**Impact of the Degree of Polymerization and Amino Group Addition on the Emulsifying Properties of Polyglycerol Esters.**

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**Highlights**

* Microwave radiation shortens the reaction time for the etherification of glycerol to polyglycerols.
* New emulsifiers based in polyglycerol were synthesized.

It is possible to produce emulsifiers with different functional properties by varying characteristics such as degree of polymerization and electric charge.

**1. Introduction**

 The conversion to valued-added chemicals of the glycerol co-produced in the growing biodiesel industry is nowadays a focus of global research and a topic of great industrial importance. Among different approaches, the glycerol polymerization emerges as a promising alternative, leading to the formation of Polyglycerol (PG). Moreover, polyglycerol has been used as raw material for the production of polyglycerol esters, which are widely used as emulsifiers in different industries [1].

The properties of the emulsifiers and their particular applications depend on their structure. In the case of polyglycerol esters, it is possible to produce emulsifiers with different functional properties by varying characteristics such as the degree of esterification [2]. However, those properties are not only determined by the hydrophobic tail but also by the hydrophilic head features, for instance, the size or degree of polymerization and the electric charge.

In this work, we synthesized new emulsifiers based in PG and also analyzed the effects of degree of polymerization of polyglycerol and the cationic charge by Lysine amino acid addition on the emulsifying properties of polyglycerol esters The degree of polymerization leads to the synthesis of polymers with a variation of molecular weights and pendant hydroxyl groups. Meanwhile, the positive charge gives to the polymers the ability to absorb on negatively charged substrates to produce an antistatic and hydrophobic effect which is useful for a range of applications such as softeners and anti-static additives in textiles and, bitumen emulsifiers due to their compatibility with a range of aggregates [3].

**2. Methods**

Microwave radiation was used as the heat source in the synthesis of polyglycerol esters to reduce the reaction times compared to conventional thermal heating [4]. In order to form polyglycerol with different degrees of polymerization, the reaction was first carried out up to the gel point, i.e., an infinite polymer network first appears and the polymerization system loses its fluidity drastically. After the termination of the gel point time, a polyglycerol sample was collected every 30 percent of the previously determined gel point. Polyglycerols with different degree of polymerization were characterized by Fourier transform infrared spectroscopy (FTIR) to confirm their chemical structure, the hydroxyl numbers were calculated according to ASTM D 4274-11 Test Method A, and molecular weight distributions were obtained using High-Performance Liquid Chromatography (HPLC) measurements.

Polyglycerol esters were synthesized using a proposed strategy of prepolymers complexes addition. Those complexes consist of glycerol esterified with (i) oleic acid and (ii) Lysine. This strategy was followed to guarantee the successful esterification of PG with each of these components. Infrared measurements confirmed the chemical structure of the synthesized complexes and their esterification reactions with PG. The hydrophilic-lipophilic balance (HLB) values of the emulsifiers from polyglycerol esters were calculated. Microscopy techniques studied the type of the resulting emulsion. The rheology, surface, and interfacial properties were also evaluated. The stability of emulsions, one of the more critical factor to be considered in the emulsion technology, was investigated and discussed at different concentrations of emulsifier and water-oil ratios (WOR) of emulsions. To measure emulsion stability, we used the half-life period.

**3. Results and discussion**

Polyglycerols with different degree of polymerization were synthesized. FTIR Results showed that functional groups presented in the reaction polymerization products are the same as polyglycerol functional groups identified in previous research studies [5]. Multimodal weight distributions were observed for all samples, and the number-average molecular weights and weight-average molecular weights showed an increase with the reaction time while the number of hydroxyl groups exhibited an expected decrease due to the progress of the polymerization. The esterification of polyglycerol with oleic acid and Lysine, through the proposed strategy of the addition of complexes, was corroborated by FTIR spectroscopy with the appearance of the bands associated with ester bonds. The hydrophilic properties of the emulsifiers increased with the molecular weight of polyglycerol. The degree of polymerization and the presence of the amino group in the modification of the PG determined the final characteristics of the type of emulsion, varying from the formation of W / O emulsions to O / W emulsions. The emulsions presented good stability that was examined using palm oil as the oil phase and distilled water as the aqueous phase.

**4. Conclusions**

The current study took advantage of the heating by microwave radiation in shortening the reaction time required for polymerization of glycerol. New emulsifiers were obtained from polyglycerol esters with fatty acid and amino acid. It was found that the structure of Polyglycerol ester emulsifiers could be tailored to stabilize different emulsion systems. The degree of polymerization and the amino group addition to polyglycerol esters influence the emulsifying Properties. Therefore, emulsifying properties of synthesized polyglycerol esters can be easily adjusted for target applications, this being of great interest for the industry of emulsion based products.

**References**

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