

A Structural Accessibility Hypothesis for Interpreting Negative Biodegradation Results in Crosslinked Photopolymer Networks

Juan Segurola

3Dresyns by Resyner Technologies S.L.

© 2026 Juan Segurola. All Rights Reserved.

Correspondence: info@3Dresyns.com · www.3Dresyns.com

ER-008 · Perspective · Version 1.8 · 2026

Abstract

This perspective proposes a structural accessibility hypothesis for interpreting negative biodegradation results in crosslinked photopolymer additive-manufacturing materials. The hypothesis is deliberately non-exclusive: an observed low biodegradation fraction may reflect intrinsic chemical recalcitrance, limited accessibility created by specimen geometry or network transport, sample-preparation effects, the selected test conditions and time horizon, or a combination of these factors. OECD ready-biodegradability methods describe a solution or suspension of the test substance in mineral medium, while controlled-composting methods such as ISO 14855-2 and ASTM D5338 quantify aerobic biodegradation of plastics under specified composting conditions. None of these methods, by itself, separates intrinsic polymer chemistry from geometry-dependent transport in a macroscopic crosslinked specimen. For rigid photopolymer thermosets, the cured network can restrict dissolution and hinder transport of large biological catalysts, while a low surface-area-to-volume ratio reduces the amount of polymer directly exposed per unit mass. The perspective therefore proposes that specimen geometry and network accessibility should be treated as explicit experimental variables when negative results are interpreted. No quantitative accessibility index is claimed. A complementary four-element research outlook considers feedstock carbon origin, network deconstruction, enzymatic depolymerisation of accessible susceptible bonds, and carefully controlled weathering or oxidation as distinct research axes. The hypothesis remains conceptual and requires direct geometry-dependence studies, transport measurements and multi-laboratory validation. It is offered as an experimental design and interpretation framework, not as a replacement for standardised biodegradability or compostability methods.

Keywords

photopolymer additive manufacturing · crosslinked thermoset networks · biodegradation testing · structural accessibility · specimen geometry · polymer transport · network deconstruction · enzymatic depolymerisation · OECD 301 · ISO 14855-2

1. Introduction

1.1 Carbon origin and end-of-life behaviour are separate questions

Sustainability claims for vat-photopolymerisation materials increasingly distinguish renewable feedstock origin from end-of-life behaviour. Biobased photopolymer formulations have been demonstrated using renewable acrylates, lignin-containing systems and other renewable-source building blocks [1,2,17–20]. The analytical question of carbon origin is well defined: radiocarbon methods such as ASTM D6866, EN 16640 and ISO 16620-2 quantify the fraction of contemporary biogenic carbon. That measurement does not establish whether the cured polymer will biodegrade, compost, persist, fragment or be recyclable at end of life.

The distinction matters particularly in vat photopolymerisation because the printing step converts liquid reactive components into a covalently connected solid architecture. Reviews of photopolymerisation and sustainable SLA/DLP materials emphasise that network chemistry, functionality, conversion, morphology and end-of-use design determine the properties of the cured article [3,4,17,19]. Feedstock origin is therefore an upstream sustainability descriptor, not an end-of-life classification.

1.2 Biobased does not mean biodegradable

A polymer can be fully or partly derived from renewable carbon and still be resistant to biological mineralisation. Conversely, a fossil-derived polymer can contain hydrolysable or otherwise degradable motifs. Reviews of biobased and biodegradable plastics explicitly caution against treating the two descriptors as interchangeable [1,13]. For crosslinked photopolymers, the relevant end-of-life variables include the chemistry of cleavable bonds, network connectivity, water uptake, morphology, environmental conditions and the accessibility of susceptible bonds to hydrolysis, oxidation or biological catalysts.

Outdoor weathering adds a second distinction: fragmentation is not equivalent to biodegradation. Photo-oxidative chain scission can embrittle polymers and generate progressively smaller fragments [5,6,24]. Unless those products subsequently undergo biological conversion and mineralisation under the relevant conditions, fragmentation alone does not satisfy biodegradation criteria. This distinction is also central to the European treatment of oxo-degradable plastics [S9,S15].

1.3 The structural accessibility hypothesis

The hypothesis advanced here is that, for some rigid crosslinked photopolymer test articles, the biodegradation fraction measured over a finite test period may be influenced by structural accessibility in addition to intrinsic chemistry. “Structural accessibility” is used qualitatively to describe the combined effect of specimen size and surface area, water uptake, network transport, and the physical state in which the test material is presented to the assay. It is not a new metric and no formula or universal scaling law is proposed.

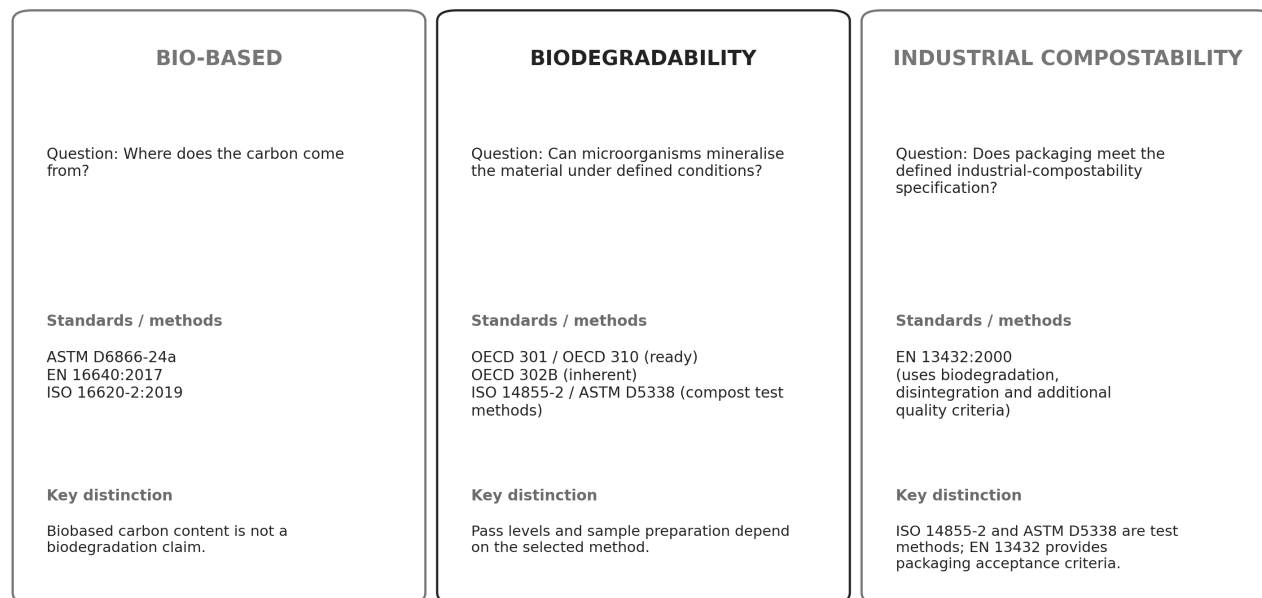
The hypothesis does not claim that standard methods are defective, nor that a negative result should be reclassified. It states a narrower experimental proposition: when a macroscopic crosslinked article is tested, geometry and transport may contribute to the observed kinetics and should be reported or varied deliberately if the objective is to distinguish accessibility effects from chemical recalcitrance.

1.4 Scope and methodology

This is a perspective and hypothesis paper. It introduces no primary experimental data. Evidence is drawn from peer-reviewed literature on photopolymer networks, degradable polymer erosion, polymer transport, enzymatic depolymerisation and sustainable photopolymers, together with official standards and European regulatory documents. Claims that cannot be supported directly by those sources are presented as hypotheses or research questions rather than as established facts.

2. Bio-based, biodegradable and compostable are distinct properties

Figure 1 separates three descriptors that are frequently conflated. Biobased carbon content addresses feedstock origin. Ready or inherent biodegradability tests address biological conversion under the conditions of the selected method. Industrial compostability is a broader specification for packaging that combines biodegradation with disintegration and additional quality criteria. The distinction between a test method and an acceptance specification is important: ISO 14855-2 and ASTM D5338 are controlled-composting test methods, whereas EN 13432 defines requirements for packaging recoverable through composting and biodegradation.



Three distinct properties. Test methods and acceptance specifications should not be conflated.

Figure 1. Distinction between biobased carbon content, biodegradability testing and industrial compostability. ISO 14855-2 and ASTM D5338 are biodegradation test methods under controlled composting conditions; EN 13432 is a packaging acceptance specification that combines biodegradation with disintegration and additional criteria.

3. Structural accessibility: network transport and specimen geometry

3.1 Crosslinked network architecture and transport

Crosslinked photopolymer networks are produced by light-initiated polymerisation of multifunctional or otherwise network-forming reactive species [3,4]. Their transport behaviour depends on chemistry, crosslink density, conversion, free volume, water uptake and morphology. Polymer-network theory and hydrogel transport literature show that diffusion of a solute through a polymer network can be reduced by obstruction, hydrodynamic drag and free-volume limitations, and that the magnitude of the restriction depends strongly on both the network and the size of the diffusing species [25,32,33,35]. These principles do not justify a single “typical” mesh size or diffusion coefficient for engineering photopolymers; such values are formulation- and cure-specific and must be measured for the material under study.

For enzyme-mediated degradation pathways, catalyst size is also relevant. Proteins and extracellular enzymes occupy nanometre-scale hydrodynamic dimensions [15]. When an enzyme is large relative to the dynamically accessible free volume of a cured network, bulk penetration can be hindered and reactions may be concentrated near the polymer–environment interface. The degree of hindrance cannot be inferred from material class alone. Swelling, heterogeneous porosity, defects, surface oxidation and progressive network cleavage can all change transport during ageing.

The distinction between polymer degradation and polymer erosion is also important. Chain cleavage is a chemical event; erosion is the loss of material from the specimen. Classical degradable-polymer theory shows that surface- versus bulk-erosion behaviour depends on the relative rates of water ingress, bond cleavage and the dimensions of the article [26,27]. Those models were developed for degradable polymer systems and should not be transferred quantitatively to a rigid photopolymer without validation, but they establish a relevant principle: specimen dimension can influence the observed mode and rate of mass loss even when chemistry is held constant.

3.2 A qualitative accessibility coupling

The hypothesis therefore couples two experimentally separable variables. The first is intrinsic chemical susceptibility: whether the cured network contains bonds or motifs that can be cleaved under the selected environmental and biological conditions. The second is structural accessibility: whether water, microorganisms, enzymes or other relevant reactants can reach those susceptible sites at a rate that is significant on the timescale of the test. Specimen geometry influences the second variable because reducing characteristic size increases exposed surface area per unit mass.

Figure 2 is deliberately qualitative. It does not claim a universal boundary between “accessible” and “inaccessible” networks. Its purpose is to make a testable design principle explicit: if structural accessibility contributes materially to the measured response, changing specimen dimension while holding formulation, cure state and test conditions constant should change the observed kinetics.

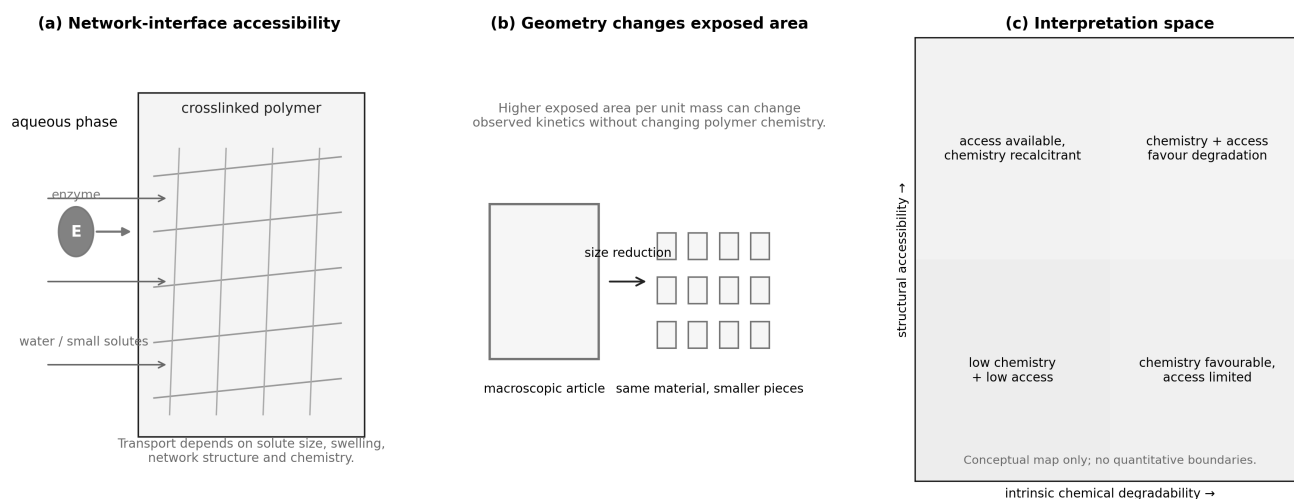


Figure 2. Conceptual structural-accessibility framework. (a) Transport at a crosslinked polymer interface depends on solute size, swelling, network structure and chemistry. (b) For the same chemistry, reducing characteristic specimen size increases exposed area per unit mass. (c) Intrinsic chemical degradability and structural accessibility are separate axes. The map is qualitative and claims no quantitative regime boundaries.

3.3 Reframing the interpretation of a negative result

A negative biodegradation result is therefore not assigned automatically to one mechanism. It may reflect a chemically recalcitrant backbone; a chemically susceptible backbone that is poorly accessible in the tested geometry; a network whose accessibility changes slowly with swelling or ageing; a sample-preparation state that is not well matched to the selected method; or a test horizon that is short relative to the relevant transformation. These explanations can coexist. The standard result remains the standard result; the hypothesis concerns mechanistic interpretation and experimental follow-up.

4. Standards landscape and what the methods actually establish

4.1 Biobased carbon content

ASTM D6866-24a determines biobased or biogenic carbon content using radiocarbon analysis [S1]. The method reports the contemporary-carbon fraction of the carbon in the sample; it is not a gravimetric determination of renewable-source mass fraction. EN 16640:2017 and ISO 16620-2:2019 similarly address bio-based or biobased carbon content using carbon-14 methods [S11,S12]. The historical development and analytical basis of radiocarbon determination of modern carbon in biobased products are described by Norton and Devlin [16].

4.2 Aqueous ready and inherent biodegradability

OECD Test Guideline 301 comprises six ready-biodegradability methods. The OECD description specifies a well-defined solution or suspension of the test substance in mineral medium and a normal test duration of 28 days. The ready-biodegradability pass levels are 70% removal of dissolved organic carbon for DOC-based methods and 60% of theoretical oxygen demand or theoretical carbon dioxide production for respirometric methods [S3]. OECD 310 is a separate ready-biodegradability method based on CO₂ in sealed vessels [S5]. OECD 302B is an inherent-biodegradability test and should not be presented as equivalent to a ready-biodegradability pass/fail method [S4].

For poorly soluble or solid substances, preparation and dispersion matter. The hypothesis in this paper does not assert that OECD methods exclude crosslinked polymers. It asks a narrower question: when the test material is a macroscopic crosslinked article or a difficult-to-disperse specimen, does the chosen preparation state introduce a geometry- or transport-dependent contribution that should be investigated separately?

4.3 Controlled composting and compostability

ISO 14855-2:2018 specifies a laboratory method for determining the ultimate aerobic biodegradability of plastic materials under controlled composting conditions by gravimetric measurement of evolved carbon dioxide [S6]. ASTM D5338-15(2021) is another controlled-composting biodegradation test method [S7]. Neither standard should be described as, by itself, a universal 90% “pass” specification. EN 13432:2000 is the European packaging specification that combines biodegradation with disintegration and additional criteria; the biodegradation requirement is expressed as at least 90% within six months under the specified framework [S2].

4.4 Reporting specimen state as an experimental variable

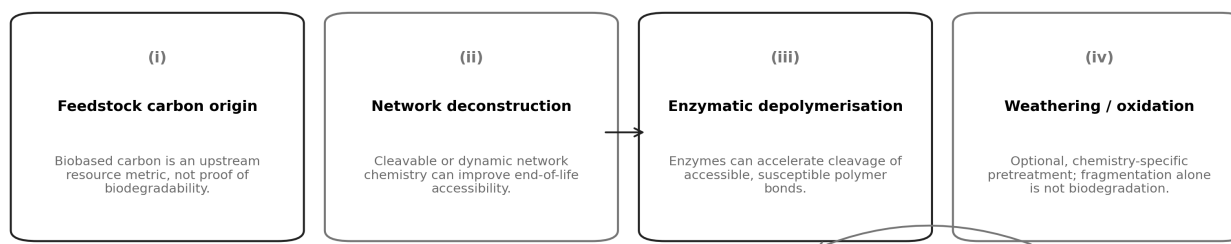
For hypothesis testing, the material state should be documented at minimum by formulation identity, cure/post-cure history, specimen geometry or particle-size distribution, mass, accessible surface-area description where available, and any preprocessing applied before inoculation or composting. This proposal is not an amendment to any standard. It is an experimental reporting layer intended to make geometry-dependent effects reproducible and testable.

5. A four-element research outlook

5.1 Four distinct research axes

The perspective separates four research axes rather than treating them as a mandatory degradation sequence. Element (i), feedstock carbon origin, is an upstream resource question. Element (ii), network deconstruction, concerns chemical or physical routes that increase end-of-life accessibility. Element (iii), enzymatic depolymerisation, concerns biological catalysis of accessible susceptible bonds. Element (iv), controlled weathering or oxidation, is an optional pretreatment concept that must be evaluated by subsequent depolymerisation and mineralisation measurements because fragmentation alone is not biodegradation.

Four-element research outlook



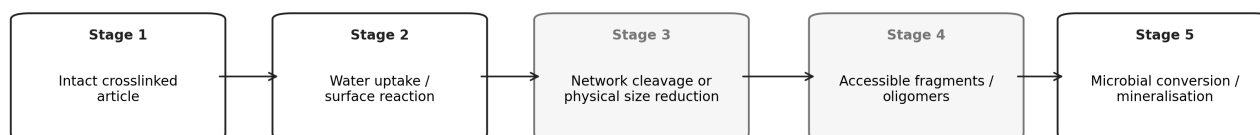
Elements (ii)-(iv) are candidate end-of-life research routes, not a mandatory sequence. Element (iv) requires subsequent mineralisation testing.

Figure 3. Four-element research outlook. Feedstock carbon origin is an upstream resource metric. Network deconstruction, enzymatic depolymerisation and controlled weathering/oxidation are candidate end-of-life research routes rather than a mandatory sequence. Fragmentation or oxidation must be followed by appropriate depolymerisation/mineralisation testing before any biodegradation conclusion is drawn.

5.2 Conceptual end-of-life state sequence

A crosslinked article can be discussed conceptually as moving from an intact network to a state in which water uptake or surface reactions occur, then to a more accessible state through network cleavage or physical size reduction, then to soluble or finely dispersed fragments, and finally, if the chemistry is susceptible and the biological system is capable, to microbial conversion and mineralisation. Figure 4 is a state map, not a kinetic law. Individual materials can bypass stages, stop at a stage, or follow different mechanisms.

Conceptual state sequence, not a universal kinetic pathway



The controlling step depends on bond chemistry, water uptake, network transport, geometry and environmental conditions. Fragmentation without chemical depolymerisation/mineralisation does not establish biodegradability.

Figure 4. Conceptual state sequence from an intact crosslinked article toward mineralisation. This is not a universal kinetic pathway. The controlling step depends on bond chemistry, water uptake, network transport, geometry and environmental conditions; fragmentation alone does not establish biodegradability.

6. Element (i): feedstock carbon origin

6.1 Routes to renewable-source photopolymer feedstocks

Published vat-photopolymerisation research has used renewable-source acrylates, lignin-containing photoactive resins and other biobased components [2,17–20]. These studies demonstrate that substantial renewable-source content can be compatible with photopolymer printing. They do not establish a universal relationship between biobased fraction and biodegradation, nor a universal mechanical penalty associated with increasing biobased content. Mechanical behaviour is formulation-specific and depends on molecular architecture, functionality, conversion and network morphology.

6.2 Reporting recommendation

For sustainability communication, biobased carbon should therefore be reported using the applicable carbon-content method and kept explicitly separate from biodegradability, compostability, recyclability and environmental-persistence claims. Any end-of-life claim requires its own evidence route.

7. Element (ii): network deconstruction

7.1 Principle

Network deconstruction is the most direct engineering response to an accessibility-limited state. The aim is not to assume that every crosslinked network can be made biodegradable, but to design bonds or exchange reactions that allow a cured network to be transformed at end of life into a state that is more soluble, dispersible or chemically accessible. Covalent adaptable networks and vitrimers provide a broad conceptual basis for reversible or exchangeable network connectivity [7–9,30,31].

7.2 Verified examples relevant to photopolymer and thermoset design

Several published systems demonstrate pieces of this design space. Aduba et al. produced vat-photopolymerised PEG-methacrylate networks containing an acid-cleavable crosslinker and showed that both crosslinker content and printed geometry affected dissolution under acidic aqueous conditions [10]. Davis, Burdick and Anseth produced photoinitiated degradable copolymer networks containing hydrolysable lactic- and caproic-acid-derived ester segments and measured hydrolytic degradation under physiological conditions [23]. Leguizamon et al. demonstrated additive manufacturing of degradable thermoset materials through ring-opening metathesis polymerisation, providing a distinct route to programmed end-of-life deconstruction [21].

Dynamic-network examples outside vat photopolymerisation provide additional design principles. Ruiz de Luzuriaga et al. demonstrated epoxy thermosets with exchangeable disulfide crosslinks that enable reprocessing, repair and recycling [22]. Adjaoud et al. analysed thermally activated transesterification in polybenzoxazine vitrimers and the role of internally catalytic tertiary-amine functionality [31]. These papers support the general feasibility of designed network exchange or cleavage; they do not, by themselves, demonstrate biodegradability of rigid vat-photopolymerised engineering resins.

7.3 Research need

The key experiment for the structural accessibility hypothesis is not simply to demonstrate that a network can be chemically deconstructed. It is to quantify whether deconstruction changes the subsequent biodegradation response under a defined method, while documenting the chemistry and size distribution of the products.

8. Element (iii): enzymatic depolymerisation

8.1 What is established

Engineered hydrolases have demonstrated high activity against ester-containing polyethylene terephthalate under optimised aqueous conditions. Tournier et al. reported an engineered PET depolymerase capable of rapid depolymerisation under controlled process conditions [11], and Lu et al. used machine-learning-aided enzyme engineering to improve PET hydrolase performance and robustness [12]. Broader reviews describe microbial and enzymatic degradation mechanisms across multiple polymer classes [14].

8.2 What is not yet established for rigid crosslinked photopolymers

Those PET results should not be extrapolated directly to rigid crosslinked photopolymer networks. Direct enzymatic mineralisation of engineering-grade crosslinked vat-photopolymerised parts has not been established by the sources reviewed here. Translation would require a susceptible bond chemistry, sufficient transport or prior network deconstruction, and evidence that the reaction products proceed beyond fragmentation or partial depolymerisation to the endpoint required by the selected biodegradation method. Enzyme incorporation directly into a photoresin should therefore be treated as a future research concept, not as a demonstrated implementation.

9. Element (iv): controlled weathering and photo-oxidation

Ultraviolet radiation and oxygen can produce oxidation, chain scission, embrittlement and fragmentation in many polymers [5,6,24]. In principle, a controlled weathering step could increase surface oxidation or reduce characteristic particle size before biological testing. However, the environmental history of oxo-degradable plastics demonstrates why this route requires caution: accelerated fragmentation without demonstrated mineralisation can increase microplastic generation rather than solve the end-of-life problem [S9,S15].

Accordingly, any photo-oxidative pretreatment proposed within this framework must be evaluated as a pretreatment only. Success would require subsequent evidence of depolymerisation and biological mineralisation under a recognised method. Carbonyl-index growth, mass loss or visible fragmentation alone are insufficient endpoints. Laboratory weathering methods such as ISO 4892-2 and ASTM G154 may be useful for controlled comparative pretreatment studies, but they are not biodegradability tests [S13,S14].

10. Limitations, competing explanations and research programme

10.1 Methodological status

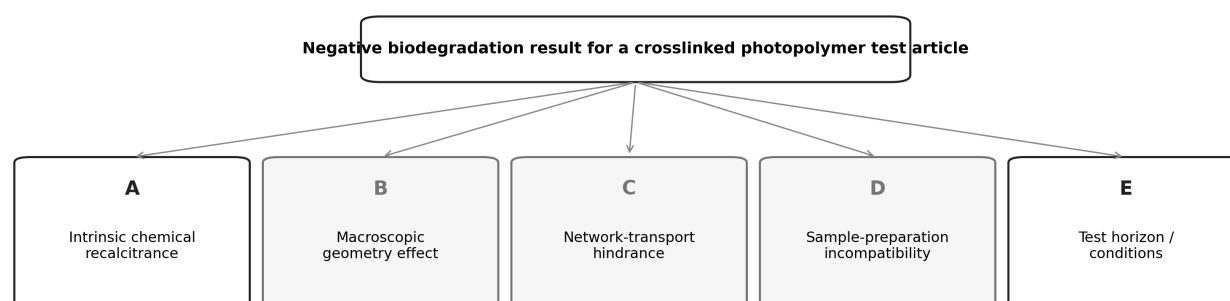
This perspective is single-author and industrial-academic in origin. It introduces no primary experimental data and does not claim that structural accessibility is the dominant explanation for biodegradation failure in any specific commercial material. The hypothesis applies most directly to rigid crosslinked photopolymer thermosets whose geometry and network structure can plausibly restrict transport. Swollen hydrogels, intentionally resorbable polyester networks and dynamic covalent materials can behave very differently [23,25,28,29]. Their existence is compatible with the hypothesis but does not prove it.

10.2 Limits of the transport argument

The present paper intentionally avoids assigning universal values to photopolymer crosslink density, mesh size, swelling ratio, enzyme penetration depth or diffusion coefficient. The polymer-transport literature provides established modelling families, including Fickian and non-Fickian descriptions, free-volume models, hydrodynamic models and obstruction models [32–35]. A predictive accessibility model for cured photopolymer parts would require experimentally determined network and transport parameters rather than generic literature values.

10.3 Five non-exclusive explanations for a negative result

Figure 5 separates five candidate explanations: intrinsic chemical recalcitrance; macroscopic geometry; network-transport hindrance; sample-preparation incompatibility with the selected assay; and the selected time horizon or environmental conditions. The structural accessibility hypothesis focuses on the middle three without excluding the first or fifth.



The causes are non-exclusive. The structural accessibility hypothesis focuses on B-D while retaining A and E as competing or coexisting explanations.

Figure 5. Five non-exclusive explanations for a negative biodegradation result. The structural accessibility hypothesis focuses on geometry, network transport and sample-preparation state while retaining intrinsic chemical recalcitrance and test horizon/conditions as competing or coexisting explanations.

10.4 Falsifiability and the critical experiment

A direct test should compare the same cured chemistry under the same assay conditions across a controlled range of characteristic specimen dimensions or particle sizes. The intervention should change geometry while minimising chemical alteration. If accessibility is important, increasing exposed area per unit mass should produce a reproducible change in observed kinetics. If biodegradation response is invariant across a sufficiently broad and well-characterised geometry range, and independent transport measurements show no meaningful restriction, a geometry-dominant interpretation would not be supported for that material system.

A second experimental tier can then introduce chemical deconstruction. Because de-crosslinking changes the material state and potentially the chemistry, it should be analysed separately from the geometry-only experiment. Characterisation of soluble products, molecular-weight distribution, residual gel fraction and subsequent biodegradation would be required to distinguish increased accessibility from creation of a chemically different substrate.

10.5 Priority research programme

The principal validation programme comprises: (1) geometry-dependence studies on identical cured formulations; (2) direct transport measurements using labelled probe molecules of controlled size; (3) network characterisation by gel fraction, solvent uptake and mechanical analysis; (4) controlled comparisons before and after network deconstruction or weathering; and (5) replication across multiple laboratories and biodegradation methods. Only such data can establish whether structural accessibility is a minor effect, a major effect, or negligible for a given material class.

11. European regulatory context

European sustainability legislation is expanding the reporting and product-design framework for polymers, including the Corporate Sustainability Reporting Directive, the Ecodesign for Sustainable Products Regulation, the Single-Use Plastics Directive, the Packaging and Packaging Waste Regulation, and the REACH restriction on intentionally added synthetic polymer microparticles [S8–S10,S16,S17]. The Packaging and Packaging Waste Regulation entered into force in 2025 and generally applies from 12 August 2026 [S10]. These instruments do not, as a general class requirement, convert the conceptual hypothesis in this paper into a regulatory biodegradability claim for photopolymer additive-manufacturing materials.

Regulatory classification remains tied to the applicable legal and standardised evidence route. The practical value of the structural accessibility hypothesis is therefore experimental: it identifies variables that may need to be controlled or reported when the scientific objective is to understand why a crosslinked material produces a particular result under a standard test.

12. Conclusions

Biobased carbon content, biodegradability and compostability are separate properties and should be reported separately. For rigid crosslinked photopolymer networks, a negative biodegradation result can have more than one mechanistic explanation. Intrinsic chemical recalcitrance is one possibility; geometry-dependent exposed area, network transport, sample-preparation state and test conditions may also contribute. The structural accessibility hypothesis does not reclassify a negative result and does not weaken the role of standardised methods. It proposes a controlled experimental programme for determining whether accessibility contributes to the measured response.

The strongest version of the hypothesis is falsifiable: if geometry and independently measured transport restrictions do not affect biodegradation kinetics for a given material under controlled conditions, structural accessibility should not be invoked as the dominant explanation for that system. Conversely, a reproducible geometry dependence would justify more detailed reaction-diffusion analysis. The next scientific step is therefore not a new index or marketing claim, but a controlled multi-geometry, multi-method validation programme grounded in polymer transport and biodegradation metrology.

Acknowledgements

The author thanks the scientific and standards communities whose published work provides the basis for this perspective, and the technical team at 3Dresyns by Resyner Technologies S.L. for verification of publicly available company information. No external funding was received for preparation of this manuscript.

Disclosure

The author is the founder and Scientific Director of 3Dresyns by Resyner Technologies S.L., a manufacturer of photopolymer resin systems. This perspective introduces no primary experimental measurement and does not use undisclosed formulation chemistry as evidence for the hypothesis. The framework is intended to be manufacturer-neutral and testable against any crosslinked photopolymer system. Bibliographic metadata for journal articles were checked against publisher or DOI records; standards and regulatory citations were checked against the issuing organisations.

References

A. Scientific literature and monographs

- [1] Álvarez-Chávez, C.R.; Edwards, S.; Moure-Eraso, R.; Geiser, K. (2012). Sustainability of bio-based plastics: general comparative analysis and recommendations for improvement. *Journal of Cleaner Production* 23(1), 47–56. <https://doi.org/10.1016/j.jclepro.2011.10.003>
- [2] Voet, V.S.D.; Strating, T.; Schnelting, G.H.M.; et al. (2018). Biobased Acrylate Photocurable Resin Formulation for Stereolithography 3D Printing. *ACS Omega* 3(2), 1403–1408. <https://doi.org/10.1021/acsomega.7b01648>
- [3] Bagheri, A.; Jin, J. (2019). Photopolymerization in 3D Printing. *ACS Applied Polymer Materials* 1(4), 593–611. <https://doi.org/10.1021/acsapm.8b00165>
- [4] Layani, M.; Wang, X.; Magdassi, S. (2018). Novel Materials for 3D Printing by Photopolymerization. *Advanced Materials* 30(41), 1706344. <https://doi.org/10.1002/adma.201706344>
- [5] Andrady, A.L. (2011). Microplastics in the marine environment. *Marine Pollution Bulletin* 62(8), 1596–1605. <https://doi.org/10.1016/j.marpolbul.2011.05.030>
- [6] Singh, B.; Sharma, N. (2008). Mechanistic implications of plastic degradation. *Polymer Degradation and Stability* 93(3), 561–584. <https://doi.org/10.1016/j.polymdegradstab.2007.11.008>
- [7] Kloxin, C.J.; Scott, T.F.; Adzima, B.J.; Bowman, C.N. (2010). Covalent Adaptable Networks (CANs): A Unique Paradigm in Cross-Linked Polymers. *Macromolecules* 43(6), 2643–2653. <https://doi.org/10.1021/ma902596s>
- [8] Scheutz, G.M.; Lessard, J.J.; Sims, M.B.; Sumerlin, B.S. (2019). Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets. *Journal of the American Chemical Society* 141(41), 16181–16196. <https://doi.org/10.1021/jacs.9b07922>
- [9] Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. (2011). Silica-Like Malleable Materials from Permanent Organic Networks. *Science* 334(6058), 965–968. <https://doi.org/10.1126/science.1212648>
- [10] Aduba, D.C.; Margareta, E.D.; Marnot, A.E.C.; et al. (2019). Vat photopolymerization 3D printing of acid-cleavable PEG-methacrylate networks for biomaterial applications. *Materials Today Communications* 19, 204–211. <https://doi.org/10.1016/j.mtcomm.2019.01.003>
- [11] Tournier, V.; Topham, C.M.; Gilles, A.; et al. (2020). An engineered PET depolymerase to break down and recycle plastic bottles. *Nature* 580, 216–219. <https://doi.org/10.1038/s41586-020-2149-4>
- [12] Lu, H.; Diaz, D.J.; Czarnecki, N.J.; et al. (2022). Machine learning-aided engineering of hydrolases for PET depolymerization. *Nature* 604, 662–667. <https://doi.org/10.1038/s41586-022-04599-z>
- [13] Lambert, S.; Wagner, M. (2017). Environmental performance of bio-based and biodegradable plastics: the road ahead. *Chemical Society Reviews* 46(22), 6855–6871. <https://doi.org/10.1039/C7CS00149E>
- [14] Danso, D.; Chow, J.; Streit, W.R. (2019). Plastics: Environmental and Biotechnological Perspectives on Microbial Degradation. *Applied and Environmental Microbiology* 85(19), e01095-19. <https://doi.org/10.1128/AEM.01095-19>
- [15] Erickson, H.P. (2009). Size and Shape of Protein Molecules at the Nanometer Level Determined by Sedimentation, Gel Filtration, and Electron Microscopy. *Biological Procedures Online* 11, 32–51. <https://doi.org/10.1007/s12575-009-9008-x>

- [16] Norton, G.A.; Devlin, S.L. (2006). Determining the modern carbon content of biobased products using radiocarbon analysis. *Bioresource Technology* 97(16), 2084–2090. <https://doi.org/10.1016/j.biortech.2005.08.017>
- [17] Voet, V.S.D.; Guit, J.; Loos, K. (2021). Sustainable Photopolymers in 3D Printing: A Review on Biobased, Biodegradable, and Recyclable Alternatives. *Macromolecular Rapid Communications* 42, 2000475. <https://doi.org/10.1002/marc.202000475>
- [18] Sutton, J.T.; Rajan, K.; Harper, D.P.; Chmely, S.C. (2018). Lignin-Containing Photoactive Resins for 3D Printing by Stereolithography. *ACS Applied Materials & Interfaces* 10(42), 36456–36463. <https://doi.org/10.1021/acsami.8b13031>
- [19] Maines, E.M.; Porwal, M.K.; Ellison, C.J.; Reineke, T.M. (2021). Sustainable advances in SLA/DLP 3D printing materials and processes. *Green Chemistry* 23, 6863–6897. <https://doi.org/10.1039/D1GC01489G>. See publisher correction: *Green Chemistry* 24 (2022) 958–959, <https://doi.org/10.1039/D1GC90138A>
- [20] Sutton, J.T.; Rajan, K.; Harper, D.P.; Chmely, S.C. (2021). Improving UV Curing in Organosolv Lignin-Containing Photopolymers for Stereolithography by Reduction and Acylation. *Polymers* 13(20), 3473. <https://doi.org/10.3390/polym13203473>
- [21] Leguizamón, S.C.; Lyons, K.; Monk, N.T.; Hochrein, M.T.; Jones, B.H.; Foster, J.C. (2022). Additive Manufacturing of Degradable Materials via Ring-Opening Metathesis Polymerization (ROMP). *ACS Applied Materials & Interfaces* 14(45), 51301–51306. <https://doi.org/10.1021/acsami.2c14411>
- [22] Ruiz de Luzuriaga, A.; Martín, R.; Markaide, N.; Rekondo, A.; Cabañero, G.; Rodríguez, J.; Odriozola, I. (2016). Epoxy resin with exchangeable disulfide crosslinks to obtain reprocessable, repairable and recyclable fiber-reinforced thermoset composites. *Materials Horizons* 3, 241–247. <https://doi.org/10.1039/C6MH00029K>. See publisher correction: <https://doi.org/10.1039/D0MH90047H>
- [23] Davis, K.A.; Burdick, J.A.; Anseth, K.S. (2003). Photoinitiated crosslinked degradable copolymer networks for tissue engineering applications. *Biomaterials* 24(14), 2485–2495. [https://doi.org/10.1016/S0142-9612\(02\)00582-3](https://doi.org/10.1016/S0142-9612(02)00582-3)
- [24] Gewert, B.; Plassmann, M.M.; MacLeod, M. (2015). Pathways for degradation of plastic polymers floating in the marine environment. *Environmental Science: Processes & Impacts* 17(9), 1513–1521. <https://doi.org/10.1039/C5EM00207A>
- [25] Peppas, N.A.; Bures, P.; Leobandung, W.; Ichikawa, H. (2000). Hydrogels in pharmaceutical formulations. *European Journal of Pharmaceutics and Biopharmaceutics* 50(1), 27–46. [https://doi.org/10.1016/S0939-6411\(00\)00090-4](https://doi.org/10.1016/S0939-6411(00)00090-4)
- [26] von Burkersroda, F.; Schedl, L.; Göpferich, A. (2002). Why degradable polymers undergo surface erosion or bulk erosion. *Biomaterials* 23(21), 4221–4231. [https://doi.org/10.1016/S0142-9612\(02\)00170-9](https://doi.org/10.1016/S0142-9612(02)00170-9)
- [27] Göpferich, A. (1996). Mechanisms of polymer degradation and erosion. *Biomaterials* 17(2), 103–114. [https://doi.org/10.1016/0142-9612\(96\)85755-3](https://doi.org/10.1016/0142-9612(96)85755-3)
- [28] Lyu, S.; Untereker, D. (2009). Degradability of Polymers for Implantable Biomedical Devices. *International Journal of Molecular Sciences* 10(9), 4033–4065. <https://doi.org/10.3390/ijms10094033>
- [29] Bryant, S.J.; Anseth, K.S. (2002). Hydrogel properties influence ECM production by chondrocytes photoencapsulated in poly(ethylene glycol) hydrogels. *Journal of Biomedical Materials Research* 59(1), 63–72. <https://doi.org/10.1002/jbm.1217>
- [30] Imbernon, L.; Norvez, S. (2016). From landfilling to vitrimer chemistry in rubber life cycle. *European Polymer Journal* 82, 347–376. <https://doi.org/10.1016/j.eurpolymj.2016.03.016>
- [31] Adjaoud, A.; Marcolini, B.; Dieden, R.; Puchot, L.; Verge, P. (2024). Deciphering the Self-Catalytic Mechanisms of Polymerization and Transesterification in Polybenzoxazine Vitrimers. *Journal of the American Chemical Society* 146(19), 13367–13376. <https://doi.org/10.1021/jacs.4c02153>
- [32] Masaro, L.; Zhu, X.X. (1999). Physical models of diffusion for polymer solutions, gels and solids. *Progress in Polymer Science* 24(5), 731–775. [https://doi.org/10.1016/S0079-6700\(99\)00016-7](https://doi.org/10.1016/S0079-6700(99)00016-7)
- [33] Amsden, B. (1998). Solute Diffusion within Hydrogels. Mechanisms and Models. *Macromolecules* 31(23), 8382–8395. <https://doi.org/10.1021/ma980765f>
- [34] Crank, J. (1975). *The Mathematics of Diffusion*, 2nd ed. Clarendon Press, Oxford.
- [35] Flory, P.J. (1953). *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, New York.

B. Standards and regulatory documents

- [S1] ASTM D6866-24a. Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis. ASTM International, 2024.
- [S2] EN 13432:2000. Packaging — Requirements for packaging recoverable through composting and biodegradation — Test scheme and evaluation criteria for the final acceptance of packaging. CEN, Brussels.
- [S3] OECD (1992). Test No. 301: Ready Biodegradability. OECD Guidelines for the Testing of Chemicals, Section 3. OECD Publishing, Paris.
- [S4] OECD (1992). Test No. 302B: Inherent Biodegradability: Zahn-Wellens/EMPA Test. OECD Guidelines for the Testing of Chemicals, Section 3. OECD Publishing, Paris.
- [S5] OECD (2014). Test No. 310: Ready Biodegradability — CO₂ in sealed vessels (Headspace Test). OECD Guidelines for the Testing of Chemicals, Section 3. OECD Publishing, Paris.
- [S6] ISO 14855-2:2018. Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions — Method by analysis of evolved carbon dioxide — Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test. ISO, Geneva.
- [S7] ASTM D5338-15(2021). Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials Under Controlled Composting Conditions, Incorporating Thermophilic Temperatures. ASTM International.

- [S8] Directive (EU) 2022/2464 of the European Parliament and of the Council of 14 December 2022, as regards corporate sustainability reporting (CSRD), as amended.
- [S9] Directive (EU) 2019/904 of the European Parliament and of the Council of 5 June 2019 on the reduction of the impact of certain plastic products on the environment.
- [S10] Regulation (EU) 2025/40 of the European Parliament and of the Council on packaging and packaging waste (PPWR).
- [S11] EN 16640:2017. Bio-based products — Bio-based carbon content — Determination of the bio-based carbon content using the radiocarbon method. CEN, Brussels.
- [S12] ISO 16620-2:2019. Plastics — Biobased content — Part 2: Determination of biobased carbon content. ISO, Geneva.
- [S13] ISO 4892-2:2013, with Amendment 1:2021. Plastics — Methods of exposure to laboratory light sources — Part 2: Xenon-arc lamps. ISO, Geneva.
- [S14] ASTM G154-23. Standard Practice for Operating Fluorescent Ultraviolet (UV) Lamp Apparatus for Exposure of Materials. ASTM International.
- [S15] European Commission (2018). Report from the Commission to the European Parliament and the Council on the impact of the use of oxo-degradable plastic, including oxo-degradable plastic carrier bags, on the environment. COM(2018) 35 final.
- [S16] Regulation (EU) 2024/1781 of the European Parliament and of the Council of 13 June 2024 establishing a framework for the setting of ecodesign requirements for sustainable products (ESPR).
- [S17] Commission Regulation (EU) 2023/2055 of 25 September 2023 amending Annex XVII to REACH as regards synthetic polymer microparticles.

Copyright

© 2026 Juan Segurola. All Rights Reserved.