Achievable pickering emulsion with a high MW, amphiphilic polyurethane polymer for suncare and colour cosmetic applications

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Introduction:

A pickering emulsion where inert solid particles position themselves at the oil-water interface offers several advantages over traditional emulsions, including increased stability against coalescence. There are, however, several formula restraints to get a stable pickering emulsion. Particles must be of an appropriate shape/morphology, wettability, concentration and presence of any other emulsifiers.

By utilizing the unique properties of a high MW, amphiphilic polymer, it enables ease of formulating pickering emulsion which differentiates this polymer from other emulsifiers. Based on a nonionic associative polyurethane technology (Fig. 1), with block polymers of hydrophobic and hydrophilic parts to provide anchoring points for pigments. It means the polymer can emulsify and stabilise a high pigment load compared to traditional emulsifiers which have lower MW and less anchoring points, thus reduced ability to stabilise high pigment load.

Figure 1 “HEUR” Technology (HEUR = Hydrophobically-modified Ethylene-oxide Urethane Rheology modifier). The polymer is amphiphilic, like a surfactant, and therefore interacts with ingredients in both the aqueous phase and the dispersed phase to create thickening and emulsion stabilization.

The polymer has a very high molecular weight, like that of polymeric emulsifiers, but it is a linear chain, no crosslink. Within the hydrophilic backbone, it consists of block sections of hydrophobic parts in green, and hydrophilic parts in blue. The polyurethane polymer behaves similarly like a surfactant in water.

Materials & Methods:

Several sunscreen systems (O/W and W/O pickering emulsion) with inorganic UV filters at high concentrations were evaluated. Accelerated stability and freeze-thaw cycles were performed to test emulsion stability.

Presence of Pickering Emulsion: Emulsion was viewed under a digital microscope Keyence VHX-2000 at room temperature for the presence of pickering emulsion at x500 and x1000 zoom.

Additionally, W/O pickering emulsion was extended to colour cosmetics applications, namely in a hydra lipstick and concealer stick.

Microstructure W/O Pickering Emulsion was viewed with fluorescence confocal microscopy. A Leica TCS SP5 laser confocal microscope (Leica Microsystems Heidelberg GmbH, Manheim, Germany) equipped with a DMI6000 inverted microscope, blue diode (405nm), Argon (458/476/488/496/514), diode pumped solid state (561nm) and HeNe (594/ 633nm) lasers and 20x PL APO CS Numerical Aperture 0,70 objective lenses was used.

Stick Harness and Stiffness: Measurements have been made using a TEXTURE ANALYSER XT PLUS, with a special fixure to hold the lipstick and a probe device that apply a force to break the lipstick. The lipstick tested was placed in the fixture at the bottom of the texture analyzer. The device is applied on the lipstick until it breaks, and the texture analyzer measures the force needed to break. There is direct correlation with this force and the resistance/ harness of the lipstick. Repeat: 6 pcs of lipstick.

Results & Discussion:

Mineral sunscreen formulas with high pigment loading (25-30% w/w) were successfully stabilised by the high MW amphiphilic polymer. The presence of zinc oxide and titanium dioxide achieved the formation of pickering emulsion, which was further stabilised by the polymer. When the formula was repeated without UV filters and without the polymer, instability and, in some instances, separation was observed.

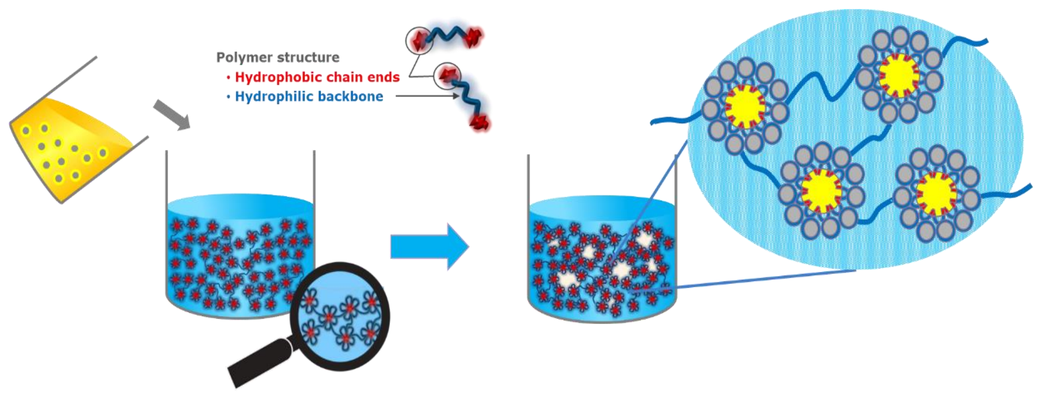
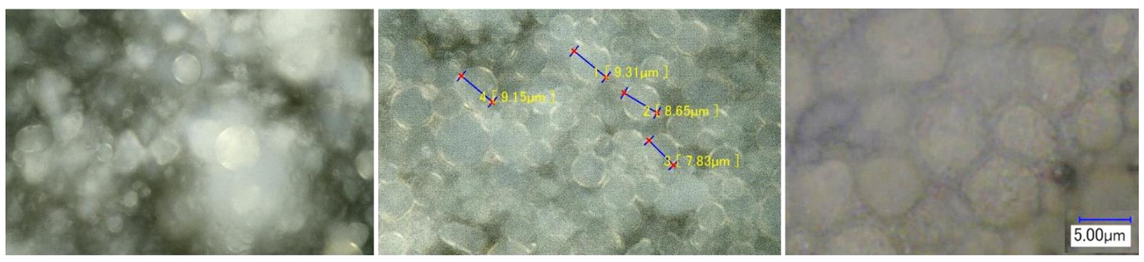


Figure 2 Diagrammatic representation of O/W pickering emulsion when utilising the polyurethane polymer from Lubrizol

For a pickering emulsion, the extra layer of solid particles sits at the interface between oil and water, providing an added stability. The polymer deposits at the interface (Fig. 2) , forming a unique U shape, with hydrophobic ends on the oil surface, and the linear backbone in the aqueous phase. The linear backbone stretches along the interface between oil and water, strengthens individual emulsion droplets and makes it easier to stabilise high pigments.
When viewing the emulsion under a digital microscope, the emulsion structure is evenly distributed, with even emulsion sizes. Sample without the polymer was unstable to be viewed clearly under the microscope, it was difficult to achieve a clear image (Fig. 3, left). We can see the pickering emulsion structure where a layer of solid particles enveloping each oil droplet. The distribution of the oil droplets is uniformly spaced and uniform in size, thanks to the unique property of the polymer in stabilising pickering emulsion (Fig. 3, right).



SU-0103 without the polyurethane polymer

SU-0103 with the polymer

Figure 3 Digital microscope of the O/W pickering emulsion sunscreen representative formula

Conclusions:

A high MW, amphiphilic polyurethane polymer provides ease when formulating pickering emulsion for several reasons. The polymer is amphiphilic, with hydrophobic ends and a hydrophilic backbone. The MW of the polymer is high, and with a linear backbone made of block copolymers it has more anchoring points to stabilise pickering emulsion. The polymer deposits at the interface, and aligns the solid particles on the interface, fixing and stabilising the pigments so they are unable to aggregate. The particle surface properties will influence o/w or w/o system. With the polymer functioning like a skeleton structuring agent, it provides flexibility to select pigments, without the need to measure contact angle. The applications of a pickering emulsion are limitless. In O/W emulsion, W/O emulsion and W/O stick.

References:

1. Ortiz, D.G., et al, 2020, Current Trends in Pickering Emulsions: Particle Morphology and Applications, Research Material Science and Engineering, Elsevier, Volume 6, pg 468-482