Click-derived triazole chitosan as a bio-based polymeric emulsifier for oil-in-water emulsions: a comparative formulation study and simulation-guided insight into interfacial stabilization

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The development of sustainable emulsifiers from renewable polymers is an important challenge in colloid and interface science. Chitosan (CS) is an attractive bio-based candidate owing to its biocompatibility, biodegradability, film-forming ability, and broad functionalization potential. However, its practical use as an emulsifier in oil-in-water (O/W) systems is often limited by weak intrinsic amphiphilicity, pH-dependent solubility, and insufficient interfacial activity under formulation-relevant conditions.
In this study, CS was structurally modified with a triazole-phenyl moiety through Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) click chemistry to tune its hydrophilic-hydrophobic balance and investigate how click-derived structural changes affect emulsion stabilization behavior. The emulsifying performances of native CS and click-derived triazole CS were comparatively evaluated in O/W emulsions using the creaming index and volume-weighted mean droplet diameter D[4,3] as principal stability descriptors. To obtain a systematic understanding of formulation-dependent behavior, the effects of pH, oil volume fraction, and emulsifier concentration were further analyzed by response surface methodology (RSM), enabling identification of stability trends, interaction effects among formulation variables, and operating windows in which each material exhibited distinct colloidal performance.
The results showed that chemical modification of CS significantly altered its emulsification characteristics, leading to measurable differences in droplet size, macroscopic phase stability, and sensitivity to formulation conditions. Compared with native CS, the modified CS exhibited enhanced emulsion stability and more robust formulation behavior over a wider condition range, including systems containing relatively high oil fractions.
Importantly, the modified CS did not exhibit uniformly superior behavior under all tested conditions, indicating that enhanced hydrophobic character alone is insufficient to guarantee optimal stabilization and that emulsion performance is governed by a complex balance among polymer solubility, conformational flexibility, interfacial adsorption, and continuous-phase structuring. In addition to emulsification performance, antioxidant activity was evaluated to assess whether click-derived modification could introduce added functionality beyond colloidal stabilization, further supporting the design of multifunctional bio-based emulsifiers.
To complement the experimental findings, molecular simulation is currently being conducted to elucidate the interfacial affinity, preferred molecular organization, and adsorption tendency of the modified CS at the oil-water interface. This simulation work aims to provide mechanistic insight into the contribution of the triazole-phenyl group to interfacial localization and molecular arrangement, with the goal of rationalizing the experimentally observed differences between native and modified CS in terms of interfacial packing and polymer-medium interactions.
Overall, this combined experimental, statistical, and simulation-based study provides a structure-property-function framework for understanding click-functionalized CS in O/W emulsion systems. The findings demonstrate that triazole-based modification is an effective strategy for tuning CS toward bio-based emulsifier applications, while also establishing a foundation for the future development of nanoparticulate or hybrid particulate stabilizers, including systems incorporating bio-waste-derived components for sustainable Pickering-type emulsification.

Keywords:
Chitosan; Click chemistry; Oil-in-water emulsion; Bio-based emulsifier; Response surface methodology; Molecular simulation

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