*IFSCC 2025 full paper (IFSCC2025−202)*

# *“Physicochemical Properties of Acrylate Copolymer Emulsions as Functional Film Formers in Cosmetics”*

**Natsumi Yamaguchi [1], Chiaki Umakoshi [1], Atsuko Ota [1], Takehiro Goto [1], Takumi Tanaka [1], Masayuki Yamaguchi [2]**

[1] Daito Kasei Kogyo CO., LTD., 1-6-28 Akagawa, Asahiku, Osaka, 535-0005, Japan; [2] Research Center for Carbon Neutral, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

## 1. Introduction

Acrylate copolymer emulsions are commonly utilized in make-up cosmetic formulations, such as mascara, eye liner and so on, as a film former. For these applications, flexibility and feeling on skin, water resistance, and removability are very important [1,2,3]. Rheological properties directly affect the feel, applicability, and stability of cosmetics [4,5,6]. Therefore, correct understanding and adjusting rheological properties are important factors that have significant impacts on product quality. This study examines the impact of rheological properties on the performance as cosmetics using acrylate copolymer emulsions.

## 2. Materials and Methods

2.1. Materials

In this study, five types of acrylate copolymer emulsions were employed (**Table 1**). Although they have the same INCI name, monomer compositions are different.

**Table 1.** Acrylate copolymer emulsions

| Name of emulsion | Polymer (INCI name) | Polymer content (%) |
|---|---|---|
| Emulsion A | Acrylates Copolymer | 50 ~ 55 |
| Emulsion B | Acrylates/Ethylhexyl Acrylate Copolymer | 55 |
| Emulsion C | Acrylates Copolymer | 50 |
| Emulsion D | Acrylates/Ethylhexyl Acrylate Copolymer | 50 |
| Emulsion E | Acrylates/Ethylhexyl Acrylate Copolymer | 50 |

Usually, acrylate copolymer emulsions in cosmetics make film on skin by evaporating water. Therefore, we evaporated the water from the above five Emulsions to make their films: Film A, B, C, D, and E. Approximately 1 mm thick films were employed as samples to evaluate physicochemical properties.

These Emulsions do not satisfy all the functions required for cosmetics at once. For example, cosmetics containing Emulsion B have adhesion property but show excessive tackiness. The other way of giving required functions from consumers to cosmetics is blending these Emulsions, i.e., polymer blend. In this study, we tried to reduce the tackiness of Emulsion B without losing its adhesion properties. For this purpose, we mixed Emulsion B and other Emulsions with a polymer ratio of 1.7:2.1 (described as Emulsion B/A, B/C, B/D, or B/E). To evaluate the physicochemical properties of these blended Emulsions, we made their films (Film B/A, B/C, B/D, or B/E).

2.2. Measurements

The physicochemical properties of the Films were evaluated by a dynamic mechanical analyzer (Rheogel-E4000; UBM, Muko, Japan). The measurements were conducted at a frequency of 10 Hz and a heating rate of 2 ºC/min. A uniaxial tensile test was performed using a tensile machine (Autograph AGS-X; Shimazu, Kyoto, Japan) at room temperature. A film sample was clamped by grips with an initial gauge length of 10 mm. The extension speed was 50 mm/min. Young's modulus was calculated as a slope of the initial linear portion of the stress-strain curves. At least 5 measurements were carried out for each sample and the average value was calculated with the standard deviation. Statistical analysis was performed by the Welch's t-test with the Holm correction. Statistical significance was set at $p$-value < 0.05.

2.3. Preparation for Liquid Foundation

We prepared W/O liquid foundations which contained 10% acrylate copolymer emulsion (**Table 2**). After heating Phase 1 to 80ºC, Phase 2 was added. They were mixed by a disper mixer at 3,000 rpm for 3 minutes and cooled to 50ºC. Phase 3 was also heated to 80ºC and cooled to 50ºC. The loss of water and dimethicone that evaporated during heating was adjusted. Phase 3 was added to the mixture of Phases 1 and 2. Then, they were mixed at 3,000 rpm for 3 minutes. Finally, Phase 4 was added to the mixture of Phases 1, 2, and 3, and they were mixed at 3,000 rpm for 1 min.

**Table 2.** Composition of W/O liquid foundation

| <Phase> | <Ingredient (INCI name)> | <%> |
|---|---|---|
| 1 | Dimethicone | 13.50 |
| | Dimethicone,PEG/PPG-18/18 Dimethicone | 4.00 |
| | Synthetic wax | 0.10 |
| | Arachidyl behenate | 0.30 |
| | Trihydroxystearin | 0.40 |
| | Laureth-7 | 0.50 |
| | Diphenylsiloxy phenyl trimethicone | 5.00 |
| | Isotridecyl isononanoate | 5.00 |
| 2 | Treated Titanium dioxide | 8.50 |
| | Treated Yellow iron oxides | 1.00 |
| | Treated Red iron oxides | 0.30 |
| | Treated Black iron oxides | 0.20 |
| 3 | De-ionized water | 40.50 |
| | Butylene glycol | 8.00 |
| | Sodium chloride | 2.00 |
| | Sodium dehydroacetate | 0.30 |
| | Tetrasodium EDTA | 0.10 |
| | Preservative | 0.30 |
| 4 | Acrylate copolymer emulsion | 10.00 |

| | |
|---|---|
| TOTAL | 100.00 |

2.4. Evaluation of the Liquid Foundations

The liquid foundation was applied to the arm. After 1 min, tissue paper was pressed to the arm to evaluate non-transfer effect. For the evaluation of creasing in application to skin, liquid foundation was applied to artificial skin (1.3 mg/cm²). After drying in an ambient environment for 15 min, the artificial skin was folded 10 times, and the extent of creasing was evaluated. Six blind experimenters performed sensory evaluation of liquid foundations. They scored one to five from the following six feelings: moist, dry, smooth, creak, slippery, and sticky. For evaluating water and oil resistance, liquid foundation was applied to artificial skin (1.3 mg/cm²). After drying in an ambient environment for 1 hour, colored water (blue) and oleic acid (red) were dropped onto the surface. Repellency of these droplets was observed.

## 3. Results

3.1. Physicochemical Properties of Films

The temperature dependence of loss tangent (tan δ) is shown in **Figure 1**. The peak temperature of tan δ is determined as the glass transition temperature $T_g$ of a Film, which is summarized in **Table 3**.

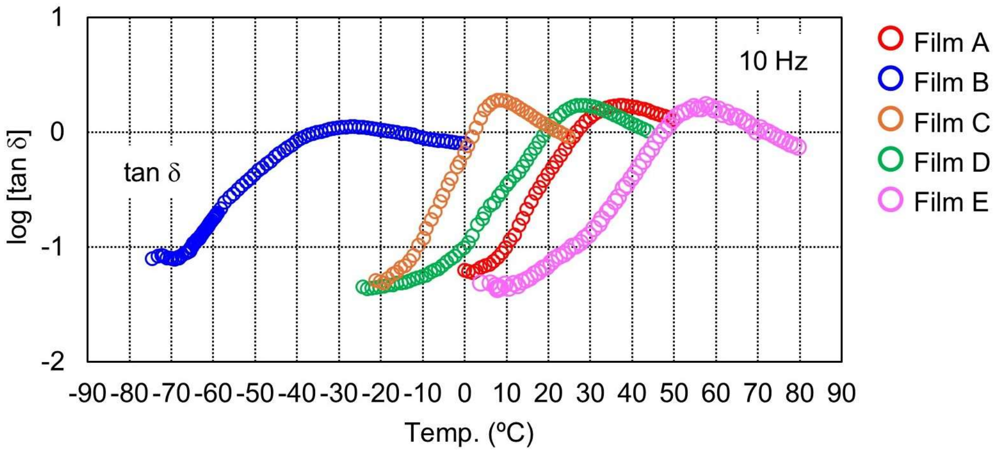


**Figure 1.** Temperature dependence of tan δ at 10 Hz.

**Table 3.** $T_g$ of the Films

| Sample | $T_g$ (ºC) |
|---|---|
| Film A | 36 |
| Film B | −26 |
| Film C | 9 |
| Film D | 28 |
| Film E | 58 |

Film B, which shows excessive tackiness and adhesion properties, exhibited a broad $T_g$ peak in the temperature range from −35 to −25 ºC (**Figure 1**). High tan δ values beyond $T_g$ indicated marked segment mobility, resulting in the sticky properties.

The uniaxial tensile stress-strain curves are shown in **Figure 2**, and **Table 4** summarizes the Young's modulus evaluated from the initial slope. As seen in the table, the Young's modulus is determined by $T_g$; i.e., The sample with higher $T_g$ showed higher Young's modulus. Although Film E having high $T_g$ and high Young's modulus showed a clear yield point, stress increased monotonically without showing a yield point for the other Films except Film C. Film C showed a constant stress in a wide strain region.

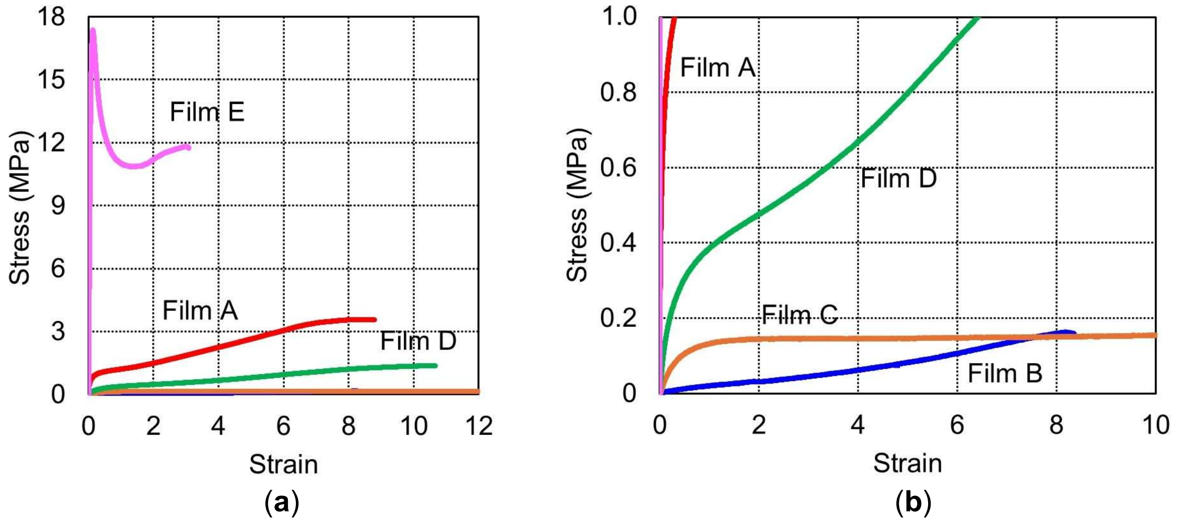


**Figure 2.** Stress-strain curves of Films at room temperature. X- and y-axis of (a) was adjusted for (b) to make it easier to see the slopes.

**Table 4.** Young’s modulus of the Films

| Sample | Young’s modulus (MPa) |
|---|---|
| Film A | 61 ± 3.7 |
| Film B | 0.027 ± 0.0049 |
| Film C | 0.38 ± 0.022 |
| Film D | 6.7 ± 0.64 |
| Film E | 227 ± 34 |

3.2. Physicochemical Properties of Blend Films

Films made from a mixture of Emulsion B and another Emulsion had two peaks ascribed to $T_g$. They were located at almost the same temperatures of individual pure Films (**Figure 1 and 3**). This suggests that they are not miscible.

As shown in **Figure 4**, flexibility of the blend Film was significantly improved by addition of Emulsion B. These results indicate that we can modify the flexibility of the film without changing the $T_g$ of the main component.

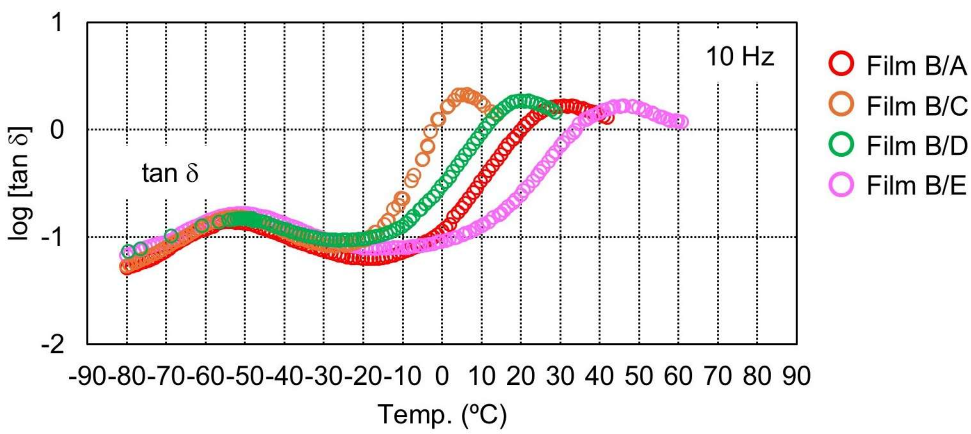


**Figure 3.** Temperature dependence of tan δ at 10 Hz of blend Films.

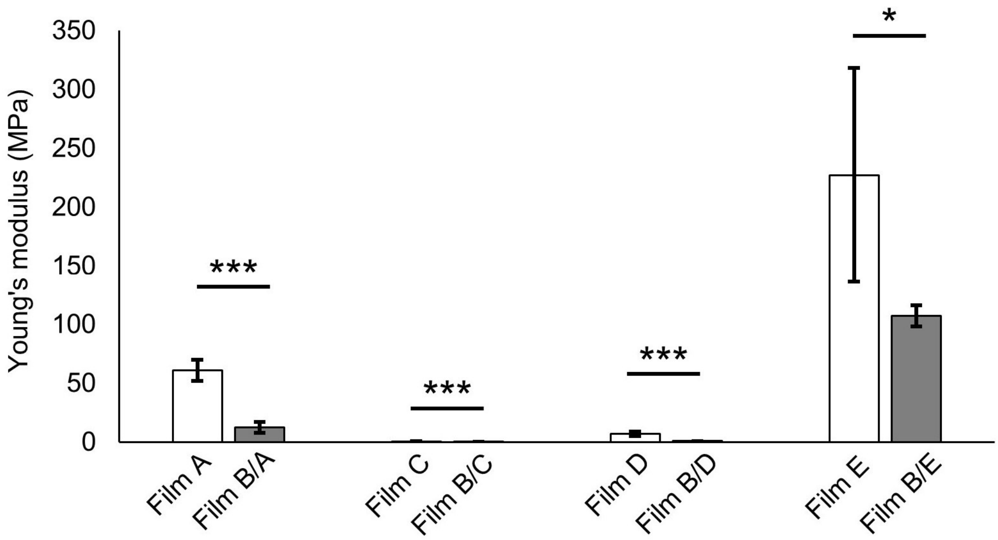


**Figure 4.** Comparison of Young's modulus evaluated by uniaxial tensile test for Films. Data are mean±SD. ***$p < 0.001$. *$p < 0.05$.

3.3. Evaluations of the Liquid Foundation

We evaluated the following functions which are needed for liquid foundation: non-transfer effect, non-creasing effect, feeling on skin, and water and oil resistance. Blending Emulsion B with Emulsion C or E improved non-transfer effect (**Figure 5**). Non-transfer effect of Emulsion D was not changed by the combination with Emulsion B, but peeling of foundation during applying was suppressed (**Figure 5**). Emulsion B/A worsened the non-transfer effect (**Figure 5**). However, non-creasing effect was improved in Emulsion B/A (**Figure 6**).

The foundation containing Emulsion A or B showed creasing clearly (**Figure 6**). As for Emulsion C, the creasing was less noticeable (**Figure 6**). Blending with Emulsion B improved non-creasing effect in Emulsion A but worsened it in Emulsion C and Emulsion E (**Figure 6**).

**Figure 5.** Non-transfer effect test. Liquid foundation was applied to the arm. After 1 min, tissue paper was pressed to the arm.

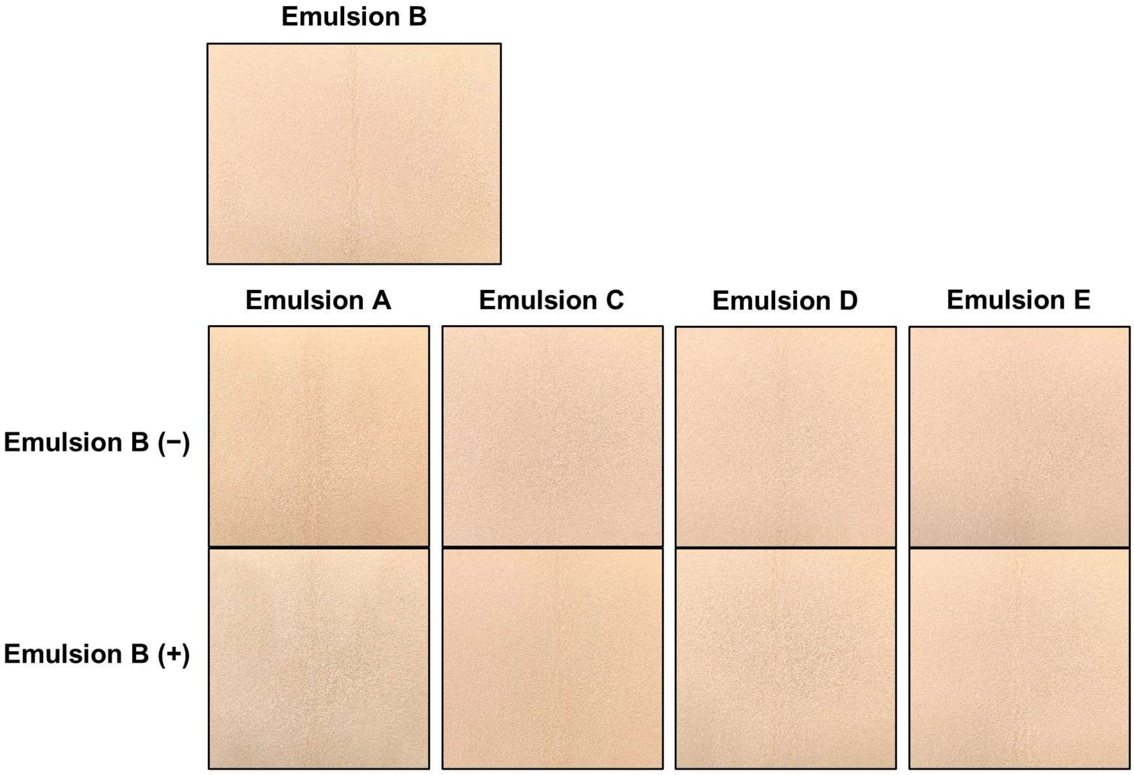


**Figure 6.** Evaluation of the creasing in application to skin. Liquid foundation was applied to artificial skin (1.3 mg/cm²) and dried for 15 minutes. After drying, the artificial skin was folded 10 times.

Emulsion B made liquid foundation extremely sticky (**Figure 7**). In sensory evaluation, blending with Emulsion B decreased dry feeling of foundation in all combinations. Emulsion B/C improved smooth feeling compared with Emulsion C. All the good properties (moist, slippery, and smooth) was improved in the foundation containing Emulsion B/D compared with Emulsion D (**Figure 7**).

The liquid foundation containing Emulsion B showed the best water and oil resistance (**Figure 8**). As for liquid foundation containing Emulsion B/A, water resistance was improved compared with Emulsion A alone (**Figure 8**). Oil resistance was improved in foundation containing Emulsion B/D compared with Emulsion D alone (**Figure 8**). Water or oil resistance were not changed in foundation containing Emulsion B/C compared with Emulsion C alone (**Figure 8**). Water and oil resistance were improved in the liquid foundation containing Emulsion B/E compared with Emulsion E alone (**Figure 8**).

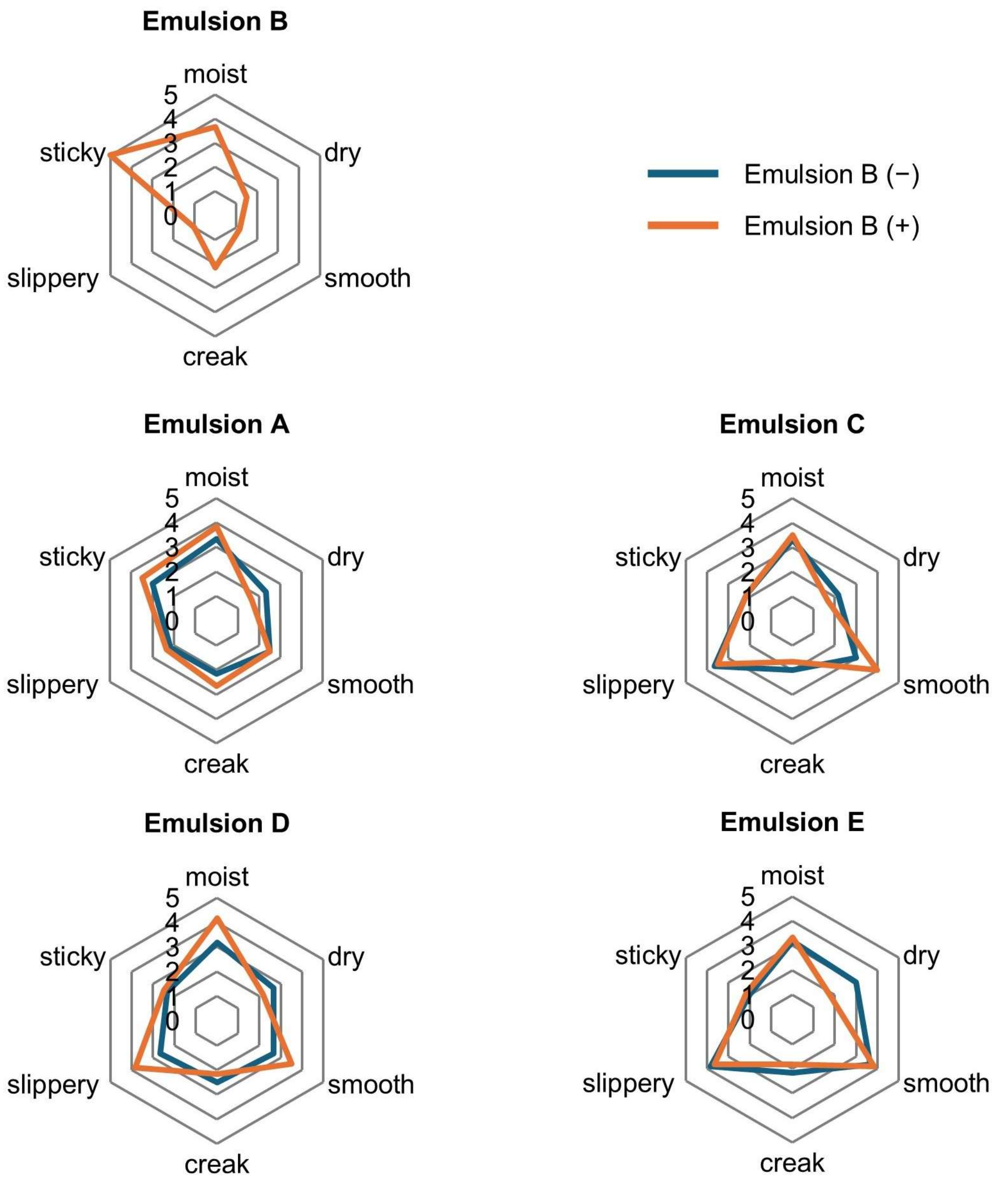


**Figure 7.** Results of sensory evaluation of liquid foundations. The experimenters scored one to five to the following six feelings: moist, dry, smooth, creak, slippery, and sticky.

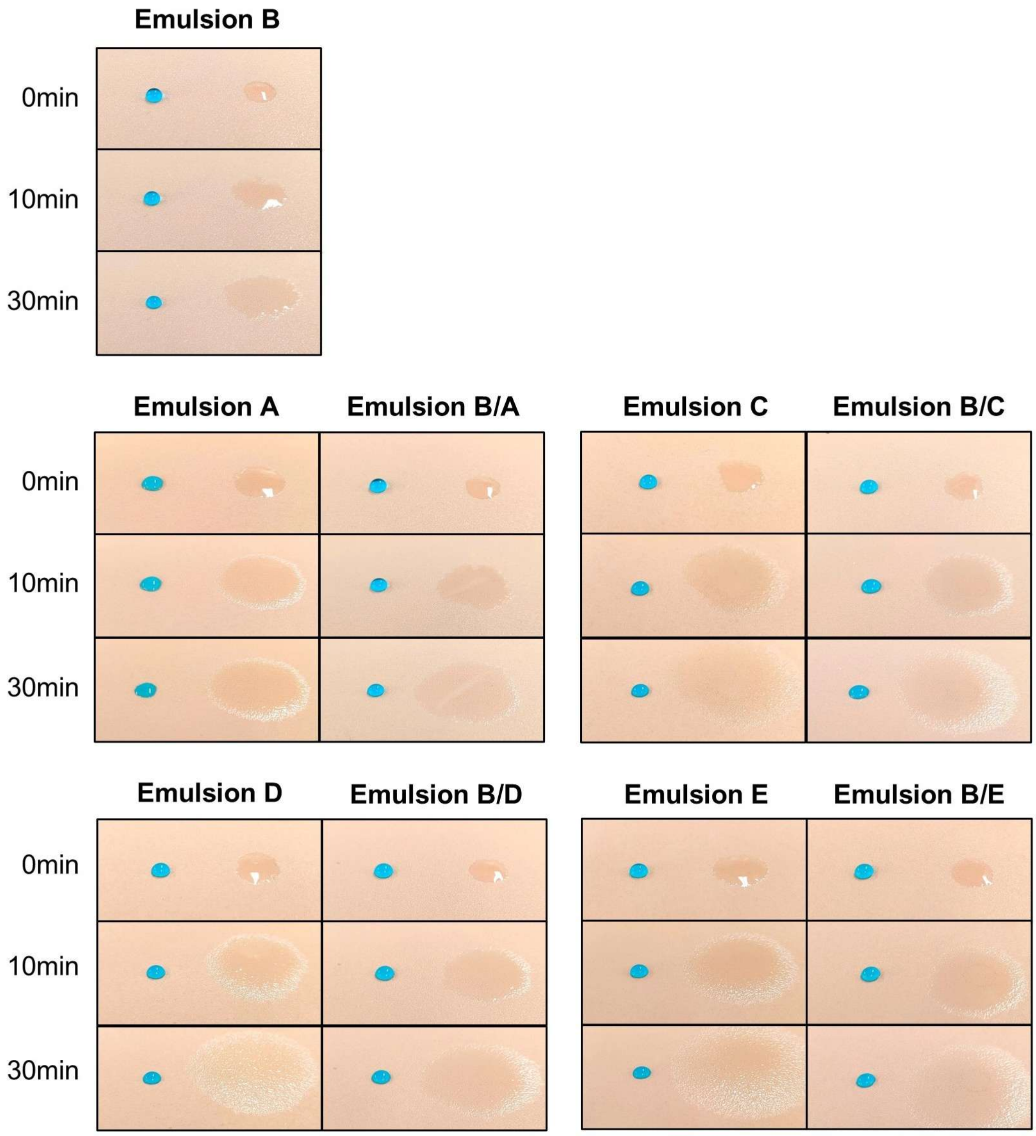


**Figure 8.** Water and oil resistance test. Liquid foundation containing an Emulsion was applied to artificial skin (1.3 mg/cm²). After 1 hour drying, colored water (blue) and oleic acid (red) were dropped onto the surface. Repellency of these droplets was observed.

## 4. Discussion

Acrylate copolymer emulsions play important roles in make-up cosmetic formulations as a film former. For cosmetic formulations, flexibility and feeling on skin, water resistance, and removability are very important [1,2,3]. Rheological properties are closely related to the feel, applicability, and stability of cosmetics [4,5,6]. In this study, we confirmed the correlation between the functions of liquid foundation and the physicochemical properties of acrylate copolymer emulsion contained in the foundation. We assessed the properties of acrylate copolymer emulsions by making their films. According to the results of dynamic mechanical analysis and uniaxial tensile test, the Film with higher $T_g$ showed higher Young's modulus (**Table 3 and 4**). These properties are also related to the hardness of the Films. The higher Young's modulus, the harder Films.

We found that the $T_g$ and Young's modulus of Films could be indicators of foundation flexibility and texture. Film B exhibited low $T_g$, broad $T_g$ peak, and low Young's modulus (**Table 3 and 4**), and the liquid foundation which contained Emulsion B alone showed creasing in application to skin because of its strong stickiness (**Figure 6 and 7**). On the other hand, Film A and E exhibited high Young's modulus (**Table 4**), and the liquid foundation containing Emulsion A or E showed creasing because of its inflexibility (**Figure 6**).

We blended Emulsion B with another Emulsion for giving moderate adhesion and flexibility to foundation. The effects of blending Emulsions on the functions of liquid foundation are summarized in **Table 5**. The symbols in the table have following meanings compared with foundation containing Emulsion A, C, D, or E alone: ⤴ (Improved), ⤵ (Worsened), → (Unchanged).

**Table 5.** Effects of blending Emulsions on the functions of liquid foundation

| Functions | Emulsion B/A | Emulsion B/C | Emulsion B/D | Emulsion B/E |
|---|---|---|---|---|
| Non-transfer | ⤵ | ⤴ | → | ⤴ |
| Non-creasing | ⤴ | ⤵ | → | ⤵⤵ |
| Water resistance | ⤴ | → | → | ⤴ |
| Oil resistance | → | → | ⤴ | ⤴ |

Blending Emulsion B with Emulsion D reduced peeling of foundation during applying, which indicates that Emulsion B improves the adherence to skin of liquid foundation. Furthermore, non-transfer effect was improved in the foundations containing Emulsion B/C and Emulsion B/E (**Figure 5**). As for Emulsion A, which gave an extremely strong non-transfer effect to foundation, it was suggested that Emulsion B gave stickiness and depressed the non-transfer effect (**Figure 5**). In the evaluation of creasing in application to skin, we assessed flexibility of the liquid foundation. For all combinations, the flexibility of the blend Films were significantly improved (**Figure 4**). However, not all combinations improved the non-creasing effect. Non-creasing effect was improved in Emulsion B/A (**Figure 6**). This result suggests that the improved flexibility of Film B/A is reflected in the foundation. There are different reasons for the decrease in non-creasing effect of Emulsion B/C and Emulsion B/E. As the reason for the little worse in non-creasing effect of Emulsion B/C, Emulsion C already had appropriate flexibility and non-creasing effect, and there was no need to add Emulsion B. Film B/E was opaque, which indicated their incompatibility. Therefore, the effect of Emulsion B with strong tackiness was remarkable as creasing. We found that Emulsion B gave good water and oil resistance to foundation (**Figure 8**). By blending with Emulsion B, water or oil resistance was improved or not changed (**Figure 8**). Blending Emulsions did not have a negative effect on water and oil resistance.

Under the conditions of this study, Emulsion B/A and Emulsion B/D were good combinations for the liquid foundation in terms of getting moderate flexibility and texture. As for Emulsion B/A, non-creasing effect was improved. Although Emulsion B/D did not improve non-creasing effect, good feeling properties (moist, slippery and smooth) were improved. We expect that changing combinations and ratio of them develops exploring ideal functionality of cosmetics.

## 5. Conclusion

The physicochemical properties of acrylate copolymer emulsions are related to the functions of liquid foundation. We can quantitatively assess the flexibility of films made by acrylate copolymer emulsions. Blending different emulsions modifies flexibility and gives new functional properties for liquid foundation, which can be utilized to optimize cosmetic product performance. Therefore, blending polymer emulsions offer a valuable strategy for achieving specific functionalities in cosmetics while adhering to regulatory standards.

## 6. Reference

1. R.Y. Lochhead, Cosmetic Nanotechnology. ACS Symposium Series 961: 3-56. (2007).
2. R. Hagino, R. Watanabe, Y. Masubuchi, M. Okuyama, M. Yamashita, J. Soc. Cosmet. Chem. Jpn., 54 (4): 323-332 (2020).
3. K. Miyazawa, N. Oguchi, Y. Yoda, J. Soc. Cosmet. Chem. Jpn., 58 (3): 282-291 (2024).
4. S. Tochioka, Y. Saito, T. Igarashi, T. Yamazawa, Y. Shibano, K. Hanyama, J. Soc. Cosmet. Chem. Jpn., 57 (3): 242-250 (2023).
5. E. Tamura, K. Ohsaki, K. Kuwahara, H. Nanbu, Y. Nabata, Nihon Reoroji Gakkaishi, 44 (5): 231-236 (2017).
6. H. Komatsu, S. Fukushima, Nihon Reoroji Gakkaishi, 5 (3): 101-109 (1977).