

# INTELLIGENT BIOPOLYMER-BASED FORMULATION STRATEGIES FOR EMULSIFIER-FREE SUNSCREEN PRODUCTS

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## Abstract

**Background:** Sunscreen products often contain a higher amount of oil phase than other types of skin care products where emulsifiers are required to stabilize the system. However, the use of emulsifiers often leads to concerns over potential skin irritations as well as loss of water-resistant properties. Besides, stabilizer systems are used for innovative textures or improved user experience. Therefore, it is vital to develop formulation strategies which enable high-performing sunscreen products free of conventional emulsifiers while addressing the functions of stabilizers at the same time.

**Methods:** Natural biopolymers (Diutan Gum, Tara Gum, and Cellulose Gum) and synthetic polymers (Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Carbomer, and Acrylates/Beheneth-25 Methacrylate Copolymer) were evaluated in a model organic UV filter-based sunscreen formulation. Structure characters and polymer-polymer interactions were investigated by rheometer. Texture and sensory of the samples were mapped. SPF 50 sunscreen formulations were developed with *in vitro* SPF/UVAPF performance and water-resistant properties evaluated.

**Results:** Biopolymers and synthetic polymers exhibited robustness in stabilizing sunscreen formations when used in combination and provided different sensorial profiles depending on the combination. Introducing biopolymers altered the rheological behaviour of the synthetic polymer-based systems and the interactions between polymers vary from polymer to polymer. High UV protection sunscreens with very water-resistant properties were developed without emulsifiers.

**Conclusion:** Different combinations of polymers can be used to formulate stable O/W sunscreen systems of medium and high UV protection with a variety of textures and sensory profiles.

**Keywords:** Emulsifier-free; Polymer; Biopolymer; Sunscreen; *In vitro* SPF; Water resistance

## **Introduction.**

Sun protection has become an indispensable skin care routine with our growing awareness of the harm of UV radiation and advance in sun care technology. However, discussions of sun care products' effect on health and safety associated with the use of UV filters are intense. Scientists and formulation chemists have been working on ways to mitigate the safety risks. Emulsifiers are one of the raw material categories that formulators can work on to minimize the skin irritation. It is well acknowledged that emulsifiers, including both non-ionic and anionic emulsifiers, are potential irritants to skin, esp. damaged or sensitive skin [1]. Furthermore, emulsifiers can function as a penetration enhancer, which may promote the delivery of organic UV filters into the dermis unfavourably [2-3]. Having an emulsifier in an oil-in-water (O/W) sunscreen product may also exert a negative impact on its water-resistant property as the hydrophilic emulsifiers used to stabilize the system will re-emulsify the system when in contact with water, leading to a loss of protection [4].

On the other hand, stabilizer systems (other than emulsifiers) are required to offer novel textures and pleasant sensations to consumers, ensuring an enjoyable user experience to encourage the use of sunscreen products. Polymers are of high interest as stabilizers for emulsions because of their high efficiency (low use level), good safety profile (no biological activity on the skin), and excellent flexibility. Because of polymers' special stabilizing mechanism, there is no need to calculate and match the required HLB values. High molecular weight hydrophilic biopolymers, a rising category in polymers, have shown their potential as a stabilizer in numerous applications such as O/W emulsions [5].

The objectives of the present study were to examine the characteristics of biopolymer-based emulsifier-free sunscreens, to understand the performance of polymer-based stabilizer

systems, and to design biopolymer-based formulation strategies to achieve emulsifier-free O/W sunscreen systems, offering moderate to high UV protection, improved water-resistant properties, and a wider variety of textures and sensorial profiles.

## **Materials and Methods.**

### Materials

Biopolymers: Sphingomonas Ferment Extract (Diutan Gum, DG) and Caesalpinia Spinosa Gum (Tara Gum, TG) were used as supply. Cellulose Gum was used as a mixture of Microcrystalline Cellulose, Sphingomonas Ferment Extract, Cellulose Gum as supply (PS).

Synthetic polymers: Acrylates/C10-30 Alkyl Acrylate Crosspolymer (EZ), Carbomer (U30), and Acrylates/Beheneth-25 Methacrylate Copolymer (L10) were used as supply.

UV filters: Ethylhexyl Methoxycinnamate (EHMC), Ethylhexyl Salicylate (EHS), Ethylhexyl Triazone (EHT), Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT), Diethylamino Hydroxybenzoyl Hexyl Benzoate (DHHB), and Phenylbenzimidazole Sulfonic Acid (PBSA) were used as supply. Inorganic UV filter particulates assessed were micro titanium dioxide (15 nm) coated with hydrated silica (TiO<sub>2</sub>-100WP) and silicone-coated titanium dioxide (TiO<sub>2</sub>-TX), used as supply.

Other ingredients: C12-15 Alkyl Benzoate, Diisopropyl Sebacate (DIS), Phenoxyethanol (and) Ethylhexyl Glycerin (PEHG), Glycerin, Methyl Gluceth-20 (E-20), Disodium EDTA, Aminomethyl Propanol (AMP), Sodium Hydroxide were used as supply.

### Methods

#### Preparation of emulsions

The water phase was first prepared using an over-head stirrer at 400 rpm until homogenous and the oil phase was added into the system under stirring. The oil phase with TiO<sub>2</sub>-TX was pre-homogenized at 10 000 rpm for 3 min before adding to the water phase. The mixture was then homogenized at 10 000 rpm for 3 min.

**Table 1.** a) Model organic UV filter-based emulsifier-free formulations (DGSUN, PSSUN, EZSUN, U30SUN, L10SUN); and b) SPF 50 emulsifier-free sunscreen formulations.

(a)	SPF 30 model formula	DGSUN	PSSUN	EZSUN	U30SUN	L10SUN
	Ingredient	Weight %				
Water phase	Deionized water	Q.S. to 100				
	Glycerin	8.00				
	E-20	5.00				
	Biopolymer	0.50/0.25	1.00/0.25	0.20	0.20	0.20
	Synthetic polymer	-	-	0.30	0.30	1.50
	PEHG	0.60				
Oil phase	Disodium EDTA	0.10				
	EHMC	7.50				
	BEMT	3.00				
	DHHB	3.00				
	EHT	2.00				
	EHS	4.50				
	C12-15 Alkyl Benzoate	10.00				
	Sodium Hydroxide	pH 5-7				

(b)	SPF 50 sunscreen chassis	(1)	(2)	(3)	(4)	
	Ingredient	Weight %				
Water phase I	Deionized water	Q.S. to 100				
	E-20	5.00				
	Glycerin	8.00				
	Synthetic polymer*	0.20/0.50/1.50				
	DG	0/0.20				
	PEHG	0.60				
Oil phase	Disodium EDTA	0.10				
	DIS	5.00				
	EHMC	7.50				
	BEMT	5.00				
	DHHB	3.00				
	Ethylhexyl Triazone	4.50				
	EHS	4.50				
Water Phase II	TiO <sub>2</sub> -TX	-	-	2.00	-	
	TiO <sub>2</sub> -100WP	-	-	-	2.00	
	PBSA	-	1.00	-	-	
	Aminomethyl Propanol	-	pH 7-7.5	-	-	
Additive	Sodium Hydroxide (18%)	pH 5-7				

\*Synthetic polymers were used at different levels: EZ at 0.2% without PBSA and 0.5% with PBSA; L10 at 1.5% as supply (0.45% active) for all conditions.

#### Microscope analysis

Optical microscopy was used to examine the microstructure of emulsion samples. A small amount of emulsion sample was placed on a microscope slide without dilution and covered by a cover glass slip. Samples were observed under transmitted light and polarizing light at 500 times magnification.

#### Rheology measurement

Rheology experiments were conducted to study structure characters of the model emulsion systems. For all experiments, a rheometer with cone and plate geometry (stainless steel, 40 mm diameter, 1.018° angle) was used. Approximately 2 g of the sample was added onto the Peltier plate Aluminium. The viscoelastic properties of the samples were assessed at 1 Hz at 25 °C between 0.01% to 1 000% strain amplitude to determine the linear viscoelastic region (LVER) by measuring the storage modulus G' (associated with energy storage) and the loss modulus G'' (associated with loss of energy). The moduli were measured from 0.1 to 100 Hz at a constant shear strain (0.5%) in the linear region at 25 °C.

#### Sensorial assessment

A sensory panel of six panellists evaluated the biopolymer/synthetic polymer-based SPF30 model emulsifier-free sunscreens (9 samples, blind-test) based on the stages and attributes below:

- (1) First stage (before application/sample appearance): glossy surface, matte surface, firmness, and pick up.
- (2) Second stage (during application): quick break effect, watery feel, creamy feel, slippery feel, playing time, and absorption.
- (3) Third stage (after application): softness, smoothness, stickiness, residue feel.

Each attribute was scored from 1 to 5 with 1 being the least and 5 the most.

#### Stability measurement

Emulsion samples were subjected to stability evaluation at room temperature (RT), elevated temperature (50 °C) for 1 month, and centrifugation test at 3 000 rpm for 30 minutes. pH and viscosity were measured at 24 h RT, 1 month RT, and 1 month 50 °C. pH was measured by pH meter and viscosity by viscometer at 20 rpm at room temperature. Visual inspection was used to assess the apparent stability of emulsion samples.

#### *In vitro* SPF/UVAPF analysis

*In vitro* SPF and UVAPF values of optimized sunscreen samples were determined by UV-2000S. A  $0.0325 \pm 0.0005$  g portion of sample was applied on a moulded PMMA plate using an automatic robot arm and transmission of light was measured before and after solar simulation following Colipa test method. Each sample was repeated at least three times.

#### Water resistance test

Static *in vitro* SPF and UVAPF values of samples applied on a moulded PMMA plate were first measured and then each PMMA plate was immersed in a 1 L vessel of a dissolution tester containing hard water solution (conductivity  $>500 \mu\text{S}$ , pH 6.5-7.5). Immersed PMMP plates were taken out after 80 min stirring at 120 rpm, air-dried for at least 30 min, and subjected to *in vitro* SPF/UVAPF analysis.

#### Statistical analysis

The results of viscosity of samples and sensory evaluations were analysed by general linear model of ANOVA at a confidence level of 95, two-sided confidence interval, and Tukey pairwise comparison to detect the difference between and across samples.

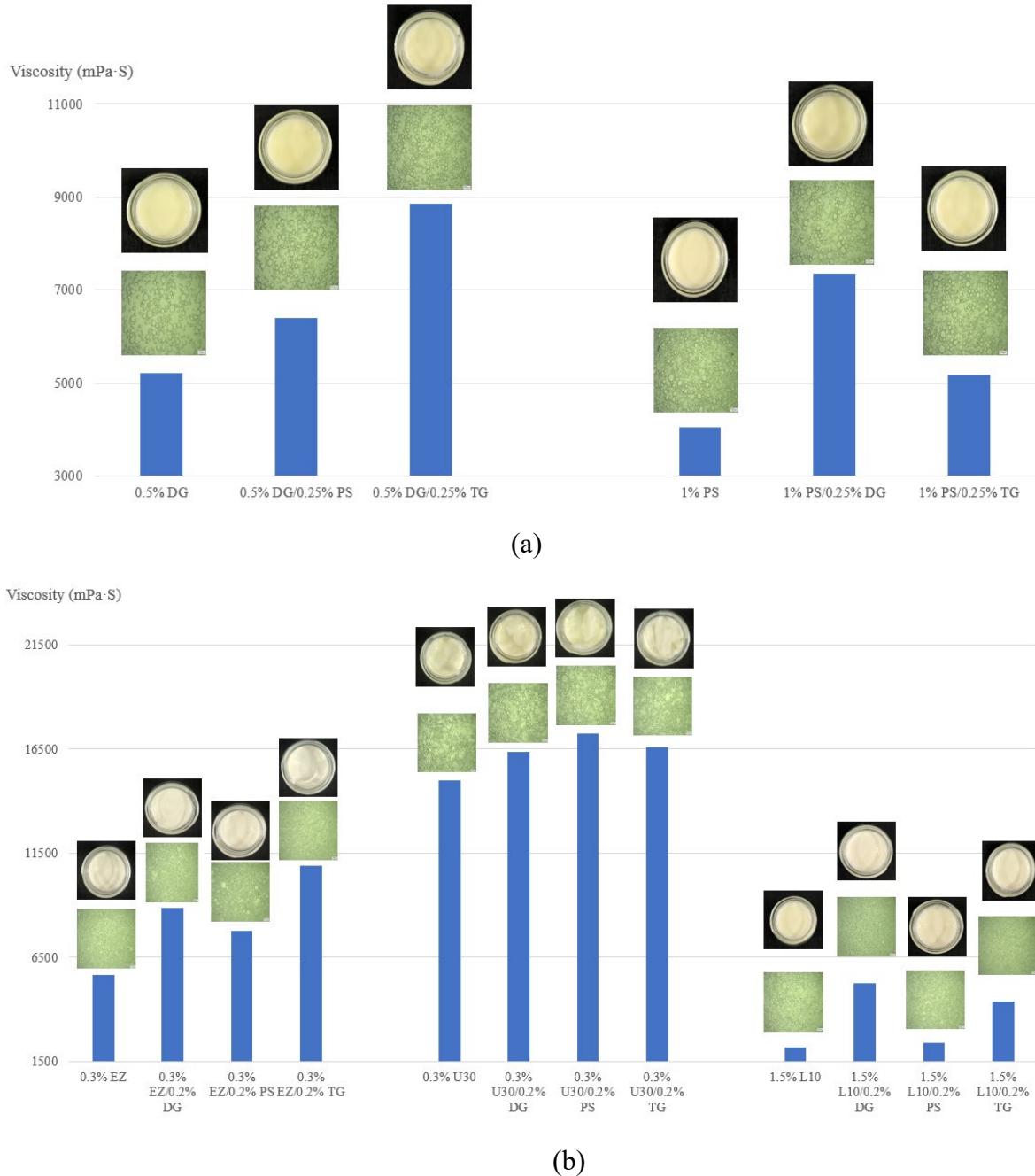
## Results.

### SPF 30 organic UV filter-based model sunscreens

#### Physicochemical characterization

Formulations stabilized by biopolymers have no significant difference in viscosity whereas the combination of synthetic polymer and biopolymer exhibited a significant difference in viscosity across three synthetic polymers ( $p < 0.05$ ). Introducing biopolymers increased the viscosity of the systems compared with the control samples (**Figure 1**). Although the mixing

of biopolymers did not significantly affect the droplet size of emulsions, the addition of biopolymers to synthetic polymers made the oil droplet sizes smaller and the droplet size distribution narrower, indicating better stability (**Figure 1**) [6].



**Figure 1.** 24 h Viscosity of biopolymer-based (a) and synthetic polymer/biopolymer-based (b) sunscreens with sample image and microscopic image ( $\times 500$  magnification).

### Structure characterization

Diutan Gum can build a viscoelastic gel system and it increased the gel strength (higher G') for all systems. There is no significant effect of Cellulose Gum and Tara Gum on the cohesive energy and yield stress of the Diutan Gum-based system. The elastic strength of the system is determined mainly by Diutan Gum. However, Cellulose Gum affected the internal structure of the system, where a small peak of loss modulus (G'') can be seen in **Figure 2A**, indicating relative motions between the particles that are not linked or fixed in the network, for instance, the mobile single particles-microcrystalline cellulose, or micro-cracks. Similarly, when using Diutan Gum in a PS-based system (**Figure 2B**), such a G'' peak is more obvious compared with the other biopolymer systems.

In the frequency sweep of Diutan Gum with Cellulose Gum (**Figure 3A**), there is a sharp decrease of G' at high frequency ( $G' \rightarrow 0$ ), suggesting the system changed and demonstrated viscous flow behaviour whereas all other systems displayed increased rigidity (increasing G'). With the only exception of the DG/PS-based system, all biopolymer-based systems showed gel-like behaviour across the low to high frequencies. For PS-based systems (**Figure 3B**), Diutan Gum improved the viscoelastic strength of the system that even at high frequencies, the system remained the behaviour of a gel whereas PS and PS/TG-based systems changed to a viscoelastic liquid ( $G'' > G'$ ).

Acrylates/C10-30 Alkyl Acrylate Crosspolymer (EZ)-based systems displayed a certain rigidity at low shear rates and showed low viscosity flow behaviour at medium to high shear rates. Although introducing biopolymers to EZ raised both the elastic portion and the viscous portion, biopolymers provided a relatively smaller LVE range (**Figure 2C**), less flexibility and higher rigidity, which indicates a more brittle behaviour of the internal structure. All G'' curves of EZ-based systems showed a slightly wide base with increasing deformation that indicates a network structure breaking down gradually.

In the frequency sweep (**Figure 3C**), both Diutan Gum and Tara Gum exhibited a vastly different behaviour compared with EZ alone and with Cellulose Gum, where DG and TG had elastic behaviour dominating over the viscous behaviour across the frequency range tested.

Instead, at high frequency, the loss modulus of EZ alone and with PS override the storage modulus, implying a change from solid-like gel to a flowing liquid.

Carbomer-based systems, with or without biopolymers, showed a similar LVE range and presented a gel-like character (**Figure 2D**). The peak of the  $G''$  of Carbomer with Diutan Gum is different from the rest, suggesting stronger deformation energy in a cross-linked network of Carbomer and Diutan Gum than the others.

In well-structured carbomer-based systems, the elastic modulus is always greater than the viscous modulus and both are almost independent of frequency (**Figure 3D**).  $\text{Tan}(\delta)$  remained below 1 across different systems and the whole frequency range, indicating the behaviour of viscoelastic gels. Such robust elastic behaviour reassured the high stability provided by the emulsifier-free system. Although the overall trends of Carbomer with biopolymers are similar to EZ's, there is no crossover between storage modulus and loss modulus at the frequency range assessed.

The rheological behaviour of the L10 (Acrylates/Beheneth-25 Methacrylate Copolymer) control sample is vastly different from the other systems. The addition of biopolymers to L10 can change the structure character completely, impart yield, and thus improve stability.

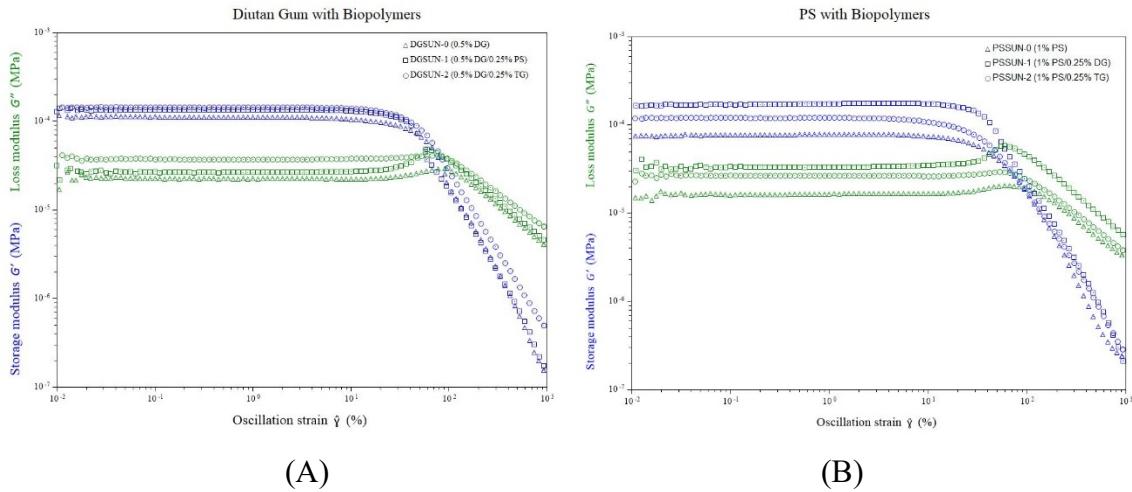
The L10 control sample showed the character of a viscoelastic liquid in the LVE range ( $G'' > G'$ ) (**Figure 2E**) and this well explains its self-levelling texture when at rest. Such rheological behaviour indicates that the formula was built without a consistent physical network of forces, though the flow process of the L10 sample can occur with an extremely low flow velocity. Unlike the other systems where an increase in  $G''$  can be seen before the breakdown of the gel, the L10-biopolymer systems exhibited a smoother decrease of  $G''$ , implying an unlinked structure that deformation energy is lost as a whole of the sample.

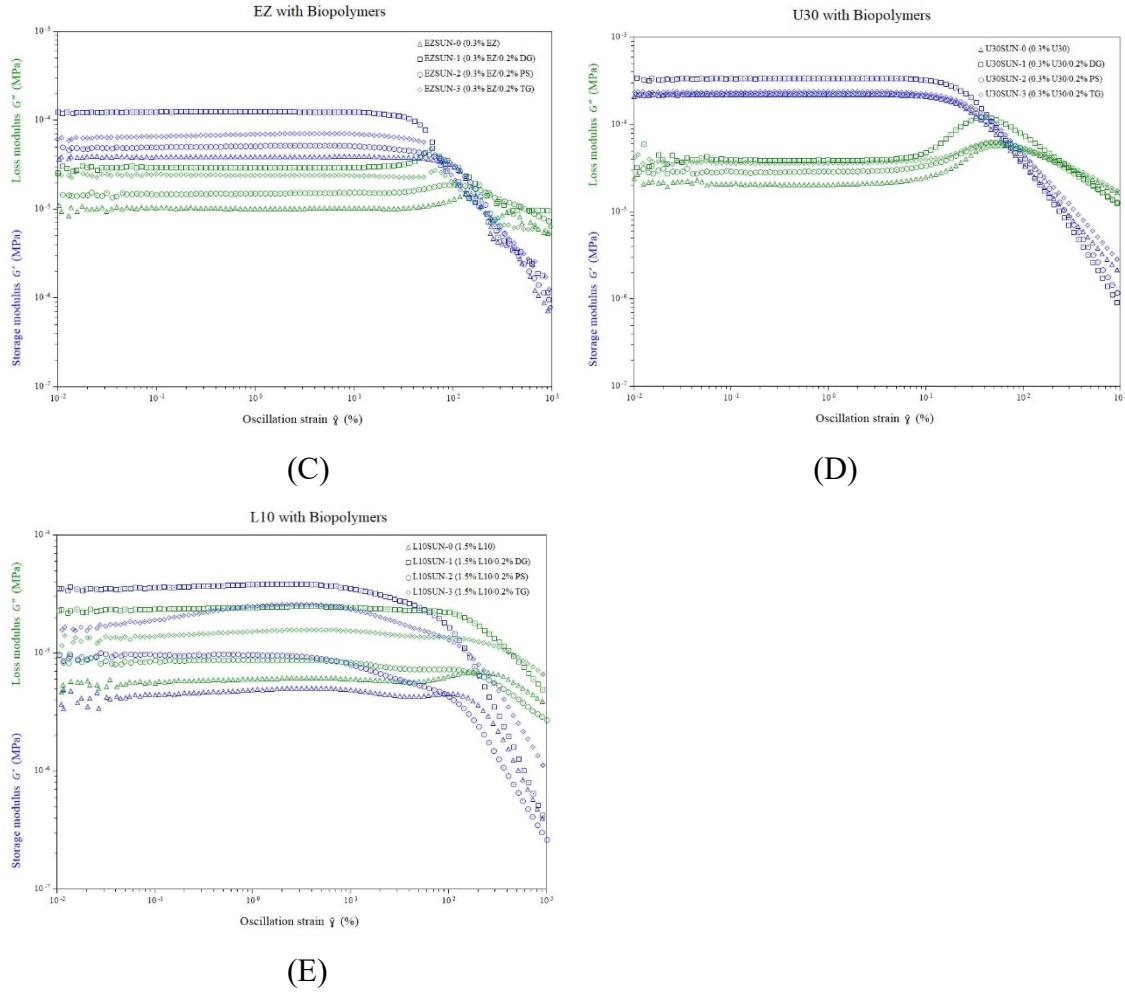
The frequency sweep of the L10 control sample depicted the bouncy texture of L10 polymer-based system that at high frequencies, the system showed higher  $G'$  than  $G''$ , decreased  $\text{Tan}(\delta)$ , like an elastic gel (**Figure 3E**). However, when exposed to very slow motions,

$G'$  was smaller than  $G''$ , indicating a slow-flowing liquid behaviour. The L10 control sample may spread gradually under its own weight when left at rest.

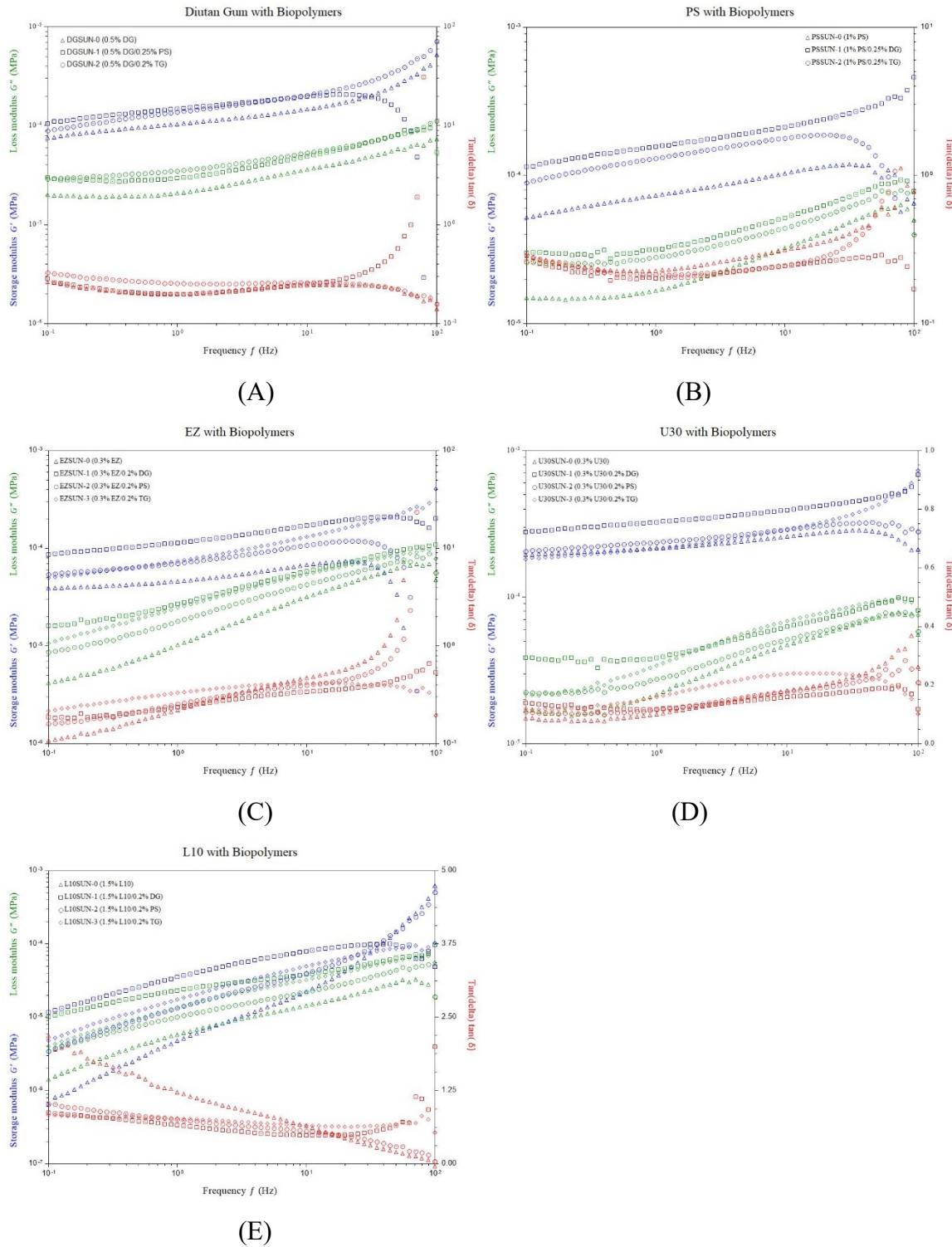
On the other hand, when biopolymers were introduced to a L10 polymer-based system, the rheology behaviour changed from a flowing liquid to an elastic solid ( $G' > G''$ ) at LVE region, most noticeably with Diutan Gum. The addition of Diutan Gum significantly increased the elasticity of the system that a yield point and a flow point can be easily captured in the amplitude sweep test (**Figure 2E**). Cellulose Gum and Tara Gum raised the storage modulus over the loss modulus as well, but to a less extent. Diutan Gum supplies a higher flow point, implying a stronger internal structure at the same use level.

Biopolymers helped build a weakly-structured system with the L10 polymer in sunscreens, where storage modulus dominated over loss modulus but increased together with frequency (**Figure 3E**).





**Figure 2.** Strain amplitude (0.01% to 1 000%) of SPF 30 model emulsifier-free sunscreens:  
 (A) Diutan Gum with biopolymers; (B) Cellulose Gum with biopolymers; (C)  
 Acrylates/C10-30 Alkyl Acrylate Crosspolymer (EZ) with biopolymers; (D) Carbomer with  
 biopolymers; (E) Acrylates/Beheneth-25 Methacrylate Copolymer (L10) with biopolymers.

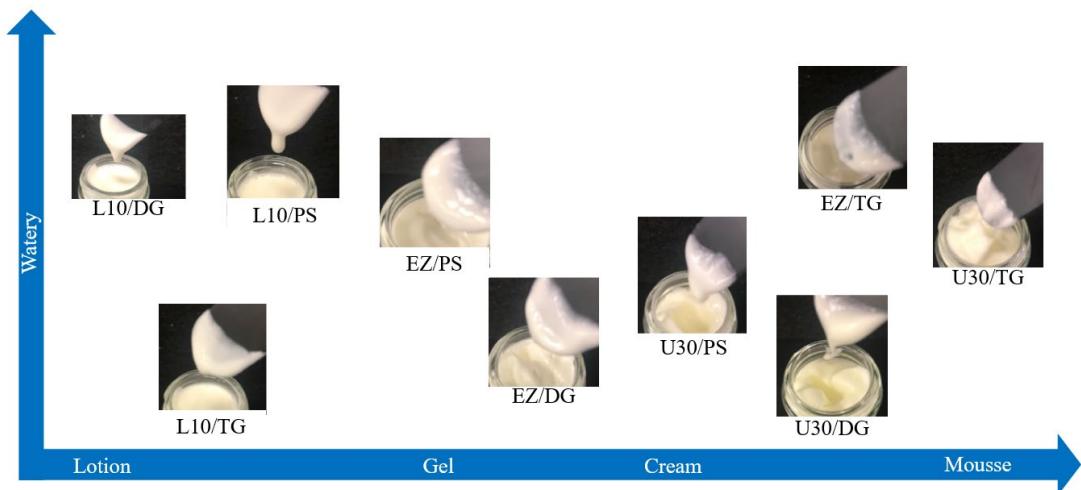


**Figure 3.** Frequency sweep (0.1-100 Hz) of SPF 30 model emulsifier-free sunscreens: (A) Diutan Gum with biopolymers; (B) Cellulose Gum with biopolymers; (C) Acrylates/C10-30

Alkyl Acrylate Crosspolymer (EZ) with biopolymers; (D) Carbomer with biopolymers; (E) Acrylates/Beheneth-25 Methacrylate Copolymer (L10) with biopolymers.

### Texture and Sensory

Different biopolymers provide various sensory because of different backbone compositions and configurations. Both synthetic polymer and biopolymer played a role in formulation appearance, glossy or matte surface ( $p < 0.05$ ). L10 and Tara Gum provided a more matte surface while EZ gave a glossier look compared to their counterpart polymers. Diutan Gum improved the slipperiness of the formulation. Cellulose Gum can reduce the rigidity of the system and promote a quicker breakdown or watery feel. Tara Gum can impart a matte and mousse-like texture. In addition, synthetic polymers have their distinctive sensory notes such as EZ and L10 for a watery and refreshing sensory, U30 for a firm and relatively creamy sensory ( $p < 0.05$ ). The selection of synthetic polymers affects the appearance, firmness, pick up, watery or creamy feel, playing time and absorption rate ( $p < 0.05$ ). Thus, combinations of different polymers can deliver different textures and sensory needs based on the product design (**Figure 4**).



**Figure 4.** Texture mapping of SPF 30 model emulsifier-free sunscreen formulations.

### SPF 50 emulsifier-free sunscreens

Based on the findings of the SPF 30 model emulsifier-free sunscreen, optimization of the UV filter system and other functional ingredients was done and evaluated with EZ alone and the

combination of L10 polymer with Diutan Gum. Because the same amount of EZ cannot tolerate high electrolyte content such as PBSA, a higher dosage of it was needed. Moreover, the compatibility of silicone-coated Titanium Dioxide with EZ was not good enough for the system studied. The combination of L10 polymer and Diutan Gum exhibited excellent versatility in different UV filter systems and stability at all test conditions (**Table 2**).

All SPF 50 emulsifier-free sunscreens proposed showed long-term stability at room temperature and elevated temperature and gave *in vitro* SPF values higher than 50. There was no significant difference in the SPF/UVAPF performance among stabilizer systems. The values of SPF retained were all higher than 50% after 80 min water immersion (**Table 2**).

**Table 2.** Overview of SPF 50 emulsifier-free sunscreens

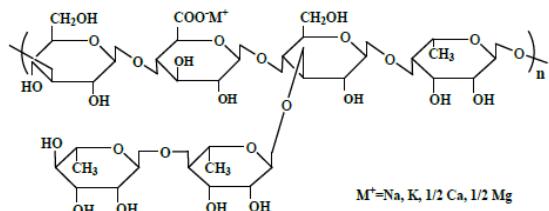
SPF 50 sunscreen chassis	0.2% EZ	0.5% EZ w PBSA	0.2% EZ w TiO <sub>2</sub> -100WP	1.5% L10/0.2% DG	1.5% L10/0.2% DG w PBSA	1.5% L10/0.2% DG w TiO <sub>2</sub> -TX	1.5% L10/0.2% DG w TiO <sub>2</sub> -100WP
RT & 50°C 1mon sample							
Microscope image (X500)							
pH	6.4	7.0	6.4	7.5	7.2	7.3	7.1
Viscosity (mPa·s)	3 560	11 700	4 180	9 140	7 920	11 860	11 520
SPF/UVAPF (Static)	64.4/16.0	75.9/17.2	76.7/14.5	62.7/16.6	66.9/15.9	68.8/14.6	72.3/15.3
SPF/UVAPF (80min WR)	47.0/14.4	57.2/14.2	46.1/10.7	47.2/14.5	53.0/12.8	39.9/12.0	51.7/14.8
SPF retained	73%	75%	60%	75%	79%	58%	72%

## Discussion.

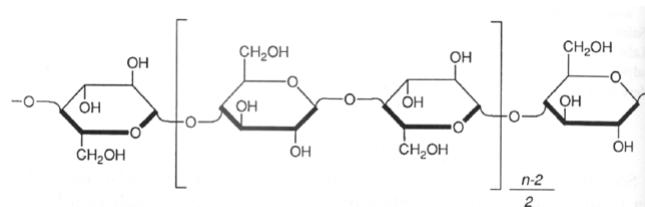
Owing to the strong stabilization capability, the proposed biopolymers and synthetic polymers can formulate SPF 30 model sunscreens with a standard formulation process. The effect of polymers on droplet size distributions is, like conventional emulsifiers, dependent on the type and concentration of the polymer used. The stability of emulsion samples is linked to the droplet size distribution. Samples of a smaller droplet size and a narrower size distribution give a better stability profile. The viscosity given by different polymers depends

on the chemical structure (backbone and crosslink level) of the polymer. Cellulose Gum, a linear unbranched homopolysaccharide, is not as good at building networks as heteropolysaccharides like Diutan Gum and Tara Gum—Diutan Gum can form a highly ordered double helix structure and Tara Gum (galactomannan) thickens through random coil hyperentanglement (**Figure 5**) [7-10].

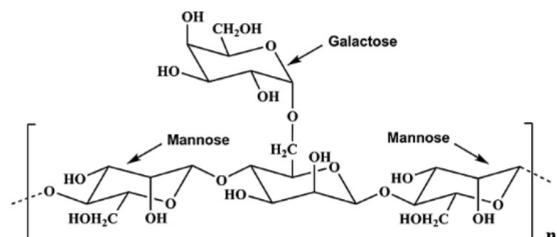
All samples showed shear-thinning behaviour and the viscosity dropped significantly upon shearing, ensuring an appropriate spreadability upon application. Differences in yielding behaviour are related to differences in conformation and interaction of polymers. Tara Gum (Galactomannan) dispersion is not elastically structured. Hence, Tara Gum alone cannot provide suspension or stability for oil components. Similarly, L10 (Acrylates/Beheneth-25 Methacrylate Copolymers) is a linear, non-crosslinked polymer that cannot build a profound yield on its own [11]. Such chemical nature of Tara Gum and L10 creates a light and watery sensory with less pilling, making them good sensory and viscosity modifiers to be used together with other elastic structure-building polymers.



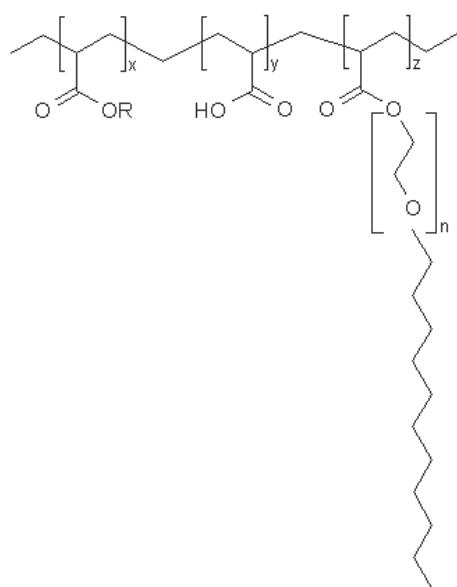
Diutan Gum



Cellulose



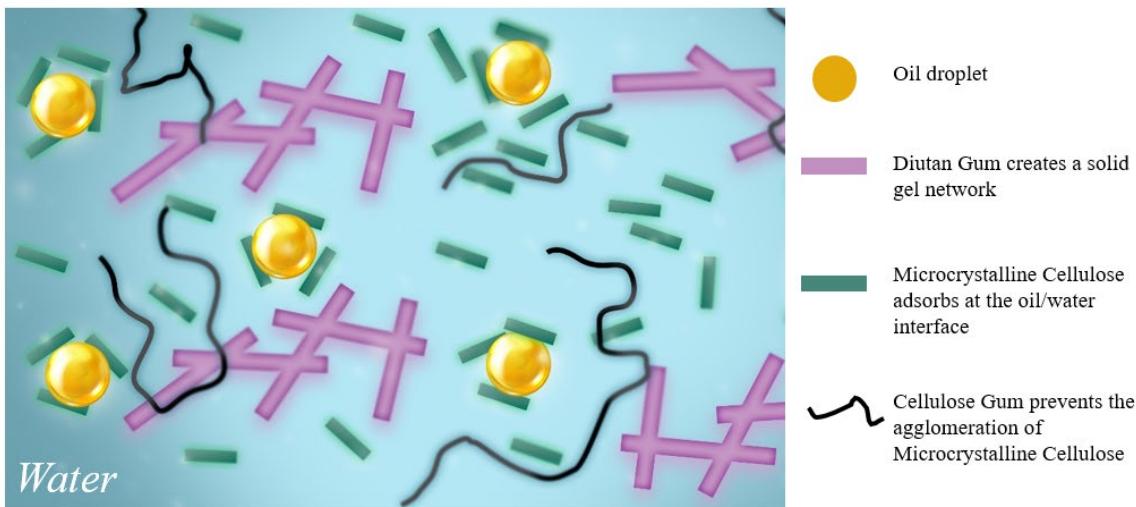
Tara Gum



Acrylates/Beheneth-25 Methacrylate Copolymer (L10)

**Figure 5.** Chemical structures of polymers [11-13].

The oscillation amplitude test results illustrate the impact of mixing polymers in a O/W sunscreen emulsion system. Different rheological behaviours were seen with different blends of polymers in terms of LVE region, elastic strength, and even deformation energy. The G" peaks observed in amplitude sweeps of DG/PS-based systems suggest stronger inner friction processes within DG and PS than other combinations. The stabilizing mechanism of Diutan Gum and Cellulose Gum is depicted in **Figure 6**.



**Figure 6.** Schematic diagram of a 3-dimension network and Pickering emulsion mechanism of DG/PS system. The rigid double helix gel structure of Diutan Gum creates a solid gel network in the aqueous phase ensuring an excellent suspension of the oil droplets. Insoluble particles of Microcrystalline Cellulose irreversibly adsorb on the oil-water interfaces, forming an effective mechanical barrier against coalescence.

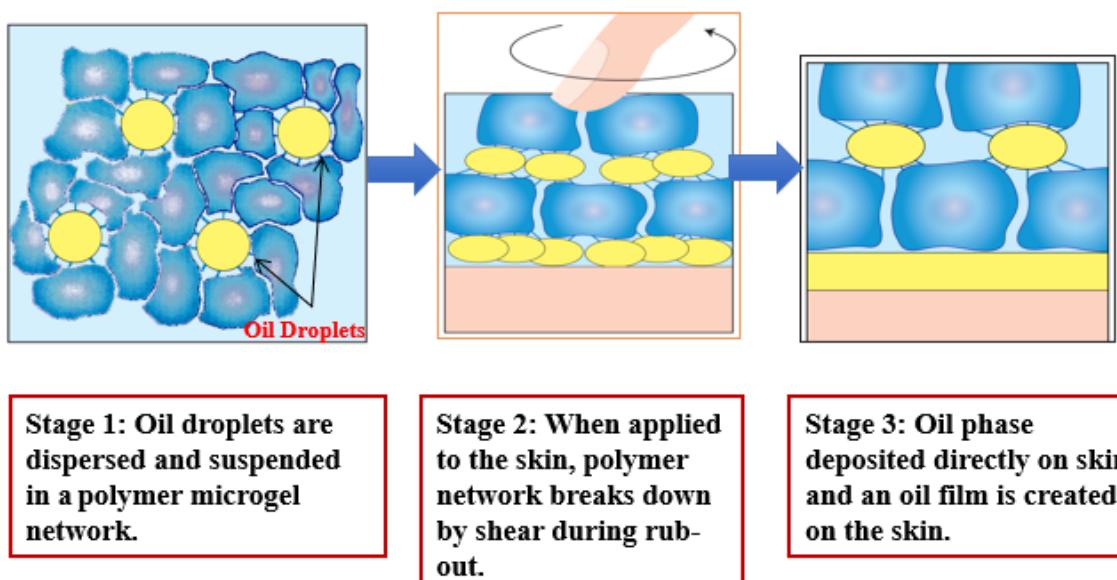
When introducing biopolymers to synthetic polymer-based systems, Diutan Gum showed the greatest impact on synthetic polymers in storing the deformation energy. The occurrence of the peak in  $G''$  curve suggests a consistent, three-dimensional network of the system at rest, and that the breakdown of the integrated bulk started with micro cracks and displayed a delay in energy dissipation. With increased strain applied, a macro crack ruptured the entire system at the end and the sample flows as a whole. Hence, in the case of non-crosslinked L10 polymer, Diutan Gum is the most efficient in building up the network. However, the strong double helix network building capability of Diutan Gum may lead to stringiness in application. Regarding stringy behaviour, Tara Gum exhibited an impact on shifting the  $\text{Tan}(\delta)$  of all the systems to the elastic end at high frequencies, promoting brittle fractures and thus reducing the stringiness [14].

As frequency sweeps give information about long-term behaviour by slow motion, stability profile can be predicted at low frequencies [14]. The rheology analysis results are in line with stability observations where the L10 control sample failed the centrifuge test with a clear

phase separation while biopolymer-based L10 samples all passed the centrifuge test. The other synthetic polymer-based systems displayed dominant elastic behaviour showing  $G' > G''$  at low frequencies or even across the whole frequency range. The rigidity of the system throughout the whole frequency range is related to the crosslink level of polymers. All Diutan Gum-based systems showed gel-like character with presumable stability at rest.

The texture and sensory evaluation of the model sunscreen formulations confirm the feasibility of using biopolymers and synthetic polymers to attain a variety of tangible product features that can help distinguish the products on the market.

The *in vitro* SPF and UVAPF analysis results further validated the efficiency of the emulsifier-free systems in fulfilling the functions of UV filters. Furthermore, the 80 min water immersion tests substantiated the hypothesis that macromolecules such as polymers can help improve water resistance because there is no re-emulsification when rinsed with water (**Figure 7**). Oil droplets are suspended and stabilized by a polymer-based network and exhibit good stability at rest. When applied onto the skin, the shear force induced by rubbing breaks down the network of polymers and the oil phase released from the structure forms a layer on the skin which cannot be emulsified when rinsed with water in absence of surface-active agents.



**Figure 7.** Schematic diagram of the mechanism of water-resistant property of O/W emulsions achieved by polymer-based emulsifier-free technology.

The SPF and UVAPF values assessed *in vitro* did not show a strong correlation with the type of polymers, nor did the degree of water-resistant level. Such observations confirm the limited interaction between polymers and the oil phase, making the performance consistent and predictable.

### **Conclusion.**

Biopolymers with excellent sustainability profiles can be used as formulation strategies to formulate stable and high-performing emulsifier-free sunscreen products, offering a well-demanded collection of textures and sensory. The findings on the polymer-polymer interaction in the O/W emulsions and corresponding rheology behaviour can be useful references for formulators to develop innovative emulsifier-free sunscreen products.

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### **Conflict of Interest Statement.**

NONE.

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