 1% 0.3 M NaCl 10% ipr-OH	36 ± 1	400 ± 7	80	1–4	60	2400
A22 1% 0.3 M NaCl 5 mM SDS	35 ± 1	510 ± 15	90	40–50	50	2000
A22 1% 1.3 M NaCl	38 ± 1	100 ± 15	100	10–20	80	2000
A22 1% 1.3 M NaCl 10% ipr-OH	32 ± 1	40 ± 5	0	Immediate penetration		
A33 1% 0 M NaCl	30 ± 1	100 ± 10	100	5–25	60	200
A33 1% 0 M NaCl 10% ipr-OH	33 ± 1	100 ± 10	90	1–5	30	10
A33 1% 0 M NaCl 5 mM SDS	32 ± 1	108 ± 10	90	1–5	30	10
A33 1.5% 0 M NaCl	27 ± 1	500 ± 50	100	10–30	60	100
A33 1.5% 0 M NaCl 10% ipr-OH	30 ± 1	500 ± 50	90	2–3	50	60
A33 1.5% 0 M NaCl 5 mM SDS	35 ± 1	560 ± 10	80	1–8	25	70
A22:A33 = 1:1	–	90 ± 10	100	25–80	65	180
A22:A33 = 1:3	–	40 ± 10	100	10–40	50	140
A22:A33 = 3:1	–	400 ± 15	100	40–50	60	2000

[1] Ref. [10].
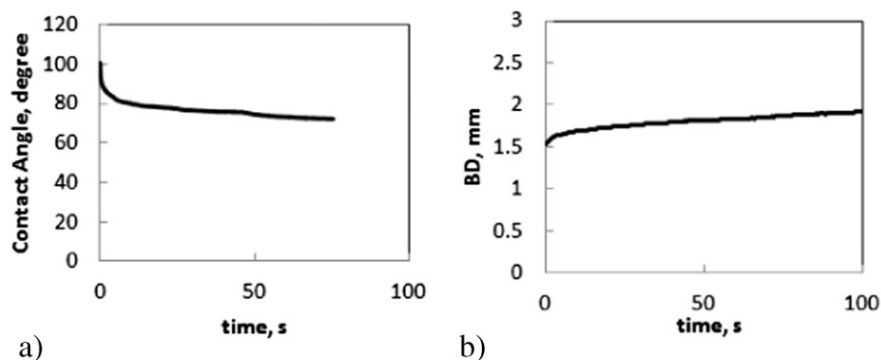
Fig. 2. A22 1% 0.3 M NaCl solution on a hair tress. a) Contact angle and b) base line diameter.

undamaged hair fibre as its primary component is keratin. However, hair tresses are a porous support. Even more than that, it has two-type porous structure: (i) pores built by an array of individual fibres (slightly different in each measurement) and (ii) a fine porous structure of each individual hair fibre (see Fig. 2(b)) [12–14]. A hair tress demonstrates hydrophobic properties not only because of the hydrophobic nature of the hair surface, but also because of air pockets in between the fibres. That is, there are three possible wetting regimes: (a) Cassie wetting, where liquid is sitting on the hair tress, without penetration inside the tress, (b) Wenzel wetting, characterized by penetration of liquid into the hair tress, (c) transition from Cassie wetting to Wenzel wetting, after some critical contact angle is reached [15–18]. All three mentioned regimes were observed.

Dynamic contact angle and diameter of the base line of the A22 polymer solution droplets on the hair tress is presented in Fig. 2. In the case of Teflon, the initial contact angle of all A22 solutions (1% polymer, 0.3 M and 1.3 M NaCl) was 110°, and fast spreading over a short period of time around 20 s was observed. After the fast spreading stage the contact angle remained around 100° and the droplet stayed on the support without changing its hemi-spherical shape. The initial contact angle on the hair tress for this polymer was about 100°. Spreading stopped after 10–20 s, and the contact angle reached the value of 80° (Fig. 2). The droplets remained on the surface of the hair tress after the initial fast spreading stage. Following this stage the total process time (until the droplet complete disappearance) was around 2000 s for both solutions (A22 1% polymer, 0.3 M and 1.3 M NaCl). During this longer stage a slow evaporation and possible imbibition of the solutions into the hair were observed. Wetting properties of the solutions were very similar in spite of a considerable difference in their viscosities.

Wetting properties of the A33 solutions on Teflon are similar to that of the A22 solutions. Initial contact angle of both A33 solutions (1% and 1.5% polymer, 0 M NaCl) on Teflon was about 100° and duration of the fast spreading stage was around 40–50 s (slightly longer than A22).

The contact angle after spreading was around 80°: the smaller contact angle in comparison with the A22 solutions is consistent with the lower surface tension of the A33 solutions (Table 1). The initial contact angle of the A33 solutions on the hair tress was about 100°. For the A33 1% 0 M NaCl the first fast stage of spreading was completed after 5–25 s. For the A33 1.5% 0 M NaCl this stage took 10–30 s. In both cases the final contact angle after spreading was around 60°. The total process time, during which the droplet disappeared completely, was 100 s for A33 1.5% 0 M NaCl and 200–250 s for A33 1% 0 M NaCl (Table 1). It is important to notice that the droplet with higher viscosity disappeared faster.

Fig. 3 shows that in the case of A33 solutions, where the contact angle reached the critical value (around 60°), fast penetration into the hair tress was observed. This resulted in a "jump" on the graph of contact angle and diameter of the base line (Fig. 3). This can be explained by Cassie–Wenzel wetting transition: before reaching the critical contact angle (around 60°) the droplet was a Cassie state "sitting" on the outer surface of the hair tress; however, after the critical contact angle was reached then penetration of the liquid into the pores inside the porous media (like the hair tress in the case) by liquid started. Schematic penetration of the liquid inside the porous media (hair tress) is presented in Fig. 4. In the case of Cassie state, liquid wetted only the outer layer of the hair tress; however, at the Wenzel state liquid penetrated inside the hair tress. Capillary transport along fibres started after the transition. Such wetting transition is also observed on other keratin-built biological tissue, pigeon feathers, when it is irradiated by nitrogen and air plasma [19].

Figs. 2 and 3 proves that the conditions for wetting transition are to reach the critical contact angle, which is around 60° in the case under consideration. This condition is satisfied for the A33 solutions and not satisfied for the A22 solution, the latter showing higher contact angle. The critical value of contact angle was obtained faster for the A33 1.5% solution than that for the A33 1.0% solution. It can be caused by slightly higher concentration of the trace surfactant carried over from the stock
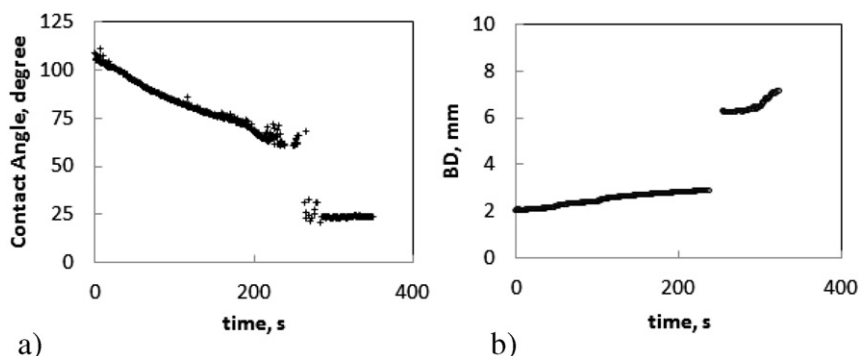

Fig. 3. A33 1% 0 M NaCl solution on a hair tress. a) Contact angle and b) base line diameter.
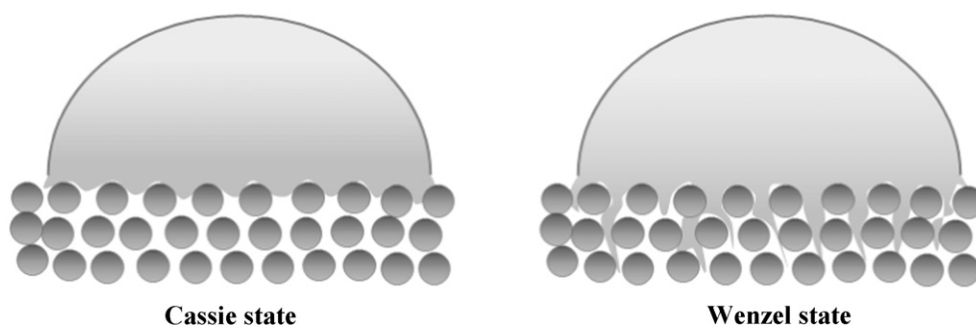
Fig. 4. Behaviour of liquid droplet on a hair tress. Cassie state: only outer layer of the hair tress is wetted; Wenzel state: liquid penetrate dipper into the hair and penetrates along the hair tress.

emulsion with the higher concentration of the polymer. The decrease of the total process time for the A33 solutions with added SDS confirms this observation. Differences in wetting behaviour of investigated solutions can be understood in terms of differences in polymer chemistry: A22 is a hydrophobically-associative polymer and has strong intermolecular associations and A33 is a microgel-type thickener that is not capable of strong intermolecular associations. It could be a reason why A33 solutions can reach critical contact angle on hair and penetrate into hair tress much faster than A22. However, other solution formulations can cause different molecule associations leading to a different wetting behaviour.

In most cases droplets of the A33 solutions behaved as described above, that is, underwent Cassie–Wenzel transition; however, there were few cases when the droplets only spread on hair tress but did not reach the critical contact angle (60°), and thus remained on the hair tress for a prolonged period of time. It could be caused by somewhat random arrangement of hair fibres on the surface of the tress (in spite of the forced alignment on the frame), and changed conditions favouring the Cassie–Wenzel wetting transition, which strongly depends on the roughness of the substrates and structure of the porous medium [16,17]. It confirms that in all experiments with hair tresses the hair arrangement plays a very important role.

The nature of the polymer determines wetting, spreading and imbibition behaviour on hair tresses. However, additives which modify the solution rheology and surface tension, including salts, solvents or surfactants, can influence the behaviour and wetting transition considerably. If certain viscosity or surface tension properties are targeted for a hair treatment, the polymer has to be carefully selected to ensure fast or slow penetration into the hair, depending on the purpose of an application.

References

[1] W. Rungjiratananon, Y. Kanamori, T. Nishita, Comput. Graphics Forum 31 (2012) 1993–2002.
[2] R.A. Lodge, B. Bhushan, J. Appl, Policy. Sci. 102 (2006) 5255–5265.
[3] C. Zviak (Ed.), The Science of Hair Care; Informa Health Care, 1986.
[4] R. Molina, F. Comelles, M.R. Julia, P. Erra, J. Colloid Interface Sci. 237 (2001) 40–46.
[5] Y.K. Kamath, C.J. Dansizer, H.D. Weigmann, J. Appl. Polym. Sci. 22 (8) (1978) 2295–2306.
[6] B.S. Lane, F. Vohra, S.K. Galazka, K.M. Nally, E.H. Agostino, G.S. Kerr, R.D. Lewis, M.T. Lund, S.D. McConaughy, Smith IIIE. D. 2012.
[7] http://www.dow.com/assets/attachments/business/pcare/aculyn/aculyn_22/tds/aculyn22.pdf.
[8] http://www.dow.com/assets/attachments/business/pcare/aculyn/aculyn_33/tds/aculyn33.pdf.
[9] A. Bureiko, A. Trybala, J. Huang, N. Kovalchuk, V.M. Starov, Colloids Surf. A 434 (2013) 268–275.
[10] A. Bureiko, A. Trybala, J. Huang, N. Kovalchuk, V.M. Starov, Colloids Surf. A. 460 (2014) 265–271.
[11] A. Trybala, A. Okoye, S. Semenov, H. Agogo, R.G. Rubio, F. Ortega, V.M. Starov, J. Colloid Interface Sci. 403 (2013) 49–57.
[12] O. Arjmandi-Tash, N. Kovalchuk, A. Trybala, V.M. Starov, Soft Matter 11 (2015) 3643–3652.
[13] A. Bureiko, O. Arjmandi-Tash, N. Kovalchuk, A. Trybala, V.M. Starov, Eur. Phys. J. Spec. Top. 224 (2015) 459–471.
[14] C. Robbins, Chemical and Physical Behaviour of Human Hair, third ed. Springer-Verlag, New York, 1994.
[15] J. Bico, U. Thiele, D. Quéré, Colloids Surf. A. 206 (1) (2002) 41–46.
[16] E. Bormashenko, et al., Langmuir 28 (7) (2012) 3460–3464.
[17] L Barbieri, E. Wagner, P. Hoffmann, Langmuir 23 (4) (2007) 1723–1734.
[18] J. Wang, D. Chen, Langmuir 24 (18) (2008) 10174–10180.
[19] E. Bormashenko, R. Grynyov, Colloids Surf. B: Biointerfaces 92 (2012) 367–371.