A Rapid Screening Method to Evaluate Waterproof Degree of Halal Mascara by Contact Angle Measurement and Adhesion Tape Test

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Abstract

Background: Waterproof character produced by film former incorporation in mascara products is one of the essential attributes for customer's preference. In accordance with the Muslim population's awareness for halal products, waterproof mascara may clash with the wudu requirement. This study aimed to find rapid screening methods to assess the waterproof degree of halal mascara products and their film former ingredients.

Methods: In-vitro test was conducted by spreading layers of film formers and mascara samples. For the immersion test, the film was immersed in reverse osmosis water. Contact angle of the water droplet on film samples was measured using a digital microscope. For the tape test, the film was pulled by pressure sensitive tape and evaluated using image analysis. The in-vivo test was performed to represent the mascara condition after wudu. Statistical analysis was conducted to determine the correlation between in-vitro and in-vivo tests.

Results: Correlation was found in in-vitro test between waterproof character with contact angle and adhesion parameter of film former. Furthermore, the developed water immersion in-vitro test in mascara can represent the actual waterproof character of finished product in women that should perform wudu, as shown by in-vivo test.

Conclusion: The findings from this study can potentially become a rapid and cost-effective method to choose a waterproof film former and guide formulation of waterproof mascara that fulfills the halal aspect of formula, thus accommodates the thriving halal cosmetic market in many muslim majority countries.

Keywords: Halal mascara, waterproof, film former, adhesivity, contact angle

Introduction

Eyes are one of the most vital organs that plays a role in beauty and facial appearance [1]. Beautiful eyes will make people's appearance more attractive, thereby increasing one's self-confidence [2]. Mascara is a type of eye makeup that is used to enhance the beauty of eyelashes with the lashes coating mechanism, giving thickening, lengthening, and darkening impressions [3]. There are several types of mascara based on the purpose of the formulation, including washable, smudge proof, and waterproof. Washable mascara can be removed by water because of its emulsions formulation (oil in water) as cream, gel, or cake. Waterproof mascara, which is made from oil-based materials, is difficult to remove by water and lasts longer than washable mascara, so many people prefer to use it [4].

Based on data in 2018, waterproof mascara is the top 5 products most sought after in the US because of its water-holding ability [5]. In Indonesia, mascara ranked as the second most widely used cosmetic during the pandemic in the eye point category [6]. Indonesia with 240 million Muslims became the largest Muslim country in the world. Therefore, the issue of halal cosmetics is significant for the global halal market which will expand at a compound annual growth rate of 6.8% until 2024 [7]. One of the crucial aspects of halal cosmetics is the product's permeability properties that allow water to pass through the coating product and contact with the skin (ablution friendly). Mascara is a product that leaves on, sticks to the substrate (lashes) for a long time, and is difficult to remove [8]. In this regard, mascara products are especially waterproof. They are feared will not meet the halal criteria because they can be the reason for the cancelation of the mandatory ablution rules before praying.

The waterproof properties of mascara products depend on the material that acts as the film former. Film formers, for example polymers or resins, will form a film on the substrate (skin or eyelashes) when applied to give a long lasting, waterproof, or smudge-proof effect. There are two types of film formers based on their properties, namely water-soluble and oil-soluble. In this study, the two types of film formers will be tested both in the form of raw materials and in mascara formulations. To date, not much research has been performed to test the waterproofness of eye make-up products and those that have focused on formulation or ingredients. In particular, the waterproofing composition and test method of mascara waterproof ability on fake eyelash substrate by immersion test in water have been previously described [9]. Another study proposed to evaluate waterproof effect with water percentage removal using forearm as substrate is reported by Kim et al. (2016) by referring to Guideline

for Evaluation Sun Product Water Resistance from Colipa [10]. Bui et al. (2019) also studied that contact angle can represent the interaction between water and foundation products which can affect the color transfer and integrity of the product [11]. Contact angle is also mentioned as a method to predict adsorption and absorption of cosmetic products to human skin [12].

Another characteristic of waterproof mascara that should be considered is its excellent adhesion to the eyelash. Some test that is done to measure adhesion is by using Tape Test and Atomic Force Microscopy (AFM) [4]. For the tape test, Bui et al. (2019) used Scotch Tape on BIOSKIN to determine the adhesion property by visual assessment [13]. However, in the previous studies, the parameters that affect waterproof ability of mascara are examined separately and independently without considering multifactor effects, including the interaction of raw materials and formulation complexity. Finally, the correlation between physical parameters such as contact angle and adhesivity is not yet discussed and validated with consumer tests.

Therefore, to address the immense needs of waterproof mascara for the emerging halal market segment, a rapid and simple screening method is developed to evaluate parameters related to waterproof ability. Through this research we assess several in vitro parameters such as contact angle and adhesion to predict the in vivo waterproof ability of mascara by consumer test. We also highlight the effect of film former ingredients as the main waterproofing raw materials in mascara products.

Material and Method

Materials

The research was done by conducting tests of film former and mascara bulk. Oil based film formers were consisted of Trimethylsiloxysilicate (FF1), VP/Eicosene Copolymer (FF2) and Acrylates/Polytrimethylsiloxymethacrylate Copolymer (FF3) . FF1 and FF2 were dissolved as 40% solution in Cyclopentasiloxane while FF3 was used as dispersed form containing 40% polymer. Water based film former consisted of Styrene/Acrylates/Ammonium Methacrylate Copolymer (FF4) and Styrene/Acrylates Copolymer (FF5) was dissolved in water as water based film former which contain 40% polymer. 2% Red Iron Oxide color

premix and 2% D&C Red no 33 were used as colorant for oil based and water based film former, respectively.

Film former materials were then incorporated in simple mascara formulation with oil-based (anhydrous) and water-based (emulsion) systems, as shown in Table 1.

Table 1. Mascara formulation of oil-based and water-based system

No	Raw materials	(wt.%)	
		Oil based	Water based
1	Wax	18.0	15.0
2	Emulsifier	-	5.0
3	Oil	2.0	9.0
4	Solvent / volatile	54.5	-
5	Water	-	40.5
6	Humectant	-	8.0
7	Thickener	10.0	3.0
8	Pigment	5.0	8.0
9	**Oil based film former (FF1, FF2, FF3)**	10.0	-
10	**Water based film former (FF4, FF5)**	-	10.0
11	Preservative	0.5	1.5

Sample Preparation

There are 4 types of tests carried out on film former and mascara samples. In-vitro test for contact angle, adhesive-tape, and water immersion were done on film former samples. Further, to check the waterproof ability, mascara bulk with the incorporated film former were also evaluated with in-vitro water immersion test and validated with in vivo consumer test. In-vitro testing was carried out by layering a film on a silica glass substrate using a film applicator (BYK-Gardner GmBH, Germany) to produce a film with a thickness of 30 μm. After spreading, the film was dried for 30 minutes at room temperature.

Contact Angle Test

Contact angle test was conducted by dropping five drops of water on the surface of the film, after which a picture of the drop was taken. Contact angle was measured using a digital microscope (Keyence VHX-7000, Japan). The distance between water dripping and taking photos should not be > 30 seconds due to the time-dependent nature of contact angle [11]

Tape Test for Adhesivity

The adhesivity test was conducted based on the ASTM D3359 Standard Test Methods for Measuring Adhesion by Tape Test. Pressure sensitive tape of Elcometer 99 Adhesive Test was placed on the surface of film former samples. The tape was rubbed firmly using a film applicator. After 120 seconds, the tape was removed by pulling it rapidly. Percentage of transferred samples onto the tape were quantified using Image Analysis Tools from Keyence VHX-7000, Japan.

Immersion Test for Waterproof

250 mL of reverse osmosis water was prepared in a beaker glass. Film samples were dipped inside the water and immersed for 8 hours. Film condition was observed every 2 hours to inspect its change over time. At the end of the observation period, the film condition was ranked (0-5) based on the remaining film that was attached on a glass plate.

In-vivo Use Test for Mascara

The in-use test was performed to represent the condition of wudu, an ablution ritual mandatory for all Muslims before performing daily prayer. Before the wudu was performed, mascara samples were applied on the eyelashes of 5 female volunteers. The mascara was applied 10 times using a product applicator and set for 10 minutes. The panelist then washed their face using tap water 3 times. The condition of mascara, before and after the washing procedure was photographed and ranked (0-5) based on change of mascara performance in eyelash and amount of smudge under eye.

Correlation Analysis

Statistical analysis was conducted to determine the correlation between in vitro waterproof character (immersion test) of film former and mascara with both contact angle and adhesivity

of film former samples. Further, correlation between in vitro immersion test with in vivo consumer test were also evaluated. Spearman's rank correlation coefficient method was used to measure the degree of association between two variables.

Results

Contact Angle Test

Results of contact angle achieved by dropping water in oil based and water based film former were shown in Figure 1 with its visualization in Figure 2. Contact angle can describe the wettability of solid surfaces with a liquid phase, in this case : film former layer with water. Oil based tends to have a higher contact angle than water based. FF1 with Trimethylsiloxysilicate has the highest contact angle value (81.30±4.382°) due to its highly hydrophobic nature compared to other materials.

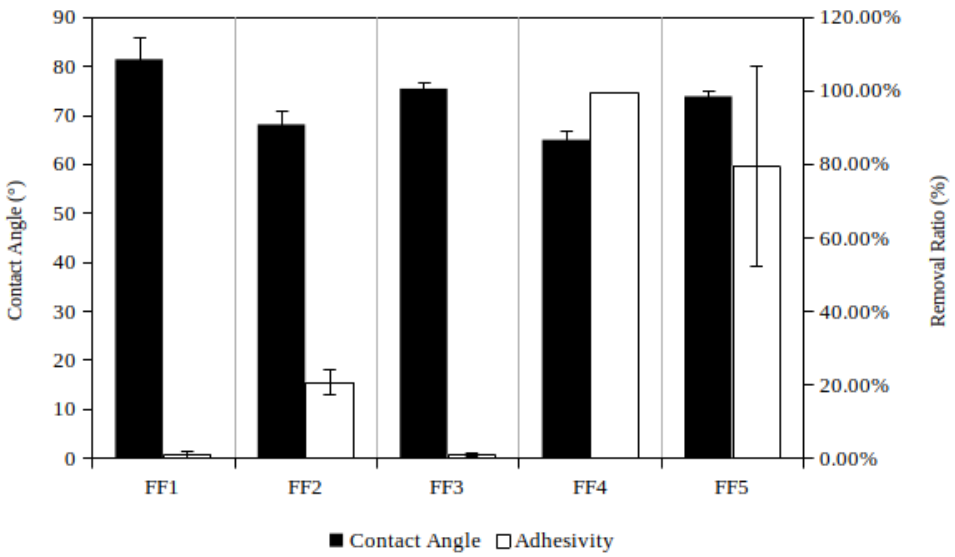

Figure 1. Contact angle and adhesivity test result in film former samples

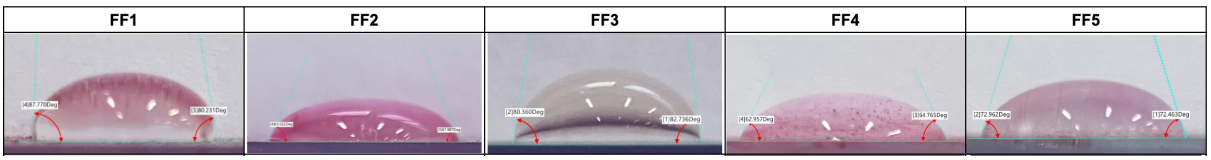

Figure 2. The visualization of the difference in contact angle formed on each film former samples

Adhesion Test

Adhesion test was conducted to evaluate the quality and value of adhesive strength between sample and substrate. Adhesion test used Keyence image analysis by measuring the percentage of film transferred to the tape from the silica glass plate. Figure 1 reported that oil-based film former FF1 and FF3 has high adhesivity with small percentage of film removal, while the contrast was shown in both water based film former (FF4 and FF5) with its low adhesivity character.

Water Immersion Test

Water immersion test showed how a layer of sample holds up well when submerged in water on day application. Table 2 showed water immersion results of film former and mascara samples. The scoring standard (value 1-5) presented in Figure 3. The result showed that the amount of removed film from substrate was higher on water based formulation. FF1 and FF2 contain hydrophobic materials that lack affinity for water, so they have low water immersion scores, both as film former and in mascara samples. As predicted, water-based FF4 and FF5 samples have higher film removal both as film former and in mascara.

Table 2. Water immersion score on silica glass plate of each material

Sample	Film Former	Mascara
FF1	0	0
FF2	0	0
FF3	3	0
FF4	4	3
FF5	3	3

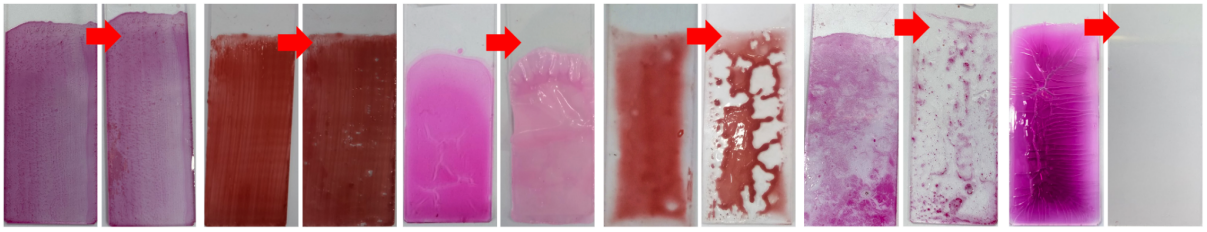

Figure 3. Visualization of scoring standard for immersion test in silica glass

In vivo test

In vivo test of mascara condition in 5 panelists (figure 4) shown that FF1 and FF3 with 0 score has no change of performance and smudge meanwhile FF2 exhibit grouping in lash and small flakes under eye. The most seen change in mascara performance and smudge amount was observed increasing in FF4 and FF5, respectively.

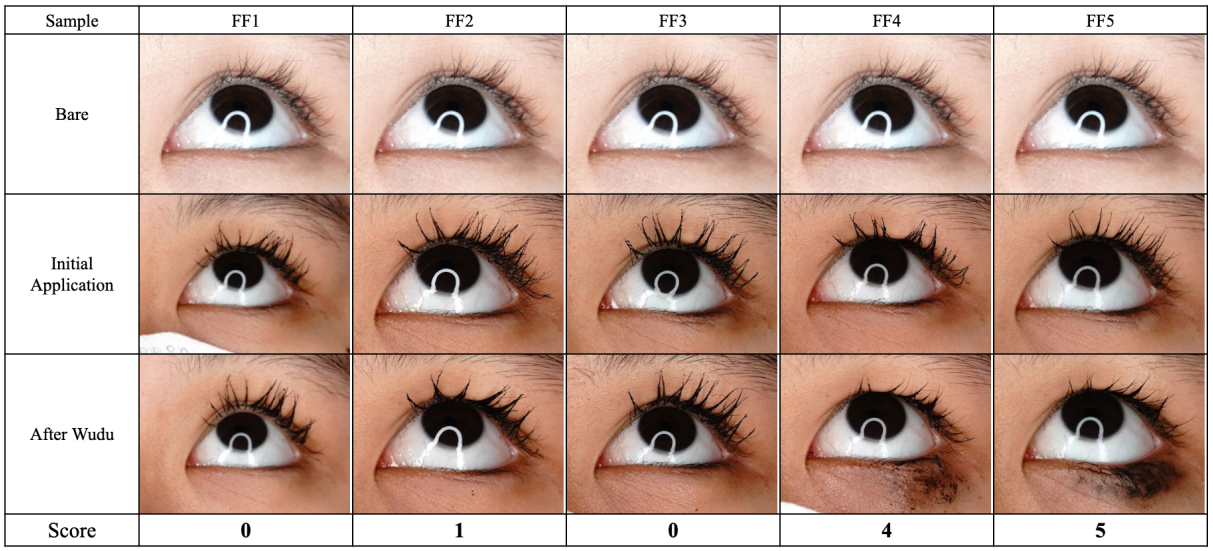

Figure 4. In vivo consumer test images of waterproof wudu test of all mascara samples.

Discussion

At present, no substrate is known to achieve the exact representation of the in vivo situation. According to the data, silica glass substrate may be used as replacement of the skin because of the similar critical surface tension of skin (27 dyne/cm) and glass (31 dyne/cm). This

became the background of silica glass usage as substrate in contact angle, adhesión, and water immersion test [12].

The contact angle describes the hydrophobicity of a material to water. From the contact angle test, samples FF1 containing Trimethylsiloxysilicate show the highest contact angle. Trimethylsiloxysilicate resins (also known as MQ resins) have been used in long-wear and non-transfer cosmetic applications to provide exceptional wear and adhesion due to their low surface free energy (SFE) [14]. Contact angle value is also correlated with surface tension between water and film, higher contact angle means greater surface tension since the material repels water [15]. This theory explained the experiment result that oil-based film formers have a larger contact angle than water based film formers. From table 3, results of the Spearman correlation test between contact angle and immersion test in film former samples showed coefficient value (r) = 0.527 and p-value = 0.361.

Table 3. Spearman correlation test between in vitro and in vivo parameters.

Parameter	Correlation coefficient (r)	P-value
In vitro film former contact angle vs immersion test	0.527	0.361
In vitro film former adhesivity vs immersion test	0.738	0.155
In vitro film former immersion test vs mascara immersion test	0.761	0.135
In vitro mascara immersion test vs in vivo waterproof test	0.889	0.044

Another parameter that is evaluated regarding waterproof ability is adhesivity. The adhesion strength of a material is based on adhesive theory, or adsorption, where a material will stick to the substrate due to intermolecular forces and interatomic forces between the two components of the material and the substrate. The intermolecular and interatomic forces that can occur are van der Waals bonds and hydrogen bonds. The van der waals bond consists of a two-pole (polar) force where the positive pole interacts with the negative pole. The adhesion mechanism by hydrogen bonds happens between hydrogen atoms with a positive charge with

electronegative atoms of other molecules between the material and the substrate. The stronger force will increase the adhesive ability of the material.

Samples of water based film former (FF4 and FF5) shows high removal of film and gives low adhesivity. This result may come from the nature of Styrene/Acrylates/Ammonium Methacrylate Copolymer and Styrene/Acrylates Copolymer that were known to have “peel off” character that refers to the ability to form thin continuous film that is easy to be removed [16]. Correlated with the water immersion test, adhesion strength will be affected by water exposure that can damage and cause separation of adhesive layer concrete interface bond [17]. Higher adhesivity represents a stronger bond between film and substrate, thus it would be harder to separate even with the presence of water [18]. Results of the Spearman correlation test between adhesivity and immersion test in film former samples showed coefficient value (r) = 0.738 and p-value = 0.115.

The Spearman correlation test between both contact angle and adhesivity with immersion test in film former samples showed higher strength of coefficient value in adhesivity. It means that waterproof ability is both the result of how film layers were affected by external impact of water (represented by contact angle) and how the film layers were attached to the substrate (represented by adhesion). The illustration can be seen in Figure 5. There may be cases of hydrophobic materials such as wax that have a high contact angle but can be easily removed by water due to its poor adhesivity [19]. Both contact angle and adhesion are independent yet give constructive impact to increase waterproofness.

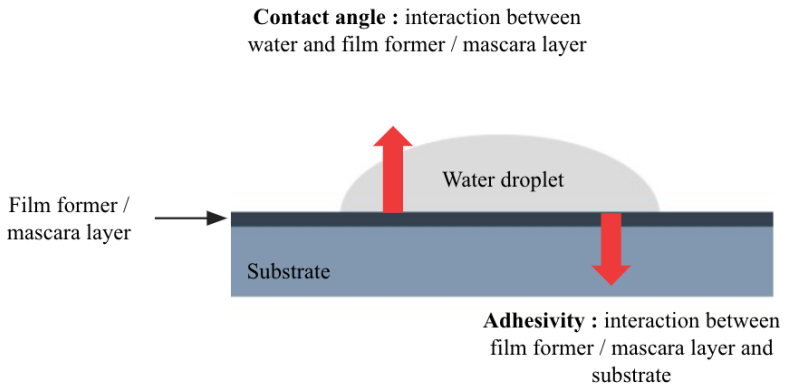

Figure 5. Illustration of constructive impact of contact angle and adhesivity to waterproof ability

After knowing the relationship between contact angle and adhesivity of film former to the waterproof ability, water immersion test then also done in mascara bulk. Spearman correlation test with coefficient value (r) = 0.761 and p-value = 0.135 show a quite large relationship between in vitro immersion test of film former and mascara. The immersion test of film former samples shows samples FF3 that consist of Acrylates/Polytrimethylsiloxymethacrylate Copolymer has a lower score as film former than any oil-based film former. This can be caused by the existence of naturally water-soluble acrylates group as the monomer of the copolymer. After incorporated to mascara formulation, other raw material addition such as wax can enhance the structure to obtain a film of good retention to the substrate, hence the good value of FF3 in mascara immersion test [20].

Further, correlation test was also done to check the relationship between in vitro immersion test in mascara with in vivo consumer test. Result showed that there is a significant correlation between in vitro immersion test of mascara with in vivo waterproof test on consumer with coefficient value (r) = 0.889 and p-value = 0.044. This indicated that in vitro immersion test in mascara is a representative method to check the quality of waterproof ability from selected high quality film former that has been incorporated in mascara bulk. Through this findings, mascara product development can be shortened and made less costly by skipping the consumer test stage for each film former screening to achieve a high quality waterproof mascara.

Conclusion

A simple and cost-effective in vitro method has been found for evaluating waterproof mascara based on contact angle and adhesiveness. There is an in vitro test correlation. Mascara with low contact angle and adhesion test tends to have a lower immersion test score. The result correlates with the in-vitro test in which less waterproof mascara shown worse wudhu test results with many peeled off film and smudge after face washing step. To create a halal market in the future, further research is needed on formulations and evaluations based on waterproof mascara permeability.

Acknowledgments

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Conflict of Interest Statement

NONE.

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