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The Challenge of Achieving Both Water-Holding Capability and Water Resistance: Innovations in Plant-Derived Multi-functional Amphiphilic Polymer Esters

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Abstract

In this study, a series of substances composed of plant-derived Polyglyceryl-2 Dipolyhydroxystearate with varying polymer compositions were synthesized, and their properties evaluated. The results of the comparative experiments on each substance clearly demonstrated that ester A1 simultaneously exhibits water-holding and water-resistant properties, which are contrasting characteristics. Furthermore, ester A1 demonstrated functionality in both water-in-oil and oil-in-water emulsion systems, forming a spreadable and robust oil film capable of imparting water resistance. This new amphiphilic polymer ester has the potential to be utilized in various formulations, including skincare and makeup products, and could potentially become a new standard in cosmetic ingredients.

1. Introduction

Polymer materials are less likely to be absorbed into the body compared to low molecular weight compounds due to their long chain structures. Therefore, they are often exempt from registration under chemical substance regulations in various countries, such as registration, evaluation, authorization, and restriction of chemicals and toxic substances control act, making them safe and compliant for use in cosmetics in terms of safety and regulatory requirements.

Previous studies have shown that combinations of polyhydroxy fatty acids and polyols are effective in enhancing emulsification, formulation stability, and water-holding capability in the development of polymer esters [1]. Thus far, esters derived from polyhydroxy fatty acids and polyols have primarily been developed as surfactants, in which the polyhydroxy fatty acid chain serves as the lipophilic group, while the polyol functions as the hydrophilic group. However, there are limited reports of their application as base materials. Notably, these esters can form complex polymeric structures, with adjustable degrees of polymerization and esterification rates. We hypothesized that this aspect could be leveraged to create base-oil materials with new functions depending on the structural design. To explore this possibility, a group of compounds with varying polymer compositions [average molecular weight (Mw), polydispersity index (Pdi)] was synthesized by controlling the esterification time and temperature of plant-derived polyglyceryl-2 dipolyhydroxystearate. A comparative evaluation was conducted to assess the viscosity, surfactant ability, water-holding capability of the esters, and their

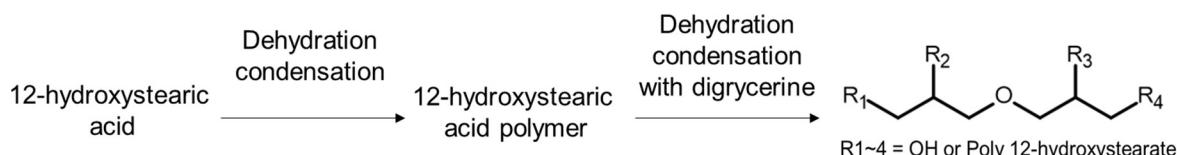
water resistance within sunscreen formulations of these compound groups. The relationship between the polymer composition of the ester and the creation of plant-based polymer esters with unique functions was subsequently examined.

2. Materials and Methods

2.1 Methods for the synthesis and evaluation of esters

2.1.1 Synthesis of esters

In this experiment, 12-hydroxystearic acid and diglycerin were synthesized in the presence of a metal catalyst under high-temperature conditions. This procedure resulted in the formation of Polyglyceryl-2 Dipolyhydroxystearate. The synthesis process was subject to a range of variables, including the heating temperature, reaction time, and the mixing ratio of 12-hydroxystearic acid and diglycerin. Consequently, 10 compounds (Ester A1-A6, B1-B2, and C1-C2) were successfully synthesized (Scheme 1).



Scheme 1. Synthesis of Polyglyceryl-2 Dipolyhydroxystearate.

2.1.2 Measurement of polymer composition (Mw and Pdi)

The polymer composition (Mw and Pdi) of a group of 10 compounds (Ester A1-A6, B1-B2, and C1-C2) was measured using high-performance liquid chromatography with the ACQUITY Advanced Polymer Chromatography System (Waters Corporation). Calibration curves were first established using 11 polystyrene standard materials with different polymerization degrees, based on molecular weight and retention time (coefficient of determination >0.999). The compounds in the group were analyzed under these conditions, and their respective Mw and Pdi values were calculated from the calibration curves.

2.1.3 Viscosity measurement

The viscosities of a group of 10 compounds (Ester A1-A6, B1-B2, and C1-C2) were measured using a cone-plate rotational rheometer (HAAKE MARS40, Thermo Scientific). The measurements were conducted at temperatures of 30°C and 50°C. The upper cone (diameter 35 mm, angle 2°) and lower plate (diameter 40 mm) were set with the sample in between and rotated at a constant speed, enabling the viscosity of each sample at the respective temperatures to be calculated based on the shear stress and shear rate.

2.1.4 Evaluation of emulsification ability

The emulsification characteristics of esters A1, B1, B2, and C1 were evaluated using a previously reported method [2]. Each ester was blended with a hydrophilic surfactant (hydrophilic-lipophilic balance (HLB): 15.0) at varying weight ratios to prepare a mixed surfactant with the desired HLB value (a). Water-in-oil (W/O) emulsions with liquid paraffin as the oil phase were prepared using the aforementioned mixed surfactant (Table 1). The particle sizes of the oil-in-water (O/W) emulsions were measured using a particle size distribution analyzer (Partica LA-960V2, HORIBA), and the emulsification state was evaluated. Based on the additivity of HLB from the properties of the O/W emulsions, the emulsification performance of esters A1, B1, B2, and C1 was evaluated.

Table 1. Formulation for O/W Emulsion for Surfactant Evaluation.

| Ingredients | | wt% |
|-------------|--------------------------------|---|
| Oil Phase | Base oil | Liquid Paraffin (Required:11.9) |
| | Surfactant for measurement (a) | The emulsifier (HLB:15) & Esters (HLB:unkown) |
| | Emulsifying stabilizer | Cetyl Alcohol |
| Water phase | Water | 87.5 |
| Total | | 100.0 |

2.1.5 Evaluation of water-holding capability

The water-holding capability of esters A1 and B1 was assessed using the following procedure. A 10 g sample of ester was heated in a water bath at 40°C, then dispersed using a mixer (IKA Japan K.K.). Water was added to the ester in increments of 0.02–0.03 mL. The endpoint was defined as the point at which no further water could be retained. The water-holding capability was calculated using Equation (1), and the maximum water-holding capability was determined at the endpoint.

$$\text{Water-holding capability} = (\text{amount of water held}) / (\text{amount of ester}) \times 100 \quad (1)$$

2.2 Preparation and evaluation of sunscreen formulations

2.2.1 Preparation of sunscreen formulations

Esters A1, B1, and C1 were utilized as base oils to prepare W/O and O/W emulsion sunscreen formulations, respectively (Table 2).

Table 2. Formulations of Sunscreens Containing Ester A1 or B1 or C1 in W/O and O/W Emulsions.

| Ingredients (INCI name) | | W/O | O/W |
|-------------------------|---|--------------------------------|--------------------------------|
| | | sunscreen formulation wt /% | sunscreen formulation wt /% |
| Oil Phase | Esters A1 or B1 or C1 (Polyglyceryl-2 Dipolyhydroxystearate) | 8.0 | 8.0 |
| | Liquid paraffin | 16.0 | — |
| | Ethylhexyl methoxycinnamate | 7.5 | 7.5 |
| | Cetyl PEG/PPG-10/1 Dimethicone | 1.5 | — |
| | Isotridecyl Isononanoate | — | 3.5 |
| UV Scattering agent | Dimethicone | — | 2.5 |
| | Titanium Dioxide | | |
| | Aluminum Hydroxide | 5.0 | — |
| | Stearic Acid | | |
| | Titanium Dioxide, Stearic Acid | — | 5.0 |
| Water Phase | BG | 7.0 | 8.0 |
| | Glycerin | 8.0 | 5.0 |
| | Phenoxyethanol | 0.1 | 0.1 |
| | Sodium chloride | 0.5 | — |
| | Ethanol | — | 10.0 |
| | Glyceryl Stearate | — | 0.8 |
| | Acrylates/C10-30 Alkyl Acrylate Crosspolymer | — | 0.2 |
| | Xanthan Gum | — | 0.1 |
| | Phenoxyethanol | — | 0.1 |
| | Potassium hydroxide | — | an appropriate amount |
| Water | | Add up to 100% | Add up to 100% |
| Total | | 100.0 | 100.0 |

2.2.2 Methods for sun protection factor (in vitro) and water resistance evaluation of sunscreen formulations

A 24.7 mg portion of the sunscreen formulation was applied to a PMMA plate (Helioplate HD6, Weneos), and left at room temperature in a dark place for 30 min. The SPF was then measured using an SPF analyzer (UV-2000S, Labsphere). Subsequently, the PMMA plate was then secured in a 30°C water bath, stirred at 100 rpm using a PB-60 type propeller (Shibata Kagaku) connected to a Three-One motor BL600 (SHINTO Scientific Co., Ltd.).

SPF measurements were taken at 20, 40, 60, and 80-min intervals. After each interval, the plate was left at room temperature in the dark for 30 min before re-measuring the SPF. The SPF at each time point was expressed as a percentage of the pre-immersion value. The SPF retention after 80 min of water exposure was used to evaluate water resistance.

2.2.3 Observation of time-dependent changes in the sunscreen formulation films underwater

A 24.7 mg sample of the sunscreen formulation, using esters A1 and B1 as base oils, was uniformly applied to a PMMA plate (Helioplate SB6, Weneos) and left at room temperature for 15 min. The state of the applied film under water was observed using a three-dimensional (3D) laser microscope (OLS-5100, Shimadzu). Subsequently, the time-dependent changes in the arithmetic mean surface roughness (Sa) were measured for both W/O and

O/W formulations by determining the gap between the water-coated PMMA surface and the lens (Figure 1).

*The Sa on the PMMA plate after application reflects the surface roughness, representing the degree of unevenness in the coating film [3,4].

Additionally, in the W/O sunscreen formulation, where the continuous phase is the oil phase, which makes it easier to compare the effects of immersion, the time-dependent changes in the 3D height image under water were observed using the same method.

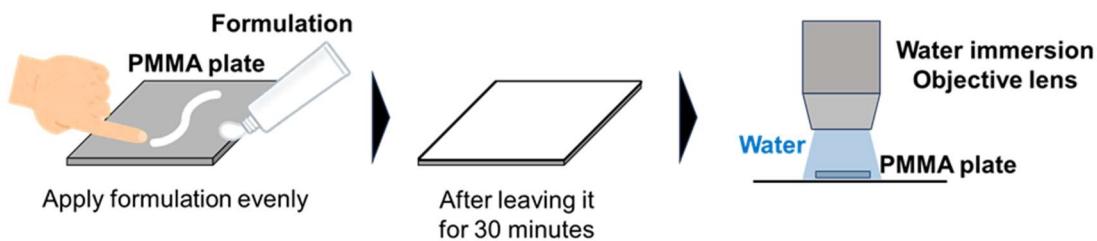


Figure 1. Method for observing underwater application film on PMMA plate.

3. Results

3.1 Evaluation of the esters

3.1.1 Polymer composition (Mw and Pdi) and viscosity of esters

The polymer compositions were classified into three groups, namely low polymerization (Group B: Esters B1 and B2), medium polymerization (Group A: Esters A1-A6), and high polymerization (Group C: Esters C1 and C2). This classification was based on the weight average molecular weight, dispersity, and viscosity of the synthesized compound group (Table 3).

Table 3. Physicochemical Properties of Ester Oils.

| Esters | Mw | Pdi | Viscosity (mPa · s) | |
|--------|--------|------|---------------------|---------|
| | | | at 30°C | at 50°C |
| A-1 | 7,800 | 1.45 | 4,800 | 1,500 |
| A-2 | 6,800 | 1.52 | 4,800 | 1,400 |
| A-3 | 7,100 | 1.56 | 4,700 | 1,500 |
| A-4 | 7,100 | 1.41 | 4,400 | 1,400 |
| A-5 | 8,900 | 1.41 | 8,350 | 2,700 |
| A-6 | 8,900 | 1.64 | 9,600 | 3,000 |
| B-1 | 4,100 | 1.76 | 2,600 | 700 |
| B-2 | 4,500 | 1.47 | 3,550 | 850 |
| C-1 | 11,800 | 1.37 | 10,350 | 3,200 |
| C-2 | 10,700 | 1.40 | 10,050 | 3,050 |

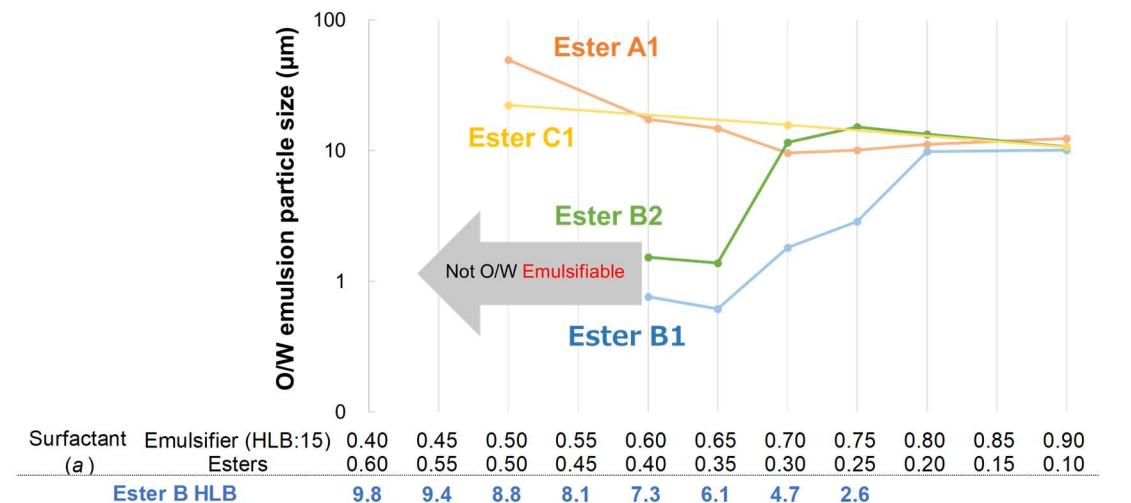
* : Weight – average molecular weight

** : Polydispersity index

*** : Mw and Pdi were measured by gel permeation chromatography.

3.1.2 Emulsification ability of esters

When esters B1 and B2 were mixed in a ratio of hydrophilic surfactant (HLB: 15) to ester in a ratio of 0.35:0.65, they produced O/W emulsions with liquid paraffin as the oil phase and achieved the required HLB value of 11.9. These emulsions exhibited fine particle sizes. Conversely, esters A1 and C1 were unable to produce emulsions with similarly fine particle sizes despite variations in the hydrophilic surfactant ratio, and maintained similar particle sizes (Figure 2).



- Varying the mixing ratios of the emulsifier and the esters.
- The HLB of Ester B is calculated based on the additivity of HLB values.
- It is determined by the balanced ratio of emulsifier and ester that emulsifies liquid paraffin most finely.

Figure 2. Measurement of median particle size in O/W emulsification.

3.1.3 Water-holding capability (maximum water-holding capability) of esters

Regarding water-holding capacity, ester A1 demonstrated a rate of 434%, whereas ester B1 exhibited a rate of 152% (Table 4). Notably, when the amount of water added exceeded the maximum absorption threshold, ester A1 maintained the W/O type, while ester B transitioned into the O/W type.

Table 4. Water-holding Capability of Esters A1 and B1.

| Esters | Water-holding Capability(%)† |
|--------|------------------------------|
| A1 | 434 |
| B1 | 152 |

† Water-holding Capability (%)
: (Maximum Water Retained)/(Amount of Each ester)×100

3.2 Evaluation of sunscreen formulations

3.2.1 SPF and water resistance

The water resistance of sunscreen formulations using ester A1 was 96% for W/O sunscreen and 75% for O/W sunscreen. In contrast, the water resistance of sunscreen formulations using ester B1 was 35% for W/O sunscreen and 31% for O/W sunscreen (Figure 3).

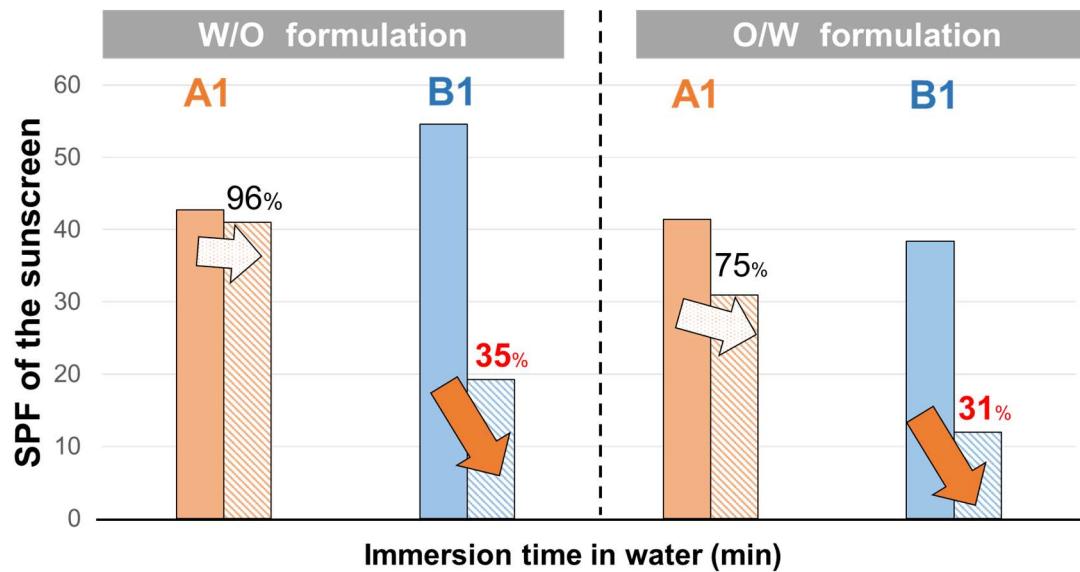


Figure 3. Evaluation of SPF & water resistance (%) in sunscreen applied on PMMA plates.

Additionally, in the standard deviation (9 points) during SPF measurement, ester C1 showed higher values compared to esters A1 and B1 (Table 5).

Table 5. Average and Standard Deviation of SPF Measurements on PMMA Plates.

| | Esters | SPF measurements | |
|-----------------|--------|------------------|----------------------------|
| | | Average | SD (standard deviation) |
| W/O formulation | A1 | 42.7 | 4.2 |
| | B1 | 54.6 | 4.5 |
| | C1 | 40.6 | 12.5 |
| O/W formulation | A1 | 41.3 | 6.2 |
| | B1 | 38.3 | 5.8 |
| | C1 | 19.2 | 10.5 |

3.2.2 Underwater application film of sunscreen formulation

The results indicated that the application of sunscreen formulations containing esters A1 and B1 on PMMA flat plates reduced the surface roughness compared to untreated (blank) PMMA plates (Figure 4). This suggests that both formulations effectively filled the irregularities of the PMMA plate and formed a uniform application film. The temporal changes in Sa of each formulation under water are also presented in Figure 4.

For the W/O formulations:

The ester A1 formulation exhibited a slight increase in Sa after 1 min of immersion, which then gradually continued to rise. In contrast, the ester B1 formulation exhibited a significant increase in Sa after 1 min of immersion, followed by a gradual decrease.

For the O/W formulations:

A decrease in Sa was observed after 1 min of immersion for both esters A1 and B1 formulations. The ester A1 formulation maintained a constant value thereafter, whereas the ester B1 formulation continued to decrease in Sa over time.

Furthermore, Figure 5 shows the time-dependent changes in the 3D height images of PMMA plates coated with W/O sunscreen formulations underwater. For the ester B1 formulation, significant expansion and peeling of the coating film observed within just 1 minute of immersion. In contrast, for the ester A1 formulation, slightly changes were observed in the coating film during 4 minutes of immersion, and the film was maintained for up to 10 minutes thereafter (data not shown).

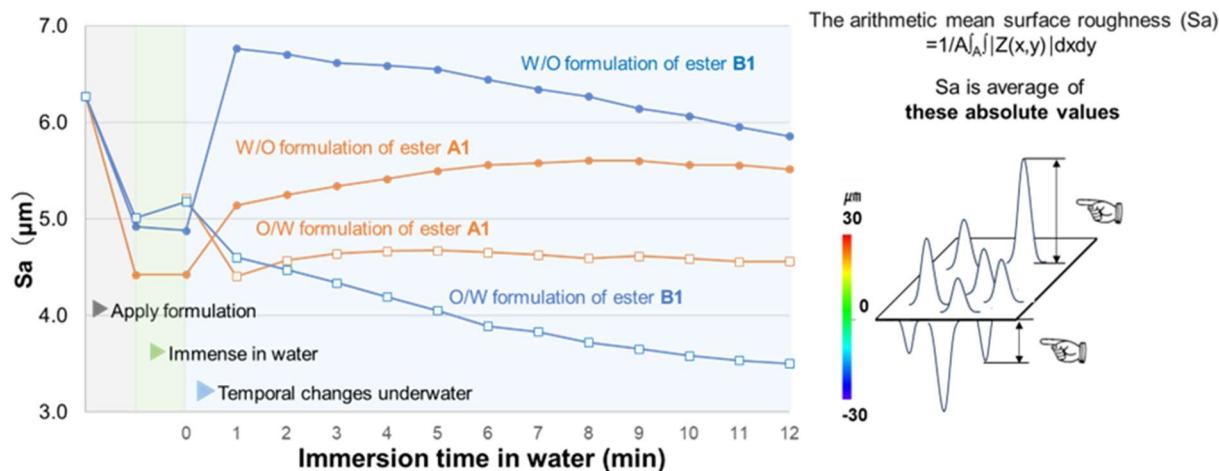


Figure 4. Temporal variation of the arithmetic mean surface roughness (Sa) of the application film in water.

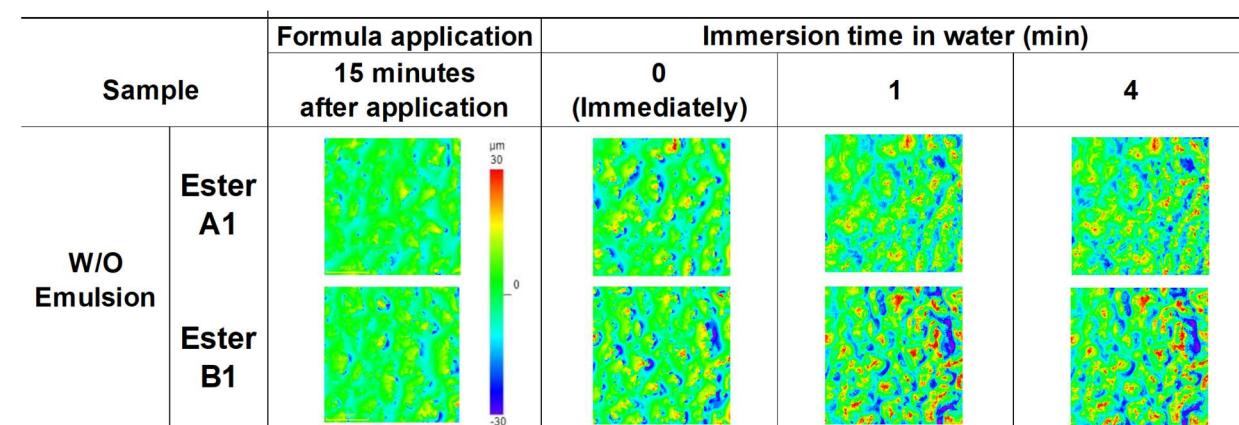


Figure 5. Time-dependent changes in the 3D height image of the application film in water.

4. Discussion

4.1 Discussion on esters

The emulsification ability of the esters was evaluated, revealing that esters B1 and B2 were capable of adjusting the HLB through interactions with hydrophilic surfactants. This

interaction resulted in the manifestation of characteristics typically exhibited by hydrophobic surfactants, as evidenced by a calculated HLB value of 6.1. Consequently, esters A1 and C1 do not possess properties analogous to those of hydrophobic surfactants, but rather demonstrate properties more closely aligned with the base oil. This difference is due to the molecular structure of each ester [5]. Compared to esters A1 and C1, esters B1 and B2 have lower weight-average molecular weights and lower dispersity, suggesting that the polyhydroxystearic acid chains in esters B1 and B2 are of a shorter length. Additionally, the presence of low molecular weight compounds that exhibit surfactant properties has been detected in esters B1 and B2. It is considered that these compounds contribute to the expression of emulsification abilities.

4.2 Discussion on sunscreen formulation

4.2.1 Water resistance of sunscreen formulation

The poor water resistance (SPF retention) observed in sunscreen formulations containing ester B1 is because ester B1 exhibited surfactant properties between the film and water, causing the film to dissolve [6]. Conversely, the sunscreen formulation containing ester A1 showed excellent water resistance results because ester A1 did not exhibit low molecular weight compounds that exhibit surfactant properties but rather had properties as an emollient, forming a strong and highly water-resistant oil film.

Observing the underwater coating films of the W/O formulation in Figures 4 and 5, it was considered that the ester B1 formulation strongly affected the coating film within 1 minute of immersion, causing expansion and delamination, resulting in a significant increase in Sa. In contrast, the coating film with ester A1 showed little change after 4-minute of immersion, with only a slight increase in Sa. Thus, the effect of immersion on the coating film was significant for the ester B1 formulation but minimal for the ester A1 formulation. In the O/W formulation shown in Figure 5, ester B1 steadily reduced Sa by expanding and filling coating irregularities upon immersion. On the other hand, ester A1 showed only a slight increase in Sa after 1 minute of immersion and did not cause expansion. In both W/O and O/W formulations, ester A1 was less affected by immersion than ester B1, and the change in Sa was minimal. These results suggest that while ester B1 caused the expansion and delamination of the coating film due to its emulsifying ability, ester A1 exhibited notable properties as an effective oily emollient agent, capable of forming a robust, water-resistant oil film with minimal sensitivity to water exposure.

4.2.2 Spreadability of sunscreen formulations

In the measurement of the SPF of the formulation of esters A1, B1, and C1, it was observed that the formulation of ester C1 showed a high standard deviation in the 9-point measurement. This variability in the measured values suggests an inability to form a uniform coating film [7,8]. Consequently, this finding indicates that ester C1 is a polymer with a high degree of polymerization and increased viscosity, rendering it unsuitable for utilization as a base oil.

4.3 Overall discussion including water-holding capability

Overall, ester A1 demonstrated superior performance in forming a robust water-resistant oil film compared to ester B1. In addition, ester A1 is a polymer ester with a moderate viscosity that is easier to spread than ester C1. Notably, Ester A1 also showed exceptional water-holding capacity—approximately three times that of Ester B1—highlighting conflicting properties of water resistance and water-holding.

The elucidation of this mechanism will be achieved through the visualization of intermolecular interactions using molecular simulations.

5. Conclusion

Through the modulation of time and temperature during the esterification of plant-derived diglycerin and 12-hydroxystearic acid, a series of compounds were synthesized. Among them, ester A1 emerged as a promising amphiphilic polyester, characterized by moderate viscosity, good spreadability, and the ability to form a strong water-resistant oil film despite its inherent hydrophilicity. This performance is attributed to the absence of low molecular weight compounds with surfactant-like properties in ester A1, as well as its optimal degree of polymerization of polyester for ease of use in cosmetics. The potential uses of ester A1 span a wide range of cosmetic products, including skincare and makeup, and its unique combination of properties may offer valuable contributions to the advancement of formulation science in the cosmetics industry.

6. References

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