Synergy of A Microbial Polysaccharide and A Hydrophobically Modified Hydrophilic Polyurethane on Thickening and Stabilization at Extreme Conditions

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Introduction:

The beauty industry has been looking for high performing ingredients to achieve innovative and quality products. With an increasing demand for various kinds of actives, requiring either high use level or specific environment to function, technology challenges come along. Extreme conditions such as low pH (≤4) (effective environment), high oil loading, and high temperature (≥50˚C), pose formulation barriers for the industry to achieve stable and quality products (1-3). Microbial polysaccharides attract great attention because of their biocompatibility, biodegradability, and sustainability (4-6). Studies have revealed that a microbial polysaccharide-Diutan Gum possesses interesting physicochemical features i.e. thickening and stabilizing (7-9). A novel combination consisting of Diutan Gum and Polyurethane-62 was investigated systematically on its performance in mucilage and emulsion systems at extreme conditions such as extreme pH environment, high oil loading, and elevated temperature. Aqueous gel formulations using Diutan Gum and Polyurethane-62 were prepared and assessed. The gel structure was investigated by rheology experiments. Emulsion systems stabilized by Diutan Gum and Polyurthane-62 were formulated and characterized to identify the capability of the combination in stabilizing the system.

Materials & Methods:

Materials

Microbial polysaccharide (Diutan Gum), Polyurethane-62 (PU-62), Cocoyl Adipic Acid/Trimethylolpropane Copolymer (CATC), Caprylic/Capric Triglyceride (GTCC), polyol (glycerin, propylene glycol, butylene glycol), uncoated non-nano Zinc oxide (ZnO) and coated Titanium dioxide (TiO2) were used as supply. Acid neutralizer used was citric acid diluted by 2-fold and basic neutralizer used was sodium hydroxide as 18% aqueous solution.

Table-1 Formulation chart for mucilage, emulsion, pigment suspension in aqueous gel and emulsion.

Phase	Ingredient	Mucilage	Emulsion	Pigment suspension	Pigment emulsion
A	Deionized water	q.s	q.s	q.s	q.s
	Diutan Gum	0.1 - 0.5	0.2	0.3	0.3
	PU-62	0.5 - 1.5	1.0	1.0	1.0
	Glycerin	-	-	-	5.0
	Propylene Glycol	-	2.0	-	-
	Butylene Glycol	-	3.0	-	-
	Phenoxyethanol	0.50	0.50	0.50	0.5
	Disodium EDTA	0.20	0.05	0.05	0.05
B	Neutralizer	q.s	-	-	-
	Oil phase	-	10 – 70	-	10 – 20
	Pigments	-	-	2 – 10	2 – 10

Formulation characterization

pH measurement was conducted using pH meter at room temperature. Apparent viscosity was measured using viscometer at room temperature. The approximate yield value of formulations was calculated by measuring at multiple shear speeds.

Transmitted light microscopy

Digital Microscope was used to access the emulsion system and pigment suspensions and emulsions. A small amount of emulsion samples was placed on a microscope slide without dilution and covered by a cover glass slip. Samples were observed under transmitted light at 500 times magnification.

Rheology

Rheometer was used to evaluate the internal structure and rheology of the system. Rheology experiments including amplitude sweep, frequency sweep, flow ramping, and temperature ramping, were conducted to study the viscoelastic properties of PU-62 and Diutan Gum systems.

Results & Discussion:

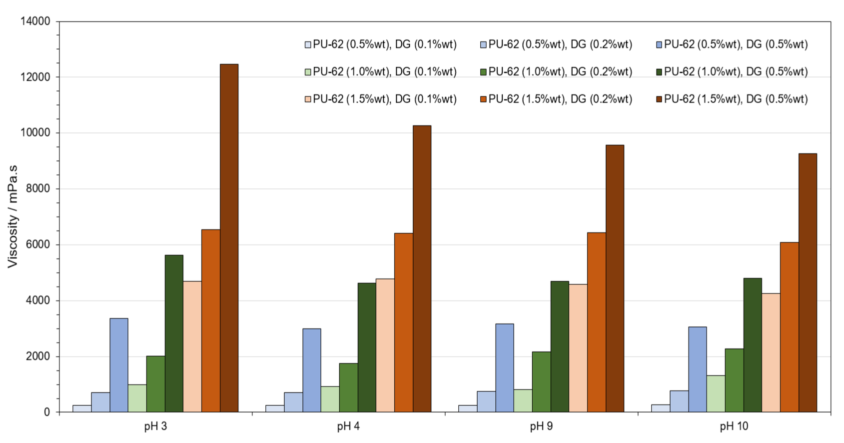

Figure-1 Viscosity of PU-62 (0.5%, 1%, 1.5 %) and Diutan Gum (0.1, 0.2, 0.5%) aqueous gel systems at extreme pH environment.

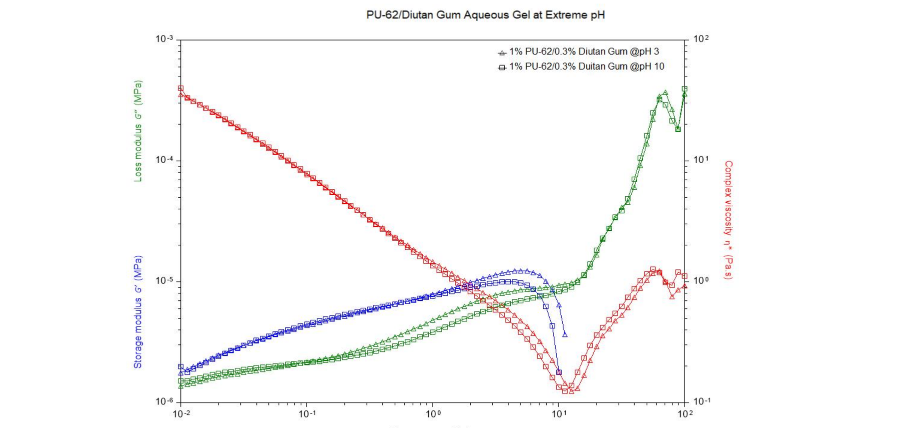

Figure-2 Rheology analysis using frequency sweep (0.01-10Hz) of PU-62 (1%) and Diutan Gum (0.3%) aqueous gel systems at pH 3 and pH 10 at RT.

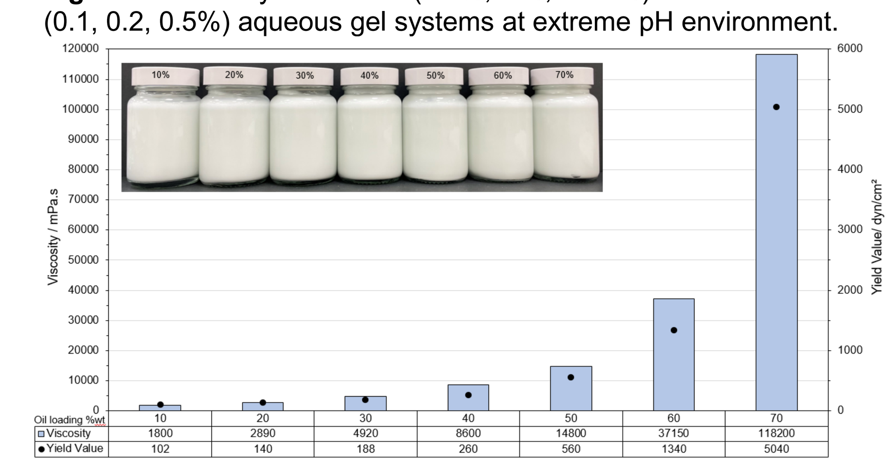

Figure-3 Oil loading capacity of PU-62 (1%) and Diutan Gum (0.2%) with 10-70% GTCC emulsion (pH range 4-5).

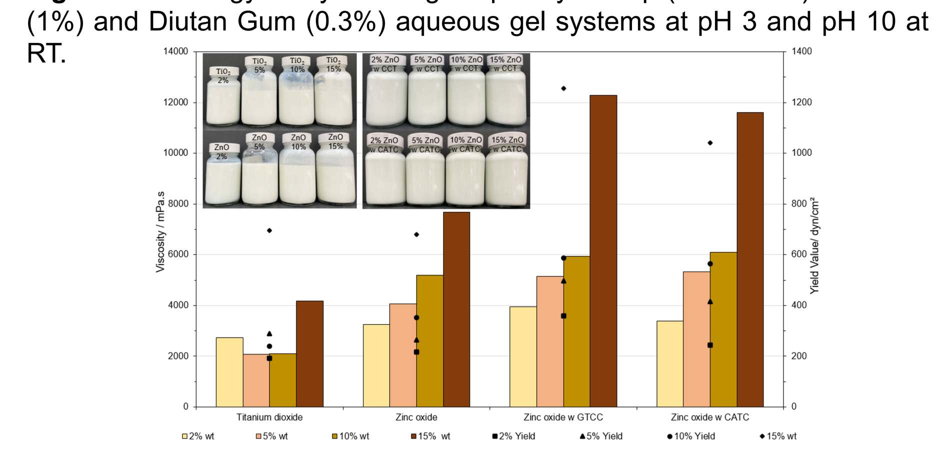

Figure-7 Suspension of 2-15% inorganic pigment aqueous gels (pH range 5-7 for TiO_2 and pH ~9 for ZnO) and O/W emulsions (pH 8-9) stabilized by in PU-62 (1%) and Diutan Gum (0.3%).

Thickening at extreme pH environment. The viscosity and yield value of aqueous gel thickened by PU-62 and Diutan Gum revealed that the water thickening properties of PU-62 and Diutan Gum were not affected by the extreme pH environment, neither the gelation strength. When existing in a high of low pH environment, PU-62 and Diutan Gum combination demonstrated the gelling properties and stability of the gel systems as the same as the systems in neutral pH range (pH 6-7) and the viscosity and yield built are directly related to the concentration and rheological properties of the polymers.

High oil loading capacity. The O/W emulsion stabilized by PU-62 and Diutan Gum exhibited a great flexibility of oil content that can be incorporated into the system. On the contrary, in conventional emulsifier-based emulsion systems, the higher the oil content usually results in larger oil droplet size in emulsion and provide lower yields values (11, 12). The mechanical spectra of 10%, 20% and 50% GTCC emulsions suggest that all emulsions were stable at rest providing an elastic response at low frequencies but at high frequencies, a viscous liquid took over indicating broken-down of entanglements and samples became more liquid like. The dependency and behavior of G′ and G″ on frequency reveal that PU-62 and DG system provides an elastic network at rest and whereas under shear, such interactions will be disrupted and material starts to flow, which ensures an ease of application for personal care products. When heated to an elevated temperature (60°C), the gel system was well retained (phase angle <45°). The system also showed good resistance to high temperature that there was no loss of gel structure.

Pigment suspension. PU-62 and Diutan Gum combination showed good compatibility with pigments tested. Both TiO_2 and ZnO can be dispersed and stabilized in the aqueous gel structured by PU-62 and Diutan Gum, although at high use level of non-nano ZnO, there was agglomeration observed of pigment particles under microscope. Although there is no suspension provided by PU-62, PU-62 can be a good dispersant for pigment because it can facilitate the wetting process by assembling the hydrophobic ends towards pigment particle and hydrophilic backbone connected to water phase on the interface. On the other hand, Diutan Gum played an important role in suspending the pigment particles. Both pigment suspension showed linear viscoelastic region with ZnO slightly greater than TiO_2.

Conclusions:

The results demonstrated high performance of the combination of Polyurethane-62 and Diutan Gum on thickening efficiency, stabilization, and suspension. The aqueous gel system displayed consistent structure robustness of the formulations at extreme pH environment and in the presence of pigments. The combination also exhibited outstanding stabilization capability for a wide range of oil loading. The rheology studies revealed that such combination provided viscoelastic structures with suspension and stability at high temperature. Emulsions stabilized by the combination showed interesting rheology behavior, which enables new sensory of formulation.

Significant synergistic effect was observed between Diutan Gum and polyurethane on thickening the system at extreme pH conditions and keeping the performance at elevated temperatures. The gel network built on double helices and florets under van der Waals forces, hydrophobic interaction and hydrogen bonding showed improved stability in extreme conditions. The emulsion system can be efficiently stabilized by such combination at low use level with a pleasant soft and silky sensation.

The synergy of Diutan Gum and Polyurethane-62 exhibits commercial importance to address challenging systems with improved stability and performance.

Aknowledgments:

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