

IFSCC 2025 full paper (IFSCC2025-1631)

"Improving Biodegradability in Non-ionic Associative Surfactant Thickeners"

1. Introduction

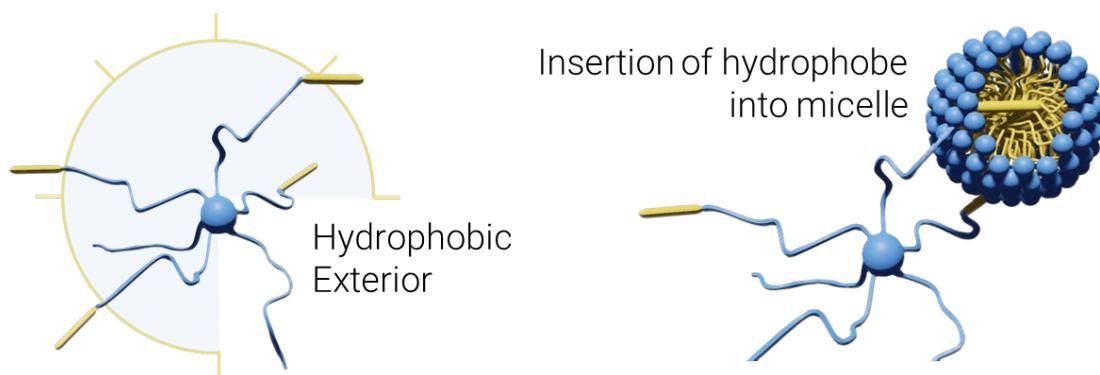
Environmental lifetime assessment has become a routine expectation in the development of new products, with a strong influence on consumer goods[1]. In particular, cosmetics and personal care formulations raise concerns due to the regular introduction into wastewater as the end of their life cycle[2]. With hundreds of millions of units sold and high package volume, rinse-off applications account for a substantial portion of personal care products entering waste streams[3]. This presents an obvious need to develop materials which can serve consumer needs with desirable performance while minimizing bioaccumulation. Research pursuing this goal requires both a reliable standard of biodegradability and an expansion of the corresponding structure-property relationship in molecular design.

To address the need for a widely accepted biodegradability metric, the Organization for Economic Co-operation and Development (OECD) has developed methods capable of evaluating the environmental persistence of manufactured chemicals. While there are many microbes capable of digesting synthetic materials, through both breakdown and assimilation, consideration of the actual conditions must be made to provide reliable methodology for evaluating general biodegradability. For this reason, the OECD 301 series of tests utilize inoculum sourced from wastewater treatment plants to provide a reasonable profile of bacteria to represent the conditions many man-made goods will be subjected to in their final fate. It has largely become considered to be a gold standard of biodegradation, with growing emphasis on the 301B test, which measures carbon dioxide generated by complete breakdown of a chemical's carbon content. However, the OECD 301 A-F tests carry very specific conditions regarding compatibility of materials with the test system, leaving some compounds to fall within a range that cannot be properly tested with respect to the methods' published scope.

It is typical for manufacturers to extrapolate existing data to new chemicals through comparison of a representative compound with a similar structure. However, there often exist certain subtleties in property-structure relationships that can drastically alter the bioavailability of materials consisting of chemical domains which themselves are well known to degrade. For example, polylactic acid is a common renewable and highly biocompatible material which has gained rapid popularity in recent decades, finding use from bulk plastic markets to fine

biomedical applications[4]. However, due to the development of highly crystalline and high molecular weight poly lactic acids, such as poly L-lactide, poly D-lactide and mixtures thereof, these materials have inhibited degradation rates due to a loss of bioavailability, from the enhanced properties which give make them attractive for applications[5].

To design materials to be sustainable, the full lifecycle must be scrutinized to identify the range of properties needed to assess renewability and biodegradability. Non-ionic associative surfactant thickeners are designed to physically link surfactant secondary structures (Scheme 1) and are used almost exclusively at concentrations <10% in mixtures containing one or more anionic, cationic or non-ionic surfactants. Sorbeth-230 tetraoleate (SOR230-TO) is an example of a highly effective non-ionic associative thickener, requiring only 0.5-4% in applications. Herein we examine the biodegradation kinetics of SOR230-TO through evaluation of structural variations. Also investigated is the impact of the presence and absence of anionic surfactant to simulate its use in consumer rinse-off products.



Scheme 1. Structure of 6-arm associative thicker and insertion of hydrophobe into micelle

2. Materials and Methods

2.1 Synthesis of Hydrophobically Modified Star Polymers

Associative thickeners were synthesized by esterification of polyethoxylated sorbitol with commercially available fatty acids. Reaction temperatures varied between 120 and 200 °C, and all were conducted under inert atmosphere. Sorbeth prepolymers were prepared with degrees of polymerization 50, 135, 230, 300, 350, and 400. Fatty acids were selected from either oleic acid, stearic acid or 12-hydroxystearic acid (12-HSA). Non-sorbeth polymers were obtained from commercially available sources.

2.2 Biodegradation Protocols

For comparative experiments, a protocol compliant with OECD 301B requirements was selected, as it represents the most rigorous condition. The concentration of conditioned activated sludge was set at 30 mg/L total organic carbon (TOC), and the test substance concentration was set at 20 mg/L TOC. For systems containing surfactants, blanks contained the equivalent amount of surfactant to allow subtraction of the corresponding degradation in the test solutions. Batches were performed in duplicate and included duplicates for the blank and benzoic acid reference standard. All OECD 310B CO₂ evolution tests were performed by a third-party, certified analytical laboratory. Results are summarized in Table 1.

SOR230-TO and sorbeth-230 pentastearate were additionally evaluated using an ISO 14851 compliant protocol. The concentration of conditioned activated sludge was set at 50 mg/L and the test substance concentration was set at a concentration of 150 mg theoretical oxygen demand per liter (ThOD/L). Batches were performed in duplicate and all ISO 14851 closed respirometer tests were performed by Aropha Inc.

2.3 Solubility Evaluation of Polymer Samples

Samples of polymer were dissolved at 10% by weight in pure water at 25° C under agitation of a stir bar. Solubility was evaluated on a pass/fail basis where passing indicates complete solvation such that no particles were visible. In cases where the polymer became clear when swollen with water but remained as a separate phase, these polymers were considered insoluble.

3. Results and Discussion

Polyethyleneglycol (PEG, or polyoxyethylene/polyethyleneoxide as PEO) polymers are highly biocompatible and biodegradable molecules which have been approved by the Food and Drug Administration (FDA) in humans for transdermal drug delivery. According to the 2009 report on alcohol ethoxylates by the Human and Environmental Risk Assessment (HERA) for ingredients of household cleaning products, a representative range of ethoxylated fatty alcohols were found to all exhibit ready biodegradability[6]. From low molecular weight up to 14 kDa, it is widely accepted that PEGs are readily biodegradable and this is supported by extensive investigations [5]. The polymer SOR230-TO has an average molecular weight of 11.4 kDa, with PEG accounting for 89% of molecular weight, positioning it in a range in which the PEG domains can be expected to biodegrade.

In contrast to linear PEG, SOR230-TO is a star polymer in which an average of 4 of the six PEG arms are capped with an oleic fatty acid ester. SOR230-TO is comprised of three classes of subunits, all of which are known to be readily and ultimately biodegradable: sorbitol, oleic acid and low molecular weight polyethylene glycol (average MW 1650 Da per arm). Primary biodegradation of the polymer architecture is expected to proceed through liberation of the fatty acid capping groups and primary polyethyleneglycol primary chains (Scheme 2). Complete mineralization of the subunits can be anticipated based on widely available data; however, the main challenge lies in the kinetics which determine the effective bioavailability during OECD 310B experiments.

Table 1. OECD 301B Biodegradation Results for Select Polymers

Sample	N	K	Alkanoate	Core	Chemical Name	28 Day Biodeg.	wt% Carbon
SOR230-PS	230	5	Stearate	Sorbitol	Sorbeth-230 Pentastearate	42.2 ± 3.2%	57.60%
SOR230-PO	230	5	Oleate	Sorbitol	Sorbeth-230 Pentaoletate	41.8 ± 2.1%	57.65%
SOR230-PB	230	5	Behenate	Sorbitol	Sorbeth-230 Pentabehenate	39.2 ± 7.3%	58.31%

SOR135-PO	135	5	Oleate	Sorbitol	Sorbeth-135 Pentaooleate	$33.8 \pm 1.9\%$	59.38%
SOR400-PO	400	5	Oleate	Sorbitol	Sorbeth-400 Pentaooleate	$17.3 \pm 4.9\%$	56.43%
SOR230-PHSA	230	5	Hydroxystearate	Sorbitol	Sorbeth-230 Penta-12-hydroxystearate	$22.3 \pm 2.1\%$	55.97%
SOR50-PHSA	50	5	Hydroxystearate	Sorbitol	Sorbeth-50 Penta-12-hydroxystearate	$17.60\% \pm 0.30\%$	60.20%
SOR230-TO-B	230	4.5	Oleate	Sorbitol	Sorbeth-230 Tetraoleate	$40.45\% \pm 0.70\%$	57.23%
SOR230-TO	230	4	Oleate	Sorbitol	Sorbeth-230 Tetraoleate	$19.60\% \pm 5.30\%$	56.82%
SOR230-TRO	230	3	Oleate	Sorbitol	Sorbeth-230 Trioleate	$11.90\% \pm 1.40\%$	56.23%
SOR230	230	0	NA	Sorbitol	Sorbeth-230	$11.10\% \pm 1.80\%$	54.25%
SOR400	400	0	NA	Sorbitol	Sorbeth-400	$18.20\% \pm 1.90\%$	54.36%
SOR135	135	0	NA	Sorbitol	Sorbeth-135	$8.80\% \pm 0.50\%$	54.07%
SOR-50	50	0	NA	Sorbitol	Sorbeth-50	$9.50\% \pm 1.30\%$	53.37%
PEG-10000	227	0	N/A	N/A	PEG-10000	$86.50\% \pm 0.80\%$	54.51%
MG120-DO	120	2	Oleate	Methyl glucose	PEG-120 Methyl Glucose Dioleate	$16.80\% \pm 0.70\%$	56.55%
PE150-TS	150	4	Stearate	Pentaerythritol	PEG 150 Pentaerythritol Tetastearate	$24.90\% \pm 2.60\%$	57.96%

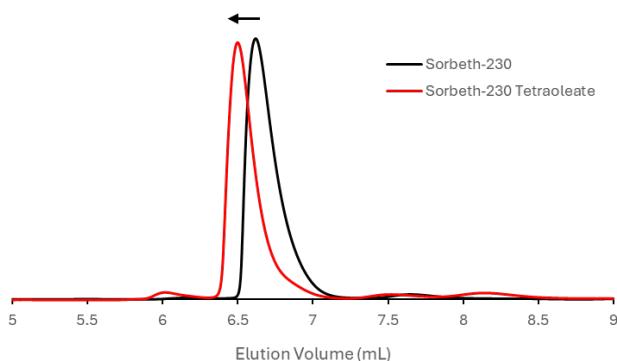
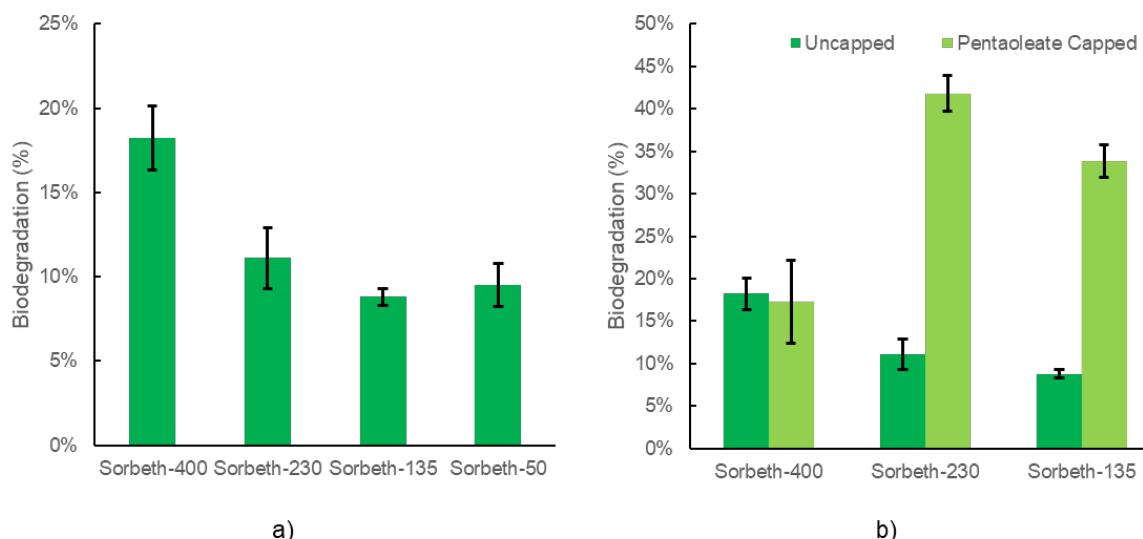


Figure 1. GPC traces for sorbeth-230 pre-polymer and esterified sorbeth-230 tetraoleate.

Initiation of ethoxylation chain growth from a sorbitol core results in the formation of a star polymer possessing 6 hydroxy-terminated chain ends. These reactive chain ends can be modified by esterification with fatty acid to form a polymer which has significant hydrophobic character due to the fatty acid effectively forming a shell. Similar results can be obtained by using initiator moieties selected from other polyols. For example, use of glycerin, featuring 3 hydroxy functionalities, will result in 3-arm star polymers. Use of either methyl glucose or pentaerythritol, featuring 4 hydroxy functionalities, will result in 4-arm star polymers. GPC analysis of esterified sorbeth star polymers revealed high conversion of the fatty acids with no detectable monomer remaining (Figure 1). Additionally, the low polydispersity of the prepolymer ensured uniformity of 3-dimensional networks formed in surfactant systems, helping to amplify the effectiveness of the material in thickening applications. For the purpose of this study, it allows for highly specific analysis of different molecular weights, increasing accuracy of structure-property relationships.

**Figure 2.** Comparison of experimental 28-day biodegradation percentage using OECD-301B protocol for a) ethoxylated sorbitol star polymers with degree of polymerization from 50 to 400 and b) sorbeth esters with an average of 5 oleic acid pendant groups per molecule.

Comparison of sorbeth-230, a 6-arm polyethoxylate with an average molecular weight of approximately 10,311 g/mol, and a linear 10,000 g/mol polyethylene oxide revealed a significant drop in biodegradation from 86.50% for the latter to 11.10% (Figure 2a). Both compounds were found to be soluble in water, indicating the difference in measured biodegradability was not directly explainable by lack of physical availability. More surprisingly, the lower molecular weights sorbeth-135 and sorbeth-50 exhibited further decreases in degradation to 8.80% and 9.50% respectively.

Table 2. Solubility results for pentaoleate modified sorbeth polymers of various DP

Polymer #	N	K	Alkanoate	Chemical Name	Solubility (10% in water)

SOR135-PO	135	5	Oleic acid	Sorbeth-135 Pentaole-	ate	Insoluble
SOR230-PO	230	5	Oleic acid	Sorbeth-230 Pentaole-	ate	Insoluble
SOR300-PO	300	5	Oleic acid	Sorbeth-300 Pentaole-	ate	Insoluble
SOR350-PO	350	5	Oleic acid	Sorbeth-350 Pentaole-	ate	Soluble
SOR400-PO	400	5	Oleic acid	Sorbeth-400 Pentaole-	ate	Soluble

To explore the impact of hydrophobic-hydrophilic balance given a similarly hydrophobic exterior character, polymers were prepared with a fixed number and species of fatty acid. For a series of polymers with 5 arms capped by oleic acid, the degree of polymerization (DP) of the ethoxylate prepolymer was varied from 135 to 400 EO. Solubility at 10% water was evaluated and it was observed that the lower ethoxylation number resulted in a loss of solubility at 300 EO and below (Table 2).

It has been well established that drug bioavailability can be increased by modifying the hydrophobic character to increase membrane interactions[7]. This concept has been applied to synthetic particles as well. Comparison of hydrophobically modified sorbeth polymers reveal that DP 230 and 135, the capped polymers had substantially improved degradability to their water-soluble counterparts (Figure 2b). However, increasing hydrophobicity alone does not appear to fully explain the observed results, as both sorbeth-230 pentaoleate and sorbeth-135 pentaoleate are highly insoluble at 10% in pure water, but the latter only exhibited a 33.8% 28-day degradation result, whereas the former reached 41.8%. It was also observed that for sorbeth-400, minimal change occurred when oleate modified, although this could be explained by molecular weight exceeding 19 kDa.

Also investigated was the use of 12-HSA as the hydrophobe. This fatty acid derivative has an added complexity of being self-condensing. Statistically, it can be expected to cap fewer arms of the sorbeth prepolymer than stearic or oleic acid at the same ratio, due to the increase of hydrophobe length by formation of 12-HSA oligomers. At a ratio of 5 to 1, SOR230-PHSA had a lower biodegradation OECD-301B result of 22.3%, compared to 41.8% observed for oleate. Reducing the DP of the prepolymer from 230 to 50, the degradability reduced moderately to 17.6% for SOR50-PHSA. However, it is interesting to note that this result was higher than the uncapped Sorbeth-50, which degraded by only 9.5% at 28 days. While the hydrophobic modification promoted higher bioavailability, the selection of the hydrophobe species appeared to be an important contributing factor as well.

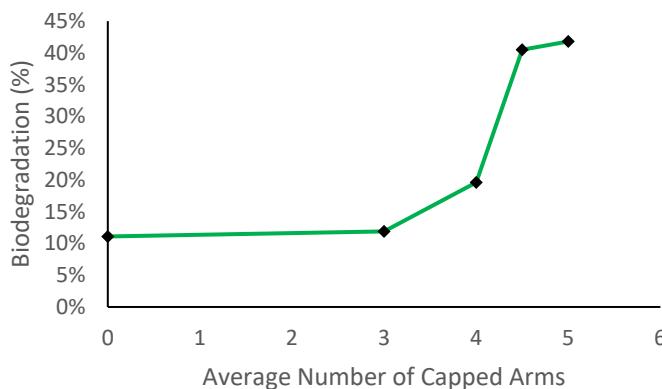


Figure 3. 28-Day biodegradation results for sorbeth-230 N-oleates by OECD 301B protocol (20 mg/L TOC), where N = 0, 3, 4, 4.5, 5.

The measured biodegradability of a substance would typically be expected to decrease as the solubility decreases and it prefers to exist in poorly available aggregates. Therefore, a reasonable hypothesis would be to expect biodegradation rates to decrease proportionally as a water-soluble material is further modified with a hydrophobic exterior. In contrast to this expectation, it was observed that rates increased substantially as the number of fatty acid groups was increased. For Sorbeth-230, as the number of oleic acid capped arms was increased from 3 to 4 of 6 arms, an increase was observed from 11.90% to 19.60% for the 28 day degradation.

An unexpected result was observed when increasing the average number of oleic acid capped arms on sorbeth-230 from 4 to 5. While a ratio of 4:1 showed a modest increase compared to the trioleate, increasing the feed ratio to 4.5 revealed a sudden increase in the 28-day degradation from 19.60% to 40.70% (Figure 3). Only a mild increase occurred from 4.5:1 to 5.0:1, up to 41.80% at 28 days, indicating a possible mechanism shift upon reaching a specific structural threshold. For different hydrophobes at 5:1, between oleic, stearic and behenic acid, no significant difference was observed, suggesting the crystallinity was not an important factor. The ability to make a small structural adjustment enabled the increase in biodegradability without substantially impacting the performance. Neither the SOR230-TO nor SOR230-PO were freely soluble in water, making the drastic change unexpected.

A common associative thickener, PEG-150 pentaerythritol tetraoleate (PE150-TO), was selected as an example of a 4-arm star polymer with a non-sorbitol core. Since ethoxylated pentaerythritol has 4 reactive arms, the maximum number of hydrophobes is lower than sorbitol's 6. The length of the polyethyleneglycol chains was 37.5 EO units, similar to sorbeth-230 which has an average length of 38.3 EO units. However, the PE150-TO only reached 24.90% degradation at 28 days and could not be further modified.

Another common material, PEG-120 glucose dioleate (MG120-DO) was found to degrade up to 16.90% at 28 days, lower than PE150-TO and SOR230-TO, but higher than SOR230-TRO. Featuring 4 polyethoxylated arms, of which only two are capped, gave it a similar structural comparison to the two uncapped arms of SOR230-TO. Also taking into consideration the lack of degradability of the uncapped sorbeth polymers, there was no apparent advantage afforded by the free hydrophilic chains.

3.1 Consideration of Target Application

In rinse-off formulations, non-ionic associative thickeners are designed to be used at low concentrations in the presence of moderate to high concentrations of surfactants. Once completely dissolved and incorporated into a surfactant system, SOR230-TO will no longer be present in collapsed aggregates but distributed between the domains of the surfactant micelles. Attempting to dissolve SOR230-TO in water without additional surfactant results in dispersion of visible particles which do not remain fully dissolved at room temperature. If we compare the structure to common non-ionic surfactants such as polyoxyethylene(20) sorbitan monololeate (Tween 80) or polyoxyethylene(20) sorbitan monolaurate (Tween 20), we find a similar design with an ethoxylated sorbitan core and a fatty acid ester capping group. Both of these surfactants have been found to be readily biodegradable, likely benefiting from high water solubility[8]. As the number of capping groups increase from one to three, such as in polyoxyethylene(20) sorbitan trioleate (Tween 85), we see a decrease in total degradation at 28 days, which falls short of the readily biodegradable threshold. Between Tween 80 and Tween 85, the hydrophilic-lipophilic balance (HLB) decreases from ~15 to ~11. The increasing hydrophobic character of the star polymers' outer shell would appear to be responsible for a reduction in overall degradability, despite the highly degradable nature of the pendant fatty acid groups. In comparison, SOR230-TO has a calculated HLB of 15.2, despite poor solubility.

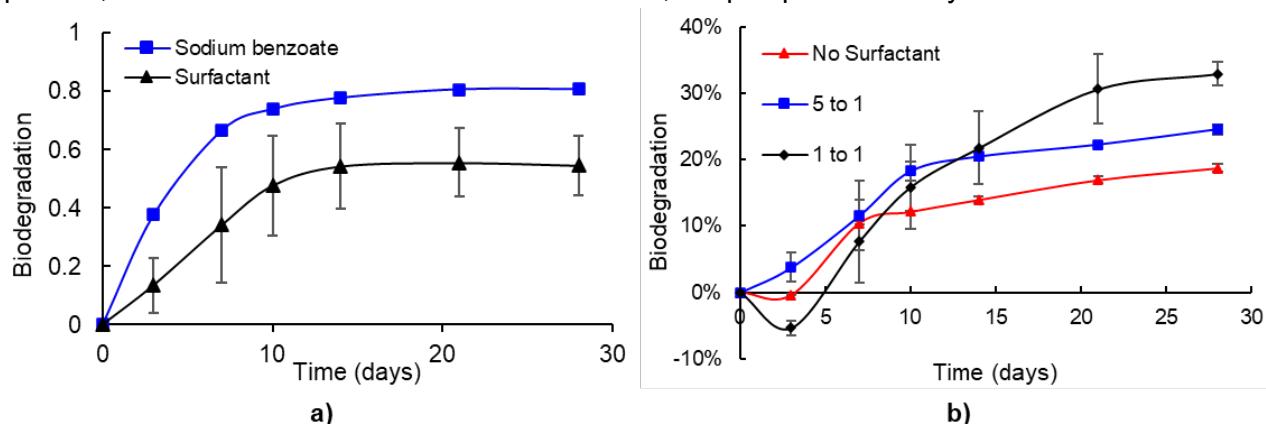


Figure 4. a) Test performed by OECD method 301B showing surfactant blank and reference standards. b) Degradation of polymer determined by subtracting blank containing appropriate concentration of surfactant (20mg/L TOC). Ratios are weight to weight sorbeth-230 tetraoleate to sodium alpha alkyl olefin sulfonate. Polymer gel stock was prepared by dissolving polymer and surfactant in water until completely homogenous.

While SOR230-TO remains aggregated in pure water, it becomes fully soluble in a typical cleanser formulation. The OECD 301 series methods were designed to mimic real-world conditions within the laboratory; in practice, associative thickeners are added to surfactants systems, which fundamentally alter the physical form. To investigate the impact of polymer activation, polymer samples were subjected to OECD 301B assays where surfactant was added at weight ratios of polymer to surfactant of 1:0, 5:1, and 1:1 in a pre-gel. As surfactant was increased, total polymer degradation increase proportionally from 15.5% to 20.5% and 35%, at 5:1 and 1:1 respectively (Figure 4). The total concentration of surfactants in solution

at a 1:1 ratio indicates both components are present in the total 20 mg/L quantities, representing a significant dilution. The surfactant itself was shown to reach maximum CO₂ evolution within 14 days. Despite the dilute concentration and rapid degradation of the surfactant, a positive response is observed in the evolution of carbon dioxide attributed to the polymer. Considering this information, we anticipate much higher rates of degradation in actual use conditions, in which polymer to surfactant ratios are more typically in the range of 1:10 to 1:100. However, further study is required to confirm this extrapolation and determine to what extent rapid degradation is possible. Further dilution was not attempted as errors were determined to be too high to obtain reasonable data while adhering to OECD 301B requirements.

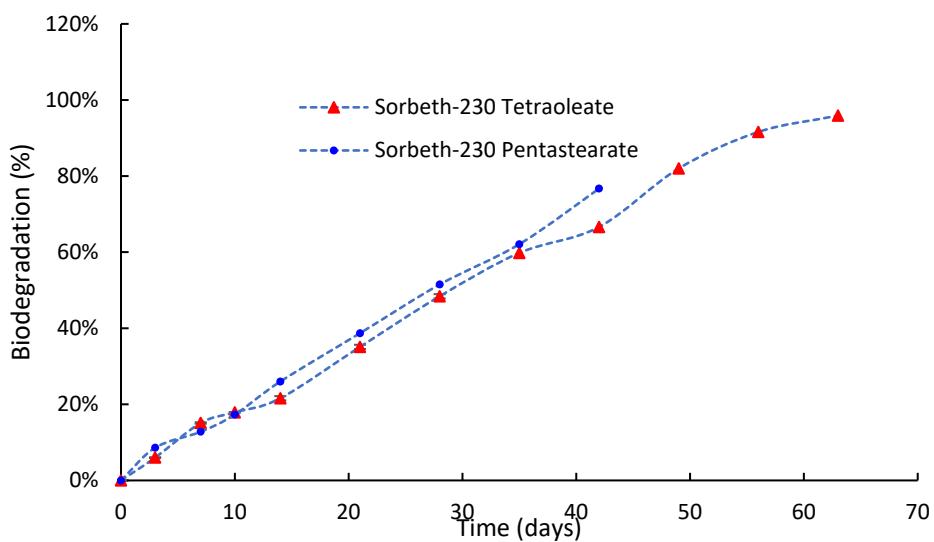


Figure 5. Results recorded for the biodegradation of sorbeth-230 tetraoleate and sorbeth-230 pentastearate using ISO 14951 protocol for biodegradation of insoluble plastic materials.

In the practice of designing industrially relevant materials, the readily biodegradable standard can be difficult to achieve, and is especially challenging for hydrophobic or poorly water-soluble compounds. The OECD 301 protocols are primarily applicable to water soluble materials, creating a gap in usable methodology for evaluation of many common materials. For polymer materials, the ISO 14851 method provides an option for the evaluation of ultimate biodegradability of poorly soluble polymers such as SOR230-TO. Up to 96% biodegradation was observed at 63 days for SOR230-TO (Figure 5). Both SOR230-TO and SOR230-PO had >60% degradation occur between 35 and 42 days. Compared to the OECD 301B protocol, the rates of degradation appeared to be similar for both polymers, with SOR230-PO displaying a slight but consistent higher result.

5. Conclusion

In this work, we presented biodegradation data that underscores the complex nature of biological processes in the context of wastewater microbiomes and their ability to break down materials introduced by consumer products. While existing literature and industrial case studies may indicate patterns that facilitate enhanced biodegradability through molecular design, there remains a distinct need to validate through experimentation. Using diligent and exhaustive

structure-property relationship studies, a balance between optimal performance and environmental responsibility can be achieved. In the case of SOR230-TO, the option to increase the hydrophobic character allowed a precipitous increase in biodegradability. Using the data obtained from the OECD 301B study, this slight alteration in the material was used to create a system capable of achieving Ultimately Biodegradable standards by ISO 14851 and reduce the bioaccumulation potential in large volume cleansing applications.

- [1] P. Ramesh and S. and Vinodh, "State of art review on Life Cycle Assessment of polymers," *Int. J. Sustain. Eng.*, vol. 13, no. 6, pp. 411–422, Nov. 2020, doi: 10.1080/19397038.2020.1802623.
- [2] C. A. R. Picken, O. Buenoz, P. D. Price, C. Fidge, L. Points, and M. P. Shaver, "Sustainable formulation polymers for home, beauty and personal care: challenges and opportunities," *Chem Sci*, vol. 14, no. 45, pp. 12926–12940, Nov. 2023, doi: 10.1039/d3sc04488b.
- [3] C. Juliano and G. A. Magrini, "Cosmetic Ingredients as Emerging Pollutants of Environmental and Health Concern. A Mini-Review," *Cosmetics*, vol. 4, no. 2, 2017, doi: 10.3390/cosmetics4020011.
- [4] T. Casalini, F. Rossi, A. Castrovinci, and G. Perale, "A Perspective on Polylactic Acid-Based Polymers Use for Nanoparticles Synthesis and Applications," *Front. Bioeng. Biotechnol.*, vol. Volume 7-2019, 2019, [Online]. Available: <https://www.frontiersin.org/journals/bioengineering-and-biotechnology/articles/10.3389/fbioe.2019.00259>
- [5] R. Nabeoka, H. Suzuki, Y. Akasaka, N. Ando, and T. Yoshida, "Evaluating the Ready Biodegradability of Biodegradable Plastics," *Environ. Toxicol. Chem.*, vol. 40, no. 9, pp. 2443–2449, Sep. 2021, doi: 10.1002/etc.5116.
- [6] K. Duis, T. Junker, and A. Coors, "Environmental fate and effects of water-soluble synthetic organic polymers used in cosmetic products," *Environ. Sci. Eur.*, vol. 33, no. 1, p. 21, Feb. 2021, doi: 10.1186/s12302-021-00466-2.
- [7] A. Falanga, R. Bellavita, S. Braccia, and S. Galdiero, "Hydrophobicity: The door to drug delivery," *J. Pept. Sci.*, vol. 30, no. 5, p. e3558, May 2024, doi: 10.1002/psc.3558.
- [8] M. Nazar, M. U. H. Shah, A. Ahmad, W. Z. N. Yahya, M. Goto, and M. Moniruzzaman, "Ionic Liquid and Tween-80 Mixture as an Effective Dispersant for Oil Spills: Toxicity, Biodegradability, and Optimization," *ACS Omega*, vol. 7, no. 18, pp. 15751–15759, May 2022, doi: 10.1021/acsomega.2c00752.