Dendritic polymer as biocompatible oil spill dispersants: molecular interactions and effectiveness

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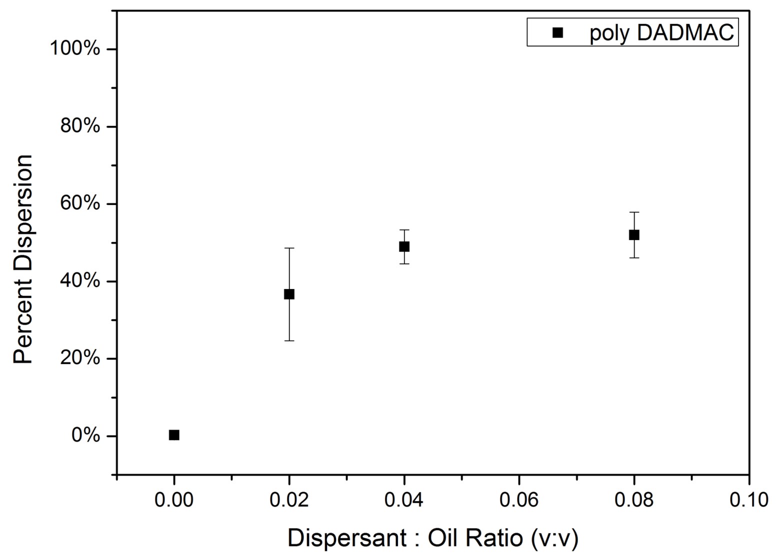
Abstract

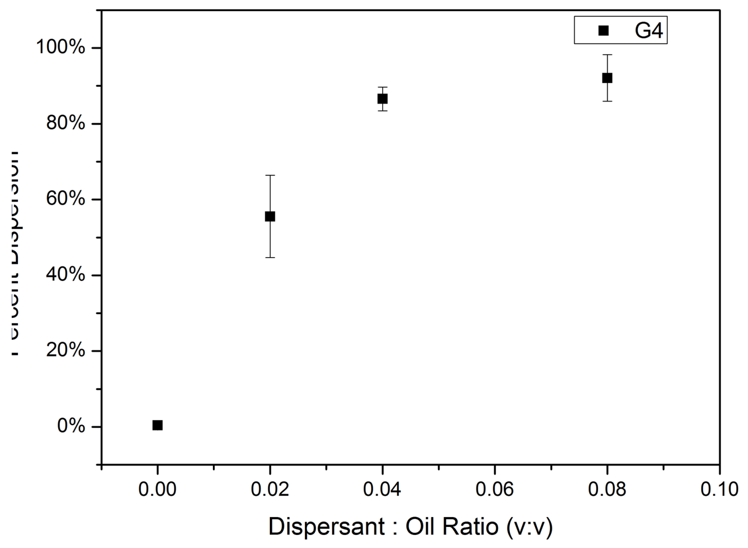
The Deepwater Horizon incident released over 200 million gallons of crude oil to Gulf Mexico; exerting an extreme impact on marine life. The dispersant Corexit 9500A was used to disperse the oil; this was the largest dispersant application in history and the first time it was used in the deep sea. Positive results from the dispersants (fewer oil-soaked beaches), mean dispersants will most likely continue to be an important component of future oil-spill remediation efforts; however, there are negative considerations to address, like toxicity. In order to develop a more beneficial material a fundamental understanding of dispersant-hydrocarbon assembly and dispersant-hydrocarbon biocompatibility are important. Recent investigations have shown that dendritic polymers are capable of encapsulating PAHs and other hydrophobic compounds, and can be engineered to increase their biodegradability. We thus hypothesize that crude oil can be dispersed using these materials. Our objective is to probe the molecular interactions between dendritic polymers and hydrocarbons, taking toxicity and biocompatibility into consideration. Lab results from dispersant effectiveness tests show that poly(amidoamine) dendrimers and hyperbranched poly(ethyleneimine) polymers increase the dispersion of crude oil. Ongoing efforts are using the interfacial tension, contact angle and bonding model to understand the mechanisms of the high dispersion capabilities. We are also examining the toxicity and biocompatibility of the dendritic polymers compared to Corexit 9500A.

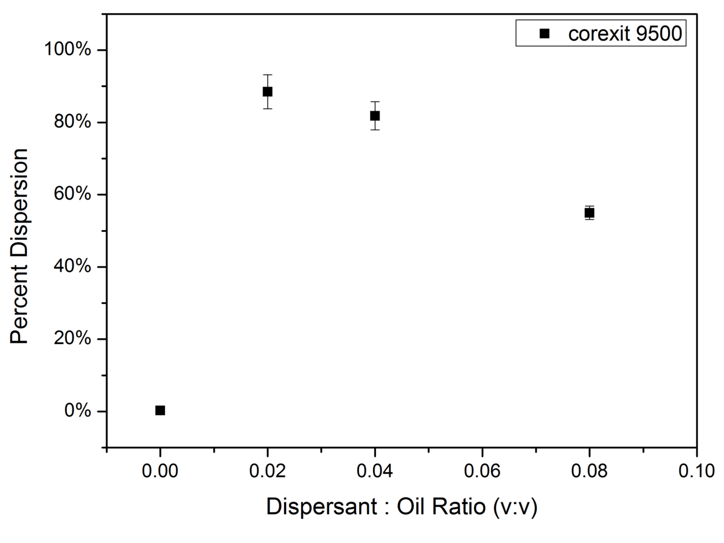
Methods

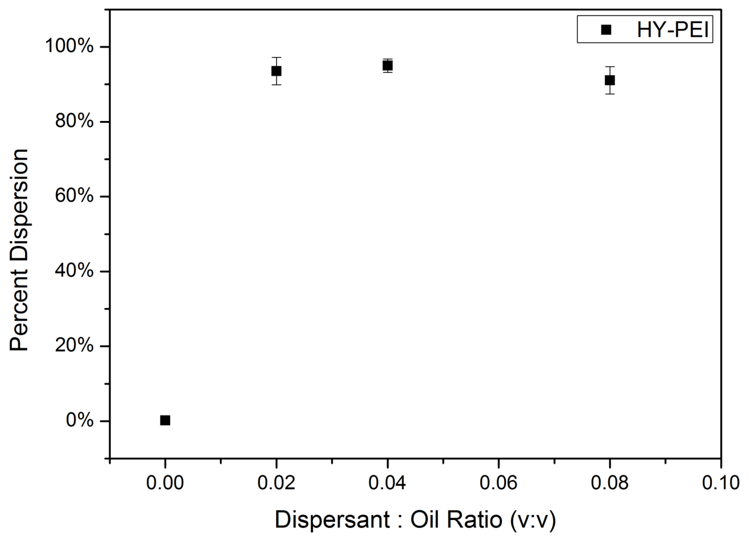
- Dispersant effectiveness tests used dichloromethane extractions to quantify dispersion. Dispersant to oil ratio (DOR) was varied. Drop size distribution analysis by microscope method .
- Photosynthesis inhibition experiments used a cyanobacterial strain, *Synechocystis* sp., grown in BG11 media and a seawater algal strain, *Dunaliella* sp., grown in DY-V media. pH indicater was added to a vial with algae, oil, and dispersants, and absorbance was measured to track pH changes caused by CO2 utilization.

Dispersion Effectiveness Results



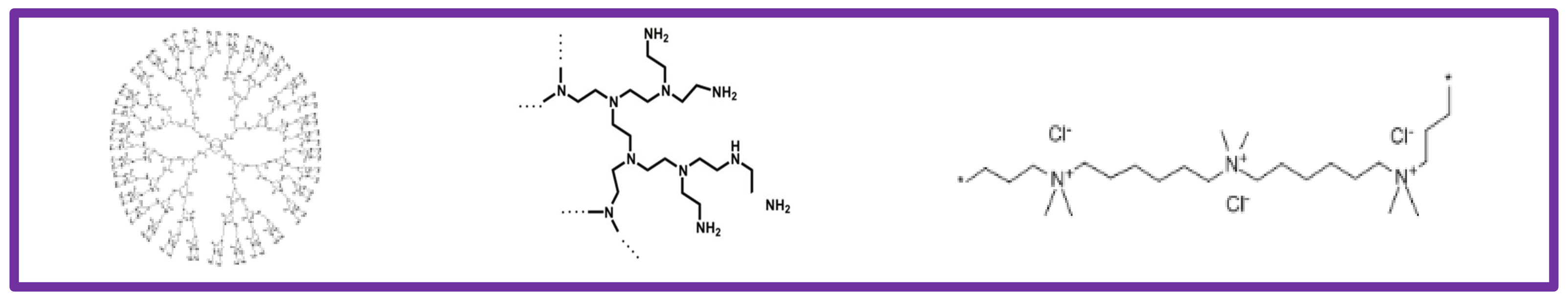




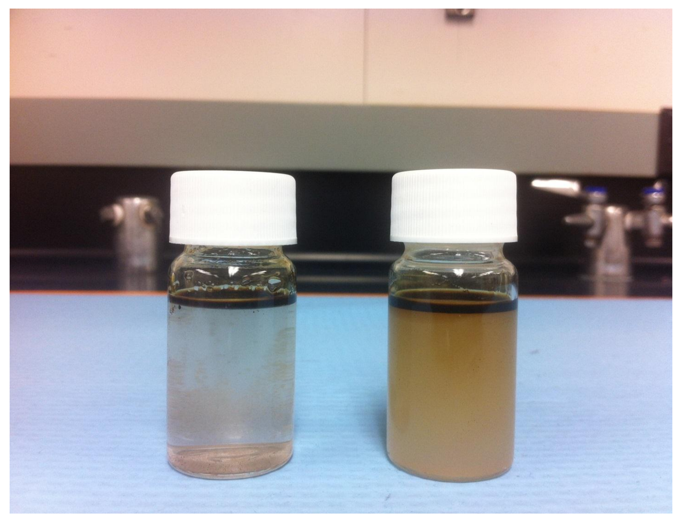


Materials

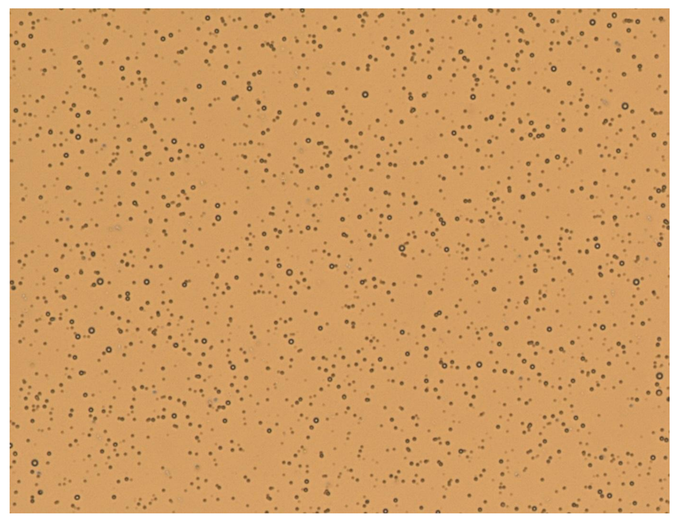
- G4-PAMAM dendrimer, formula $[NH_2(CH_2)_2NH_2]$:(G=4);dendri $PAMAM(NH_2)_{64}$; MW: 14,214
- Hyperbranched polyethylenimine polymer (or HY-PEI, formula (-NHCH2CH2-)x[-N(CH2CH2NH2)CH2CH2-]y); MW:1200/1800/10000/70000/750000
- Polydiallyldimethylammonium chloride (polyDADMAC)
- Corexit 9500
- Louisiana light sweet crude (LLS) oil



Drop Distribution

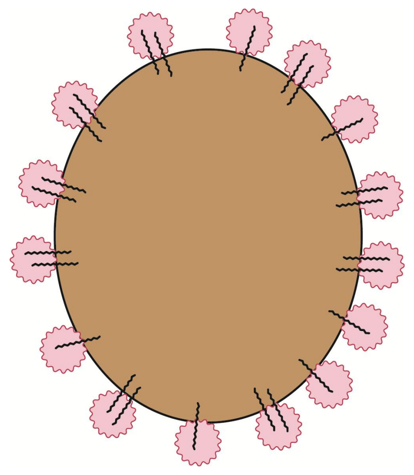


(a) Oil in water (b) oil with HY-PEI in water

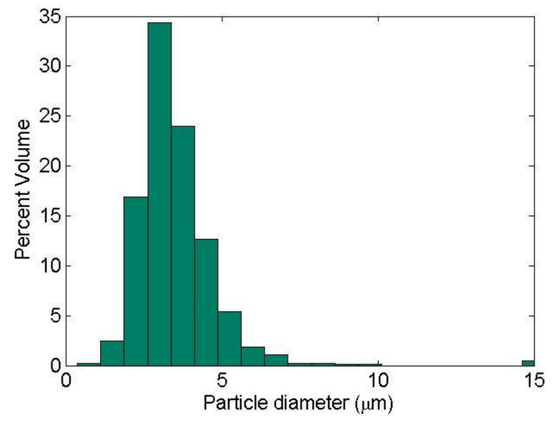


Oil droplet under microscope (dispersed by HY-PEI)

Pendent drop (a) mixture of oil and Corexit (b)oil only



Model of oil and polymer interaction



Drop size distribution of dispersed oil by HY-PEI

Acknowledgement

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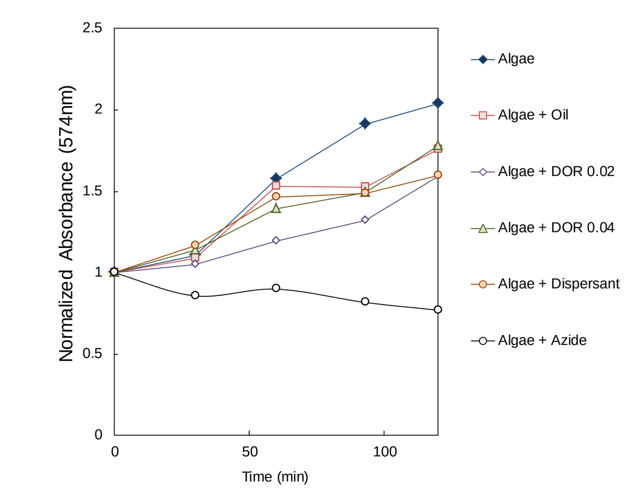
- Nalco provided Corexit 9500

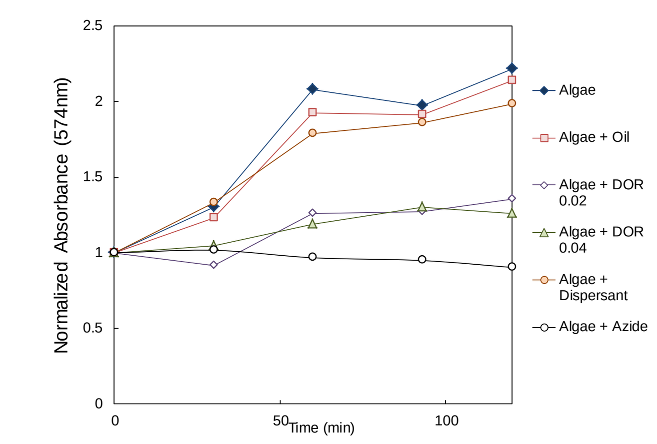
Ongoing and future work

- Evaluation of other dendritic polymers for dispersant effectiveness and toxicity.
- Molecular dynamics modeling to elucidate interaction mechanisms between oil and dispersants.
- Evaluation of interactions between dendritic polymers and natural organic matter when dispersing oil.
- Investigation of distribution and fate of dendritic polymers and hydrocarbons in algal cells.

Toxicity Results



Photosynthesis inhibition results from HY-PEI with *Dunaliella*.



Photosynthesis inhibition results from HY-PEI with *Synechocystis*.

Conclusions

- Dendritic polymers demonstrate oil-dispersing effectiveness due to their hosting capacity for hydrocarbons. The amphiphilic nature of the polymers allows them to remain soluble even after hydrocarbon capture.
- The oil-dispersing ability of HY-PEI is as good or better than Corexit 9500, particularly at higher DOR.
- G4 dendrimers were less toxic than Corexit in terms of photosynthesis inhibition for the saltwater algae *Dunaliella*. The result was different for the fresh-water cyanobacteria *Synechocystis*; G4-oil combinations were inhibitory, G4 alone was less harmful, and Corexit caused minimal inhibition. Thus, speceis and matrix are important for photosynthesis inhibition tests, and likely for other toxicity tests.

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