The ***NIKE*** Challenge:

Alternatives to Azodicarbonamide in Footwear Foams

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Greener Solutions: A Safer Design Partnership | Fall 2023

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Executive Summary

Foamed plastic materials are ubiquitous in everyday consumer products, ranging from yoga mats to footwear. Azodicarbonamide (ADCA), a fine yellow crystalline powder, is the industry standard blowing agent to make foamed plastics because it is a cheap and versatile additive. Our industry partner ***NIKE*** uses ADCA to foam their midsoles. Thermal decomposition of ADCA yields carbon dioxide, carbon monoxide, nitrogen, and ammonia gasses which are confined within the polymer matrix producing a porous, foamed material. The generation of these gaseous products has led to the classification of ADCA as a respiratory sensitizer. Additionally, non-gaseous decomposition intermediates and byproducts that are known to be toxic also form as a result of ADCA decomposition, yet their exact hazard endpoints remain unknown. ADCA has been assigned the label of Substance of Very High Concern by ECHA. The toxicity of the ADCA's evolved decomposition products has led to concerns about manufacturers' health and safety leading to an increasing sense of urgency within the industry to find a suitable, cost-effective alternative to this blowing agent.

Within this scope we have identified three strategies that when employed simultaneously can lead to the phase out of ADCA. Various points of intervention have been considered. Firstly, we lay forward possible drop-in replacements strategies. Alternative chemical blowing agents - inorganic carbonates - have been identified to potentially directly substitute ADCA in the midsole foaming process. This strategy can be most easily implemented in current manufacturing processes. Going one step further and eliminating chemical blowing agents altogether, we have identified mechanical foaming as a feasible strategy. Supercritical foaming has already been commercialized in footwear, however it would entail a larger disruption to the current manufacturing process. Finally, additive manufacturing is a midsole production strategy that eliminates foaming entirely and has also started to find application in the footwear industry.

Simultaneously researching alternative technologies, we sought to evaluate each strategy in terms of health and environmental hazards compared to our baseline ADCA. We therefore developed a hazard screening process outlined by Green Screen for Safer Chemicals. Uniquely, our evaluation also encompasses life cycle analysis and carbon footprint. With the exception of additive manufacturing, which is still being developed for large scale application, each of our strategies is deemed greener compared to ADCA.

We have come to the conclusion that a synergistic approach of employing all three strategies - possible for different tiers of shoe lines - will be most effective and quick in phasing out ADCA. However, additional considerations beyond the blowing agent are important to consider. For example, the polymer composition, additives and, processing parameters will need to be adjusted when replacing ADCA.

1. Introduction

1.1 Azodicarbonamide: a ubiquitous industry blowing agent

Azodicarbonamide (ADCA), a yellow powder with the chemical structure shown in Figure 1, serves as a blowing (also termed foaming) agent in various industrial applications. A blowing agent is a substance that yields a porous structure via a foaming process within a material matrix as it undergoes hardening or a phase transition. First used in the 1940s for the foaming of rubber, the industrial application of ADCA expanded in the 1970s with the rise in plastic and rubber production. As of 2017, it was estimated that ADCA was utilized in 80% of foamed plastic products in Europe. ADCA is the industry standard blowing agent because it is easily manufactured at scale, is a cheaply accessible chemical for suppliers, and it is widely compatible with a variety of manufacturing formulations and methods. Because ADCA decomposes during the manufacturing process, the chemical is deemed undetectable in the final product (1). Examples of consumer products in which ADCAis utilized to foam the polymeric material include yoga mats and footwear.

ADCA's mechanism of action is thermal decomposition. Decomposition begins by elevating reaction temperatures above 200°C. The primary gaseous decomposition products of ADCA are nitrogen (65%), carbon monoxide (32%), as well as ammonia and carbon dioxide (3%) (2). As the decomposition progresses, the release and entrapment of these gasses into the polymer matrix contributes to the expansion and foaming properties of ADCA that yields the desired porous material. Additionally, there are secondary intermediates and byproducts that can form via the decomposition pathway, including formaldehyde, formamide, urea, urazole, and (iso)cyanic acid (3). It is important to note the specific reaction pathways to these products on factors including temperature, pressure, and the presence of other reactants in the formulation. The compatibility of the ADCA decomposition pathway within a variety of polymers, such as ethylene vinyl acetate and polyvinyl chloride, and the so-it-seems lack of problematic residual chemicals in the final product are the reasons that ADCA is ubiquitously employed.

1.2 ***NIKE's*** Application of ADCA in Midsole Foams

A key component of ***NIKE***'s high-performance footwear is the midsole, a porous foam that is responsible for providing comfort, returning energy or bounce back to the athlete and enabling muscle and joint recovery. The midsole contains 70% by weight ethylene-vinyl acetate (EVA) polymer and 30% by weight fillers and processing additives, which are added to the formulation to achieve certain performance and technical parameters. Examples include calcium carbonate, ADCA as the blowing agent, crosslinking agents for certain material properties and a zinc(II)-oxide catalyst that decreases the decomposition temperature of ADCA from 200°C to 135°C. ***NIKE*** does not produce their midsoles in-house, but rather purchases them from suppliers in Asian nations. The process of injection molding is utilized to manufacture ***NIKE*** midsoles with the desired mechanical and performance properties (Figure 1).

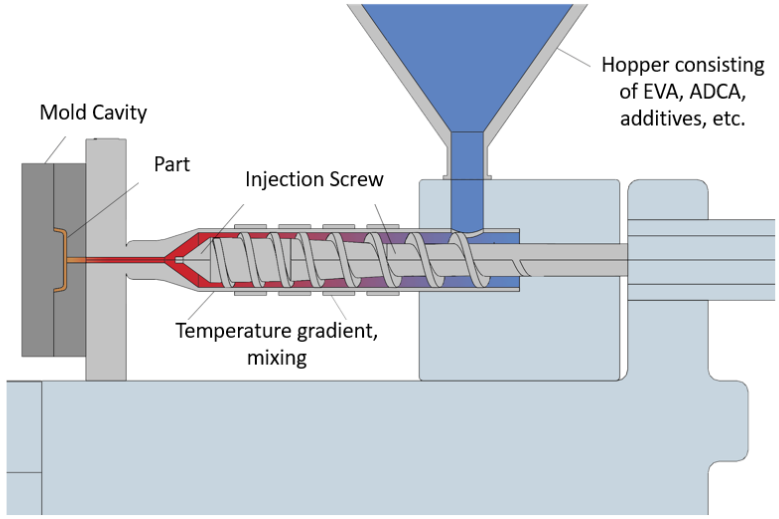


Figure 1. Schematic of the injection molding process (4).

Initially at temperatures of 80 - 90 °C, EVA is physically mixed and melted with filler materials and additives, including ADCA, and then pelletized. This is gravitationally supplied via a hopper and pushed, mixed, and melted along the length of the heated chamber. Simultaneously, thermally activated crosslinking reactions and ADCA decomposition begins. The screw forces the EVA melt through a nozzle and into a closed mold cavity, with the desired midsole shape. In the mold cavity at 170°C, ADCA decomposition and crosslinking is further induced. After 7 minutes in the mold cavity, the midsole foam is removed and placed in a stabilization tunnel for 45 minutes where it is subjected to controlled cooling from 70 °C to 45 °C in order to solidify (5,6). This reduces overall material stress, leading to higher performance shoes.

1.3 Baseline Assessment of Azodicarbonamide

1.3.1 Assessment of Baseline Chemicals

The mechanism of action by which ADCA thermally decomposes into gaseous products, thus forming trapped bubbles that yield the porous foam, is also the reason why ADCA is considered toxic. Each chemical in the mechanism of action has known health and environmental hazards identified by authoritative lists. As seen in Figure 1, there is known concern at every level. ECHA identifies ADCA as a Substance of Very High Concern due to its classification as a respiratory sensitizer. ADCA is a skin and respiratory irritant, possibly causing occupational asthma and potentially being developmentally toxic (7). Particularly ammonia is highly toxic towards humans, leading to naval, eye and throat aggravation as well as skin irritation. Sensitization can occur via inhalation and skin contact (8). Workers who manufacture the EVA foam are most significantly subjected to this toxic gas, as they are exposed to the highest concentrations of decomposition gasses as the mold cavity is opened. Another concern pertains to ammonia trapped within the foam and released slowly over time. Due to ***NIKE***'s large-scale manufacturing and shipping networks, their footwear travels in sealed containers on the ocean for many weeks, leading to the accumulation of ammonia. Therefore, port workers who initially

open the shipping containers are at the highest risk of exposure to large concentrations of ammonia. In addition, the aforementioned secondary byproducts and intermediates are concerning. These intermediates are reported to be carcinogenic to humans, although specific hazard endpoints are yet to be consistently defined because of the variety of possible intermediates. Figure 2 summarizes the main health concerns related to ADCA and its decomposition products. These will serve as our baseline chemicals, as we explore and compare alternative strategies.

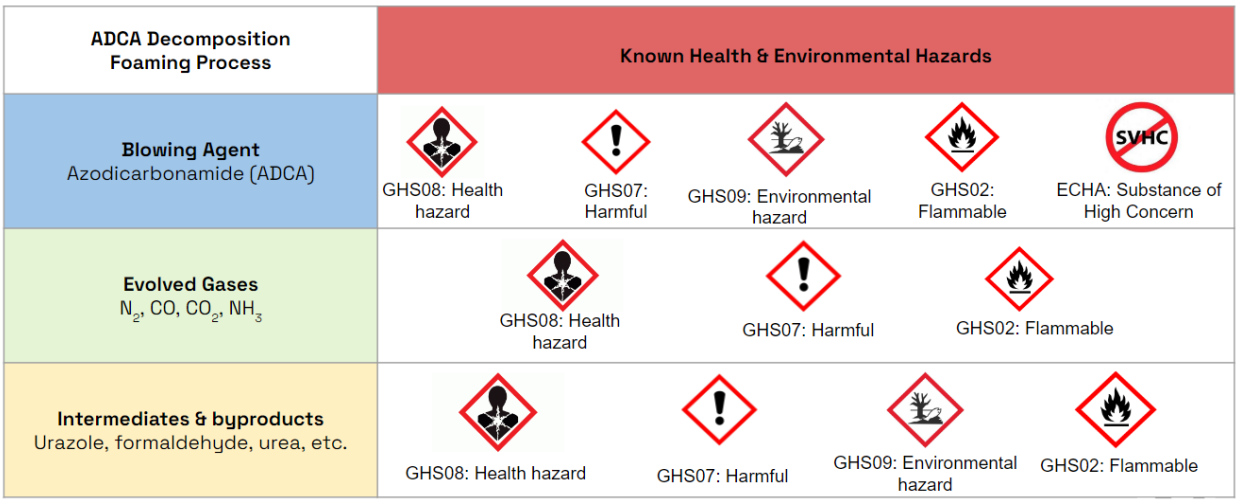


Figure 2. Documented GHS Hazard Pictograms for ADCA Decomposition Foaming Process.

1.3.2 ***NIKE's*** commitment to Green Chemistry

NIKE's 'Move to Zero' initiative towards zero-carbon and zero-waste by 2025 outlines their strong commitment to sustainability and environmental protection. With over 4,000 chemicals used in footwear and apparel manufacturing, the company places a significant emphasis on responsible and effective management of the chemistry employed in the creation of products for consumers, in order to reduce environmental impact and consumer / worker safety. Primarily, the ***NIKE*** Chemistry Playbook serves as a communication tool for this cleaner chemistry strategy and sets supplier expectations. In this Playbook, ***NIKE*** outlines a chemical prioritization strategy that combines regulatory compliance with proactive efforts to promote cleaner chemistry internally and phase out toxic chemicals. Additionally, ***NIKE*** has an internal Restricted Substance List, which defines toxic chemicals that are not to be used in manufacturing by ***NIKE*** or their suppliers. Currently, ADCA is not on the Restricted Substance List. However, ***NIKE*** is a signatory of an industry-wide initiative entitled the Zero Discharge of Hazardous Chemicals Program (ZDHC), which recommends avoiding the use of ADCA where possible and minimizing worker exposure, due to its role as a respiratory sensitizer. ZDHC plans on banning the blowing agent in the near future. Taking together ***NIKE***'s internal green chemistry commitments and the industry-wide movement towards phasing out ADCA, ***NIKE*** is committed to being an industry leader and finding an alternative, less toxic blowing agent for the midsoles of their footwear.

2. Challenge & Approach

2.1 Challenge Statement

Given the toxic decomposition products of ADCA–the known gaseous products ammonia and carbon monoxide and lesser defined byproducts such as formaldehyde and formamide–and ***NIKE***'s commitment to adding ADCA to its Restricted Substance List, our challenge for this project is to identify and evaluate potential alternative blowing agents to foam EVA-based midsoles for ***NIKE*** footwear. We will present alternative strategies, incorporating various points of intervention: alternative chemical blowing agents, blowing methods, and foam manufacturing / synthesis methods. At the conclusion of this project we will also put forward our recommended course of action to phase out the use of ADCA.

2.2 Approach

Throughout the search for strategies to replace ADCA in midsole foams, the viability of the potential solutions were judged by considering several factors:

1) Ease of implementation
2) Technical performance
3) Health hazards & environmental impact
4) Cost

Notably, although all factors contribute in a meaningful way to conclude on the feasibility of a greener solution, the cost factor is regarded as the least impactful parameter. Ease of implementation, describing the need for altering existing production processes, is hard to quantify and is therefore discussed more qualitatively. The technical performance of the greener solution strategies has many components ranging from a plethora of different mechanical properties to product-specific factors such as degradation resistance. Ultimately, health hazards and environmental impact of the current process is compared in detail to the proposed greener solutions.

2.2.1 Mechanical & Performance Criteria

As the main cushioning layer of the shoe, the midsole foam must fulfill a variety of mechanical (or technical) criteria that lead to optimal footwear performance. Relevant material properties that have been determined for midsoles manufactured using ***NIKE***'s current injection molding process with EVA foam blown by ADCA are outlined in Figure 3a (9). The compression set and shrinkage of the foam are key criteria as permanent deformation after compression is undesired in footwear. It is important to note that ***NIKE***'s midsole manufacturing process has been optimized for large scale production with ADCA as the blowing agent. For example, zinc(II) oxide is introduced into the formulation as a catalyst to lower the decomposition temperature. This means that replacing ADCA introduces a multitude of changes into a highly engineered process. As shown in Figure 3b, beyond the blowing agent, the polymer composition, additives and

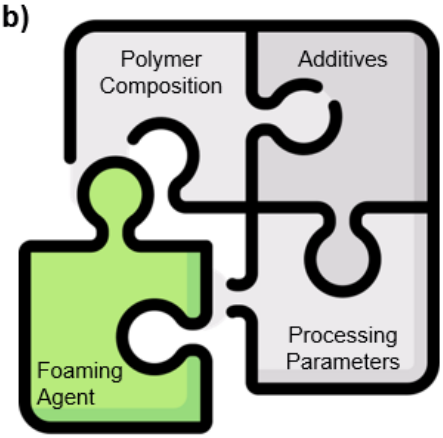
processing parameters all contribute to producing the optimal midsole foam. Thus, the mechanical properties will change when replacing ADCA and factors beyond the blowing agent will need to be re-evaluated. Therefore, as we introduce our alternative blowing agent strategies as ADCA replacements in this report, direct one-to-one comparisons in which only ADCA has been removed with the rest of the midsole composition remaining identical will be difficult. It will seem like there is a lack of fair comparisons especially pertaining to mechanical parameters and performance of the midsole. When assessing the ADCA replacement strategy, we urge some thought towards how the broader manufacturing process may also need to be optimized.

2.2.2 Health and Environmental Hazard Assessment Criteria and Baseline

a)

MATERIAL PROPERTIES	MCS
COMPRESSION SET (%):	60
ABRASION RESISTANCE:	Not Determined
HARDNESS, ASKER C:	32–60
SHRINKAGE (%):	2
TENSILE STRENGTH (kg/cm²):	20
SPECIFIC GRAVITY (WATER=1.0):	0.19–0.22
ELONGATION LENGTH (%):	200–400
TEAR (kg/cm):	10
SPLIT TEAR (kg/cm):	2.5
MELTING POINT (°C):	Not Determined
THERMAL CONDUCTIVITY:	Not Determined
FLASH POINT (°C):	Not Determined

b)



Health and Environmental Hazard Assessment Criteria Guidelines

Figure 3. Mechanical Performance of ADCA-foamed EVA (9).

Group I Human Endpoints			Group II Human Endpoints				Physical Hazard	Ecotoxicity	Fate
Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Endocrine Activity	Acute Mammalian Toxicity	Systemic Toxicity	Neurotoxicity	Skin,Eye, Respiratory Irritation / Sensitization	Flammability	Aquatic Toxicity	Persistence Bioaccumulation

Figure 4. Human Health and Environmental Hazard Endpoints.

We utilized a human and environmental hazard screening process to understand the current process utilizing ADCA and to compare new strategies. It is a comparative hazard assessment, following the criteria established by the Green Screen for Safer Chemicals (10). As seen in Figure 4, we rank hazards among 18 human health and environmental hazard endpoints, which are grouped in subcategories (i.e., Group I Human Endpoints).

Each strategy employs a different set of raw chemicals in the processing, resulting in varying health risks. In order to quantitatively assess the hazard of each health endpoint, we examined the distribution of hazards for each strategy and compared their respective quantities

or estimated composition potency. In addition to this, to ensure accuracy in our assessment, we assigned different weights to each health endpoint group, providing a quantitative outcome. Group I Human Health endpoints, aligning with global and national regulations, address hazards with potential for chronic or life-threatening effects, even at low doses, and intergenerational transfer, and thus will be regarded as priority concern. On the other hand, Group II and II* Human Health endpoints, while crucial for assessment and categorization, are often less of concern due to its estimated potency in the context of the challenge. Reflecting their manageable nature, Group II and II* health endpoints will be considered to pose the second priority concerns. Finally, the physical hazard endpoints will be considered to present the third priority. With this approach, the aim was to focus on endpoints affecting worker health and product degradation.

L	Presumed Safe
L	Low Hazard
pC	Potentially Concern
M	Medium
H to M	High to Medium Hazard
vH to H	very High to High Hazard
	Data Gap

High Confidence	Agreement within multiple sources, primarily relied on ECHA and other authoritative lists
Medium Confidence	Sourced from single authoritative list (i.e. ECHA)
Low Confidence	Preliminary studies and computational models provides evidence, presumed safe due to food additive use

Figure 5. Hazard and Confidence Ranking Guide.

With these priorities in place, we first determine specifics about the chemical's role (e.g., binder, main compound, intermediate) and potency (Figure 5). Then to evaluate hazard endpoints, we evaluated each chemical we identified from a strategy based on a literature consisting of provided documentation, patents, and journal articles. We considered various authoritative and screening lists, ECHA, preliminary studies and computational models to assess available hazard information for each chemical (11). For each component, we determined the specifics of the chemical within the process and estimated relevant potency. By determining this, we were able to consider each chemical's hazards with the focus of worker health and future product degradation.

We then categorically assigned hazards from low to high hazard and determined a confidence level ranking to maintain transparency. We had high confidence when multiple sources were in agreement, medium confidence when evidence of the assigned hazard was found on an authoritative list, and assigned low confidence for preliminary studies, computational models, and presumed safety due to historical use, such as food additive use.

Existing Strategy Health and Environmental Hazard Assessment

Common name	Group I Human Endpoints			Group II Human Endpoints				Physical Hazard	Ecotoxicity	Fate	
	Carcinogenicity/ Mutagenicity	Developmental/ Reproductive Toxicity	Endocrine Activity	Acute Toxicity	Systemic Toxicity	Neuro-toxicity	Skin, Eye, Respiratory Irrit. / Sens.	Flammability	Aquatic Toxicity	Persistence	Bio-accumulation
Ethylene	M			L	M			vH to H	M		
Vinyl acetate	vH to H	M	M	M	M	M	vH to H	vH to H	vH to H		
Ethylene-vinyl acetate (EVA)	L			*M*				H to M		vH to H	pC
Azo-dicarbonamide (ADCA)		*M*					vH to H	vH to H	M		pC
Carbon dioxide	*L*	*L*	*L*	L	M	*L*	*L*	L	*L*	L	*L*
Carbon monoxide		vH to H		vH to H	vH to H			L		L	
Ammonia		*pC*	vH to H	vH to H	*vH to H*		vH to H	L	L	L	L
Formamide	M	vH to H	vH to H		M		*L*				
Formaldehyde	vH to H	M	M	vH to H	vH to H		H to M	vH to H	vH to H	L	
Tetrahydrofuran (THF)	vH to H	*M*	M	*pC*	M	*pC*	vH to H	vH to H			

Figure 6. Hazard table for existing midsole foaming process.

Figure 6 showcases the hazard table for the current ADCA strategy, including EVA which is the baseline foam. EVA is omitted in future strategies if there is sufficient evidence that the polymer is used in the same capacity as this strategy.

Utilizing our hazard assessment approach on the current foaming agent, ADCA, revealed numerous bolded hazards, indicating a high level of confidence in the identified hazards. Notably, the gas byproducts—carbon monoxide, ammonia, formamide, and formaldehyde—display approximately seven bolded hazard levels, ranging from very high to high, specifically for group I health endpoints. Even at limited quantities in a single process, the cumulative multi-dose exposure poses high hazards for group II health endpoints. This observation is crucial as it underscores the elevated concern regarding worker exposure during the manufacturing process due to the high potency of these hazards.

3. Strategies

Throughout the search for strategies to replace ADCA we identified various points of intervention. The least disruptive replacement strategy is a drop-in replacement, which would directly switch out ADCA for an alternative chemical blowing agent. Changing the foaming process from a chemical reaction to a mechanical process is a second strategy that we have identified. Albeit, mechanical foaming involves a greater degree of intervention into ***NIKE***'s current manufacturing process. Finally, the additive manufacturing strategy removes a foaming process altogether and builds the midsole from the bottom-up. This is the most disruptive replacement strategy we are proposing.

3.1 Drop-In Replacements

3.1.1 Avoiding Regrettable Substitutes

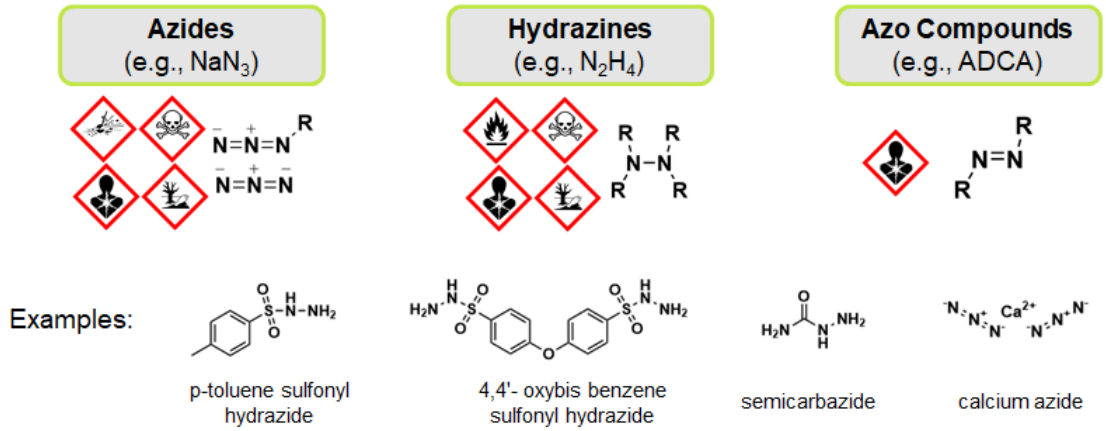


Figure 7. Nitrogen-producing chemicals pose a risk of regrettable substitution.

A drop-in replacement for ADCA would encompass any chemical that could fulfill the role of the blowing agent without many changes to the existing production process. Preferably, like ADCA, it is an N_2-evolving blowing agent. Therefore, drop-in replacements are generally regarded as the most desirable option for finding greener solutions to hazardous chemicals in industry as they can be easily implemented. Unfortunately, groups of chemicals that are likely to evolve nitrogen gas at elevated temperatures pose significant health and environmental hazards (Figure 7). The potential for thermally-induced nitrogen gas evolution is linked to the nitrogen-nitrogen bonds found in azides, hydrazines, and azo compounds. However, these functional groups are directly related to their associated hazards of being explosive, corrosive and flammable. Additionally, for a blowing agent that produces nitrogen, ammonia will always also be a byproduct. The examples of blowing agents shown in Figure 6 are slowly being phased out by industry (12-16).

3.1.2 Sodium Bicarbonate

An alternative to nitrogen-producing blowing agents are compounds that generate carbon dioxide upon thermal decomposition. Likely the most prominent and widely-used example is sodium bicarbonate, also known as baking soda.

Mechanism of Action

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 \uparrow + H_2O \uparrow$$
$$Na_2CO_3 \rightarrow Na_2O + CO_2 \uparrow$$

Figure 8. Thermal decomposition of sodium bicarbonate to produce carbon dioxide.

The thermal decomposition of sodium bicarbonate decomposes at temperatures of around 80-100°C, in which water and carbon dioxide are evolved (17). Further decomposition of the formed sodium carbonate increases the volume of carbon dioxide (Figure 8). This decomposition temperature range is too low to be considered applicable to the current process, as handling of EVA in a molten state requires temperatures of up to 90°C. However, the decomposition temperature of sodium bicarbonate can be increased by adding stearic acid or other carboxylic acids (18).

The advantages of utilizing sodium bicarbonate as a blowing agent is that it is widely accessible at a low price, it is compatible with a variety of polymer mixtures and its tunable decomposition temperature. One consideration that has to be made when switching from an N_2 to a CO_2-evolving blowing agent is that the high diffusion rate of CO_2 leads to a coarser, less flexible foam. This may require re-optimization of additives to yield the desirable mechanical properties of the foam.

Technical Performance

Solvay is currently advertising “functionalized bicarbonate” as an alternative to ADCA and other hazardous blowing agents for various foaming applications, including midsoles (19,20). The exact composition of the bicarbonate-based blowing agent is unknown but is composed of a combination of potential additives (Figure 8). Whereas the function of some compounds, such as fumaric acid acting as a co-blowing agent, is apparent, the reasoning for many additives remains unclear.

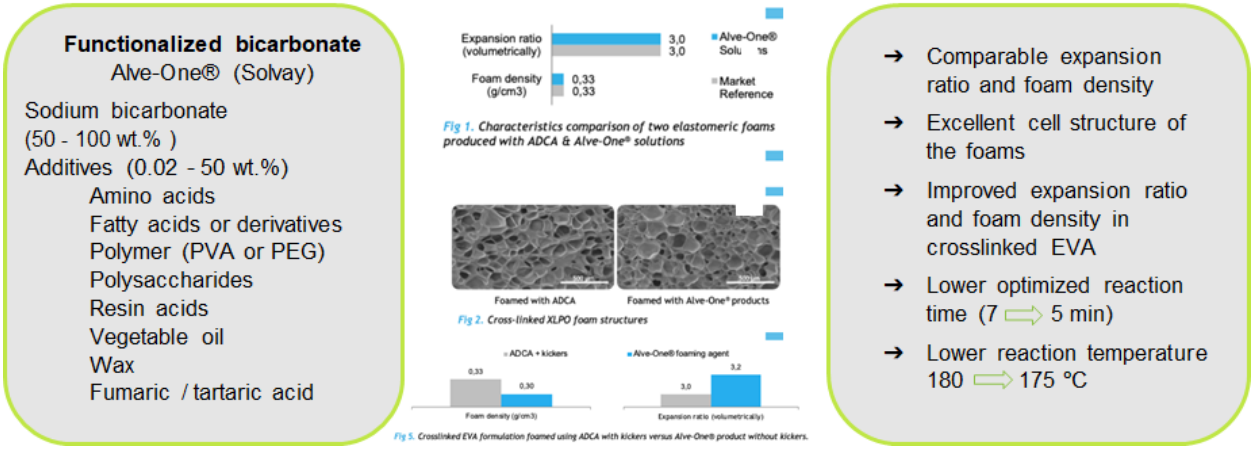


Figure 9. Alve-One ® "functionalized" bicarbonate from Solvay (20).

Solvay reports comparative studies with ADCA-based EVA (Figure 9). Important parameters such as foam density, cell structure, and expansion ratio appear to be comparable to high-end EVA foams. Furthermore, both reaction temperature and time are reported to be lower when using the functionalized bicarbonate. Although these results seem promising, there remain questions about the mechanical performance of the produced foams and the effects of the additives on the life cycle of the polymer composites.

3.1.3 Zinc Carbonate

Aside from bicarbonates, inorganic carbonates, such as zinc carbonate, could also be considered for application as blowing agents (21). Generally, carbonates decompose at higher temperatures compared to bicarbonates, which may pose a challenge.

$$ZnCO_3 \rightarrow ZnO + CO_2 \uparrow$$

Figure 10. Thermal decomposition of zinc carbonate.

An advantage of carbonates as blowing agents is the water-free evolution of carbon dioxide (Figure 10). The decomposition temperature of zinc carbonate lies between 225 - 245 °C, which is considerably higher than the optimal temperature range for EVA processing. Nonetheless, inorganic carbonates could be used in combination with other polymers, such as cross-linked PVC foams or moisture-sensitive polycarbonates (22).

3.1.4 Health and Environmental Hazard Assessment

Common name	Group I Human Endpoints			Group II Human Endpoints				Physical Hazard	Ecotoxicity	Fate	
	Carcinogenicity/ Mutagenicity	Developmental/ Reproductive Toxicity	Endocrine Activity	Acute Toxicity	Systemic Toxicity	Neuro-toxicity	Skin, Eye, Respiratory Irrit. / Sens.	Flammability	Aquatic Toxicity	Persistence	Bio-accumulation
Polyvinyl acetate	*L*	L		L	L	L	L	L	vH to H	M	pC
Vinyl acetate	**vH to H**	**M**	**M**	**M**	**M**	M	**vH to H**	**vH to H**	vH to H		
Sodium Bicarbonate*~	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	L	*L*
Maltodextrin*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	L	*L*	*L*
Resin acids and Rosin acids				*pC*			M	L	**pC**		*pC*
Epoxidized Soy Bean Oil				*pC*			M		*pC*		
Beeswax*	*L*	*L*	*L*	*pC*	*L*	*L*	*pC*	*L*	*L*	*L*	*L*
Fumaric acid*	*L*	*L*	*L*	L	*L*	*L*	**M**		pC	*pC*	
Carbon dioxide~	*L*	*L*	*L*	L	*M*	*L*	*L*	**L**		L	
Sodium Carbonate*~	*L*	*L*	*L*	pC	*L*	*L*	**M**	*L*	*L*	L	*L*
Zinc Carbonate	pC						*M*		**M**	L	
Zinc Oxide	*L*	*M*	H to M	L	**M**	*M*	vH to H	**L**	vH to H	*vH to H*	
Water	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	**L**	*L*

Figure 11. Hazard table for Drop-in replacement foaming agents.

Analyzing the hazard assessment for the drop-in replacement strategy depicted in Figure 11 reveals that a significant portion of the chemicals indicates presumed safe hazard levels. The sodium bicarbonate strategy, incorporating many edible chemicals, is credited with reducing potential hazards to workers.

Additionally, zinc carbonate suggests a potential hazard related to carcinogenicity, albeit without bolding, indicating a moderate confidence level. Despite this, it may warrant consideration. In contrast, zinc oxide presents a notable amount of hazards, ranging from very high to high, concerning skin/eye irritation/sensitization and ecotoxicity. Nonetheless, given the lack of a high confidence level, it may not necessarily be deemed highly toxic.

3.2 Mechanical Foaming

3.2.1 Supercritical Fluids

Inspiration

Aerogels are a class of materials with extremely low densities and high porosities. Although they can be polymeric, most mature applications involve ceramics and metals. Aerogels' low density and porosity mirror the desired structures for ***NIKE*** midsoles. Because of this, we initially explored the possibility of creating 'aerogel midsoles.' While we ultimately determined this to be infeasible, we did derive significant inspiration from aerogels' manufacturing process (23).

At a high level, aerogel synthesis is a two step process: gel generation and gel drying. A gel is a 'semi-solid'; i.e. solid immersed in a liquid medium. By weight, gels are primarily liquid. Gels typically form via precipitation of a solid structure within a solvent. Once the surrounding solvent is removed, only the solid structure remains (the aerogel). For the sake of example, we

will discuss silica aerogel, a porous material that often uses methanol in its synthesis. Once the silica gel is formed, the methanol must be removed. It cannot simply evaporate, as capillary action of the evaporating solvent on the silica pores would create stresses, break bonds, and lead to an overall collapse and densification of the solid structure.

To dry the silica gel without collapsing the structure, methanol must be removed via a supercritical fluid process. Supercritical fluids are a phase of matter in which substances display both properties of gas and liquid (Figure 12). They exist at high temperatures and pressures. Unlike typical phase transitions such as liquid to gas, it is difficult to define a specific thermodynamic point where a gas/liquid transitions to a supercritical fluid (24). Key to aerogel, supercritical fluids have no surface tension, meaning they can be removed from the solid structure without imposing damage. However, it is difficult to bring solvents to a supercritical state. So, solvents are replaced with substances that are easier to make supercritical, often carbon dioxide or nitrogen. In the case of silica aerogel, carbon dioxide is often chosen, as it is less miscible with methanol than nitrogen. Skipping over some of the finer details, the silica gel is put into a chamber, liquid carbon dioxide is pumped in, methanol is removed, and the carbon dioxide is brought to a supercritical state. Once this has been done, the carbon dioxide is removed via a pressure gradient, leaving behind the intact aerogel structure (25).

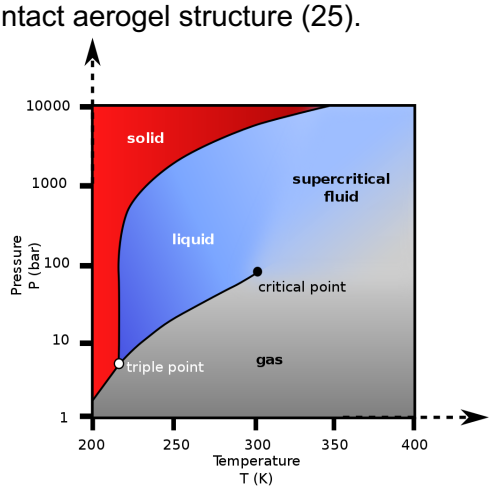


Figure 12. Phase diagram of carbon dioxide; reproduced from Wikipedia (26).

Although we do not consider the sol-gel process a viable way to create a porous EVA structure, we found utilizing supercritical fluids compelling. Looking further into this, we encountered literature detailing a process called ‘supercritical foaming.’ In this, the initial sol-gel step is skipped, and supercritical fluids are used directly to create porous structures. Supercritical foaming also appears to be more commercially mature for polymeric materials compared to aerogel synthesis, an ideal condition for our use case.

Fundamentals of Supercritical Foaming

There is abundant literature delving into the intricacies of supercritical foaming and its practical implementation in an industrial setting (27,28).

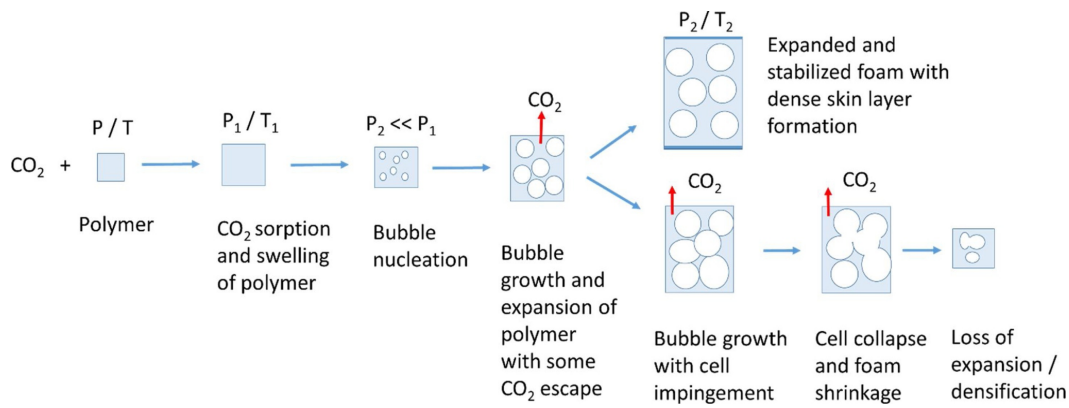


Figure 13. Overview of supercritical foaming process; reproduced from Maio & Kiran (27).

To foam a generic polymer with this technique, it must become saturated with a supercritical fluid (typically carbon dioxide or nitrogen). This is done under high pressure and, in some cases, high temperature such that the polymer is in a molten state and the fluid is supercritical(Figure 13). Once a saturated solution of polymer melt/supercritical fluid is achieved, the pressure and temperature are rapidly dropped, causing the carbon dioxide or nitrogen to leave the solution and leave behind bubbles within the polymer. The polymer quickly solidifies, leaving a porous structure 'frozen' in place. The appropriate temperature and pressures, as well as the rate of pressure drop and the rate of cooling, are specific to every polymer system, and thus must be optimized for that system. If non-optimized conditions are used, the close-cell pore structure can begin to coalesce into a large cavity. Polymers are not stiff enough to support large voids, so the material will pull together due to its elasticity. This is called 'densification,' and it must be avoided to properly foam a polymer (27).

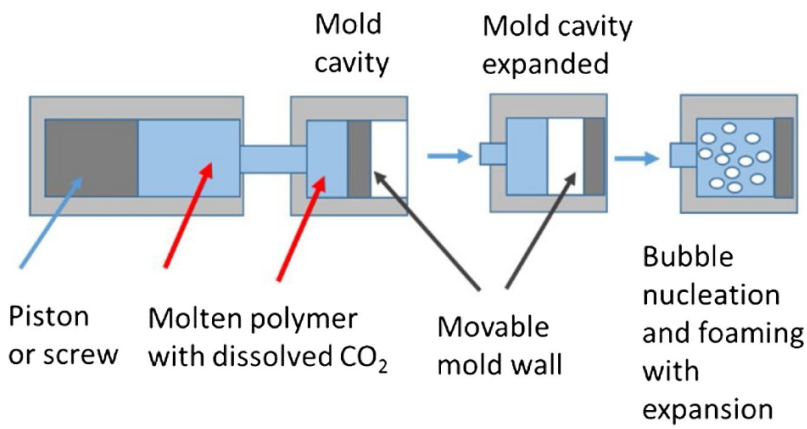


Figure 14. Schematic of injection molding with supercritical fluid; reproduced from Maio & Kiran (27).

The literature and interviews with the ***NIKE*** team indicates that supercritical foaming is compatible with their current midsole production process: injection molding (24). The supercritical fluid is mixed with the molten polymer via the turning of the apparatus' screw (Figure 14). The depressurization and temperature drop needed to nucleate bubbles within the foam occurs when the mold cavity is expanded. This is similar to ***NIKE***'s current process, where ADCA generated nitrogen escapes the polymer matrix when the mold is expanded, leaving behind nucleated

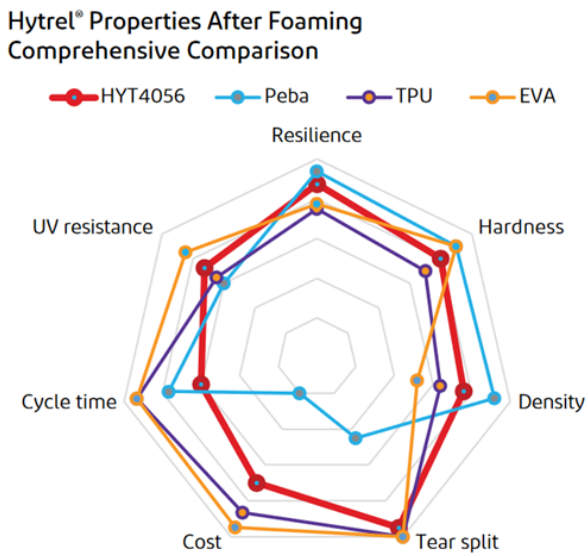
bubbles. The temperature range of current instrumentation is compatible with supercritical foaming, however the mold pressure would need to significantly increase. This calls for retrofitting of current instrumentation in manufacturing processes that utilize ADCA (29).

Technical Performance

Generally, midsole foams produced by supercritical foaming (SCF) can compete, and sometimes outperform, their chemically-foamed counterparts. Importantly, all of the commonly used polymers, thermoplastic polyurethane (TPU), ethylene-vinyl acetate (EVA), thermoplastic polyester (TPPE), and polyether block amide (PEBA), have already been translated into supercritical midsole foams. This highlights the competitiveness of SCF in comparison to other foaming strategies. Suppliers already provide a wide range of SCF-foams:

1) BASF sells SCF-based Elastollan, a TPU foam that can compete with other high-performance midsoles.
2) Arkema provides its PEBA-foam using supercritical foaming to companies like ***NIKE***, New Balance, and Under Armour.
3) DuPont markets a “green” TPPE-foam as high-performing and recyclable, which is directly linked to the avoidance of chemical blowing agents.

Although in-depth comparisons of specific mechanical performance parameters are difficult to find, DuPont provides a good comparison between commercial midsole foams and their SCF-TPPE foams (Figure 15). The figure shows very good mechanical performance with increased tensile strength and elongation as well as lowered compression set compared to ADCA-based EVA. Notably, the split tear of the TPEE foam is lowered, which may be avoided by using a different polymer with SCF processes.



Midsole Results Using Foamable Hytrel®

Test Item	Unit	EVA	TPEE
Hardness	ASKER C	40-45	40-45
Specific Gravity	g/cm3	0.19-0.20	0.14-0.18
Tensile Strength	kg/cm2	22	45
Elongation	%	156	300
Split Tear	N/mm	2.29	2.0
Resilience	%	60	70-75
Compression Set	%	40	25

Source: Data from customer trials

Insole Performance Using Foamable Hytrel®

Test Item	Unit	
Density	g/cm3	0.1-0.12
Hardness	Shore C	25-30
Tensile Strength	MPa	2.8
Elongation at Break	%	280
Method A Tear (Trouser)	N/cm	35
Compression Set	%	25
Ball Resilience	%	75-80

Figure 15. Comparison of mechanical performance for commercially available midsole foams to DuPont's SCF-based Hytrel foam (30).

3.2.2 Health and Environmental Hazard Assessment

Common name	Group I Human Endpoints			Group II Human Endpoints				Physical Hazard	Ecotoxicity	Fate	
	Carcinogenicity/ Mutagenicity	Developmental/ Reproductive Toxicity	Endocrine Activity	Acute Toxicity	Systemic Toxicity	Neuro-toxicity	Skin, Eye, Respiratory Irritation / Sensitization	Flammability	Aquatic Toxicity	Persistence	Bio-accumulation
Carbon Dioxide	*L*	*L*	*L*	L	M⁺	*L*	*L*	L	*L*	L	*L*
Nitrogen	*L*	*L*	*L*	L	*L*	*L*	L	L	*L*	*L*	*L*

Figure 16. Hazard table for Mechanical Foaming process.

Figure 16 highlights that the supercritical foaming strategy does not contain many hazards as it does not produce hazardous gas byproducts and uses either CO_2 or N_2, not both. When in use, the CO_2 did show medium hazard level, but not with high confidence. The EVA polymer formation is the same as the existing strategy. Given the context of this process and lack of specific literature on a number of endpoints, we have extrapolated some of our hazard rankings based on a literature review of the process and our known benchtop experience in the lab. Overall given our designated priorities, this assessment suggests the few chemicals used pose overall low risk.

3.3 Additive Manufacturing

3.3.1 3D-Printing Technology

Additive manufacturing (also known as 3D printing) is currently used to construct shoe components. Adidas, for example, produces its “4D shoe” line with 3D printing (31). Adidas partners with Carbon, a Bay Area 3D printing company, to produce shoes with an intricate lattice structure (Figure 17). Carbon produces the midsoles of these shoes via a process generically known as vat polymerization, during which photons activate polymerization reactions at specific, desired sites. In the following paragraphs, we will discuss forms of vat polymerization known as stereolithography (SLA) and digital light processing (DLP). Carbon employs an augmented form of DLP to produce Adidas’ shoes, and we will note the key innovations Carbon implements to produce high resolution, high performance shoe lattices.

Figure 17. 3D-printed midsoles of ADIDAS sport shoes replace midsole foams (32,33).

During vat polymerization, photons shine into a chemical vat filled with a viscous mixture of solvent, resin (a polymerizable substance composed of monomers and oligomers), and photoinitiators. The photons activate the photoinitiators, which proceed to chain the monomers and oligomers into a polymer network (Figure 18).

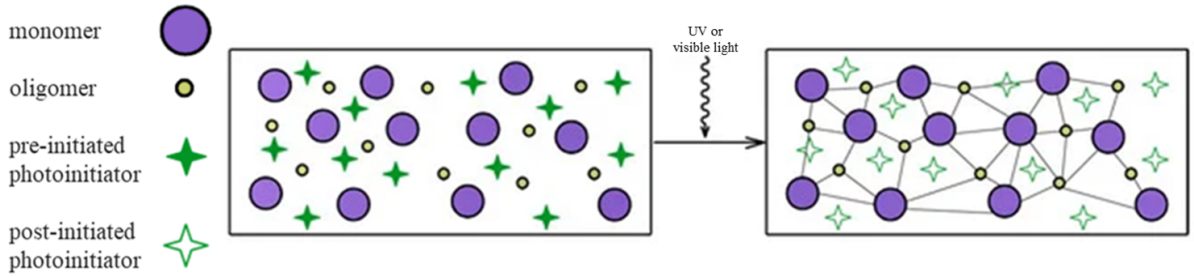


Figure 18. Photoinduced polymerization during the vat process (34).

In SLA, the photon source is a laser while in DLP, it is a digital light projector. In the case of SLA, the laser translates about the solid-liquid interface. The laser sits underneath the vat and shines through a transparent window (Figure 19). After the laser has completed translating across

a given layer, the building platform (to which the forming solid is adhered) raises, and a new liquid-solid interface forms. This process repeats until the part is complete. Because the time to complete each layer is a function of laser translation speed, the SLA printing process is slow. Additionally, the non-simultaneous solidification of a layer can introduce non-uniformities. DLP addressed this issue by replacing the laser with a projected light image. All desired polymerization sites are immediately exposed to the light image, so solidification is both faster and more uniform (34). SLA and DLP are limited in the solid details they can produce: SLA by the laser beam diameter and DLP by the digital image resolution. Current techniques allow for micron scale features; however, pores formed via ADCA reach nanometer sizes.

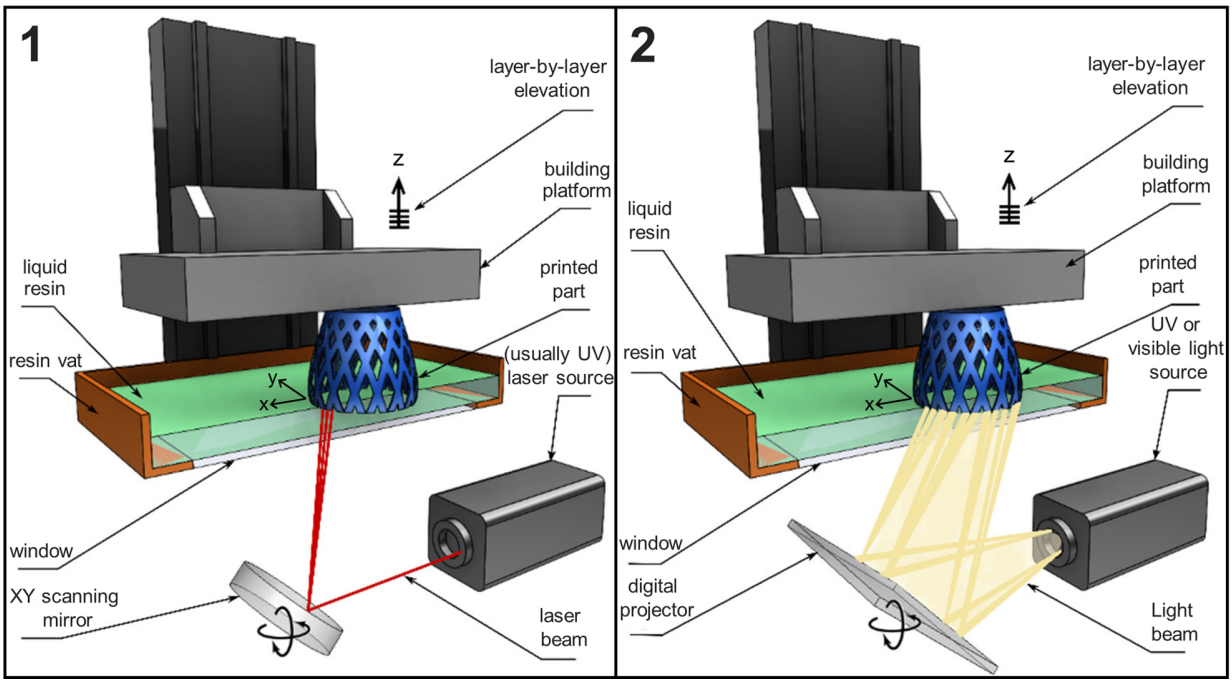


Figure 19. Instrumentation and processing in (1) SLA & (2) DLP (34).

Carbon developed continuous liquid interface production (CLIP) to further reduce undesirable non-uniformities. During CLIP, a digital light image shines through a transparent, oxygen permeable window, allowing for oxygen to diffuse to the solid-liquid interface. As the light solidifies resin, oxygen creates a “dead zone” the width of a human hair between the actively growing solid and the window (35). Resin flows into the dead zone and solidifies. While SLA and DLP grow parts “layer-by-layer” (i.e. each layer must solidify to completion before the building platform is raised), Carbon’s process is continuous, and is therefore significantly faster and precise (34).

For midsoles, Adidas and Carbon have found that photo-curable resins have insufficient mechanical properties once polymerized. As a result, they combine photo-curable resin and temperature-curable resin for their CLIP process. During CLIP, light solidifies the photo-curable resin into the desirable midsole shape. Then, this piece is heat treated, and the temperature-curable resin polymerizes into a polymer network (Figure 20). The photo-cured resin acts as a scaffolding in this process; it polymerizes in a highly controlled shape via CLIP and locks the

temperature sensitive resin into place. Then, during heat treatment, this resin polymerizes inside the scaffolding. This gives the midsoles both the desired geometry and the desired mechanical properties.

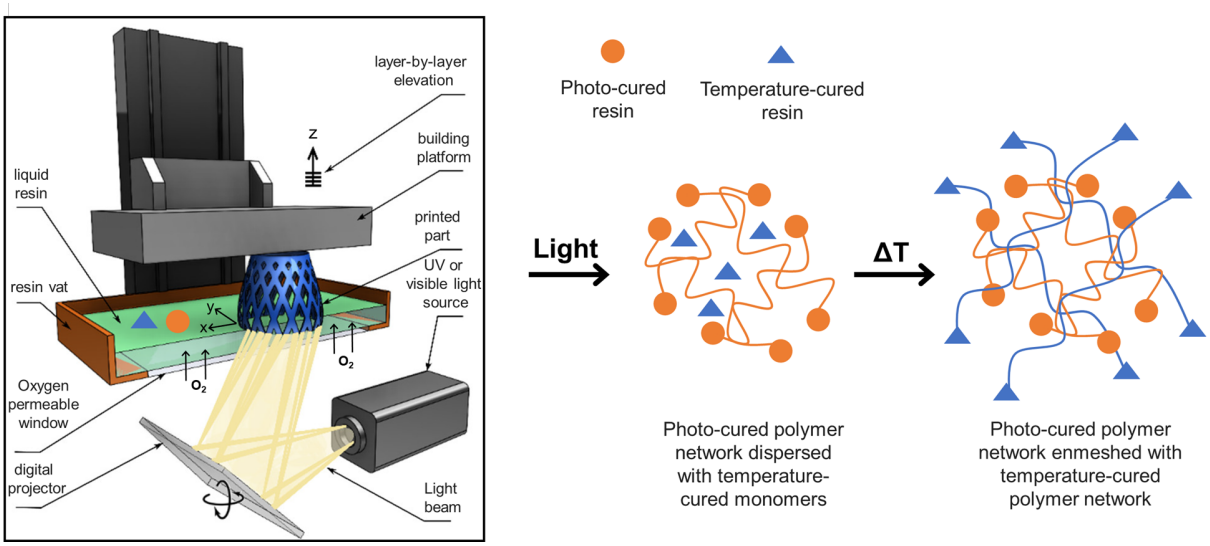


Figure 20. A simplified overview of Carbon's midsole production process (36).

Why Additive Manufacturing? Why not?

Additive manufacturing has some distinct advantages over chemical foaming agents. It is highly tunable, providing midsole macroscopic geometry optimization. This tunability allows for materials' property adjustment that is either difficult or impossible with chemical foaming agents. For example, the 3D printed midsole lattice can behave in such a way that it is stiffer in axial stresses compared to shear stresses, meaning the shoe will preferentially deform in shear. Or, for a different application, engineers can vary midsole stiffness along the length of the midsole. These are just a few examples of property adjustment that 3D printing introduces.

However, vat polymerization has some critical flaws that makes its implementation more difficult. First, Carbon has patented its most technologically mature form: CLIP. Carbon presumably has existing agreements with Adidas that would prevent or inhibit collaboration with ***NIKE***. So, to achieve the speed and precision the oxygen permeable membrane gives DLP, ***NIKE*** would need to explore other areas. Second, vat polymerization introduces significant hazards. It requires solvents, polymerization initiators, monomers, oligomers, among other chemicals that enhance function. Of course, some of these hazards exist in the polymerization of EVA for existing ***NIKE*** midsoles. However, photoinitiators and photo-curable resins are not present in the current process, and they present significant hazards (Figure 23).

Takeaways

Additive manufacturing is a mature technology for high performance midsole manufacturing. Adidas has proven this. However, it contains many hazards and removing them is a technical challenge. So, we will briefly discuss a potential way to achieve some of the favorable macroscopic mechanical properties of 3D printed shoes, while avoiding the hazards. We believe there is much space to explore the mold design of ***NIKE*** midsoles (Figure 21). ***NIKE*** could modify their molds such that the injected EVA would conform to specific, desired geometries.

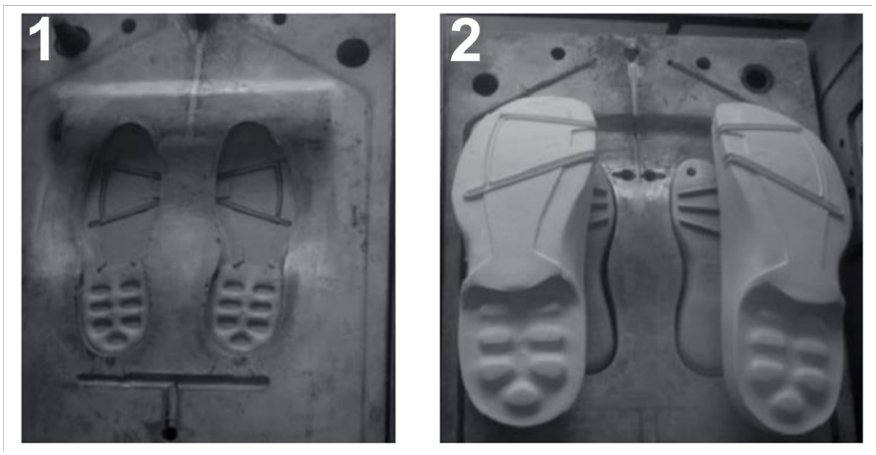


Figure 21. Pictures of the (1) mold cavity and (2) completed foamed part (29).

The first change necessary would be to change the orientation in which the mold opens and closes relative to the mold cavity (Figure 22).

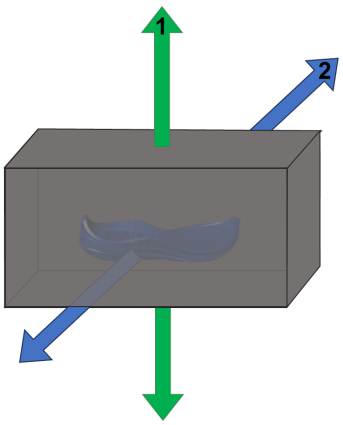


Figure 22. Crude representation of midsole mold. The front panel is slightly transparent so the internal blue mold is visible. Green arrow (1) is the orientation in which the mold currently opens. Blue arrow (2) is our proposed orientation.

With a reoriented mold, ***NIKE*** would then have the option to place rods parallel to the direction of mold opening (Figure 22). Rods, in this case, could span many form factors, not just

cylindrical. Manufacturers could not attach the rods to both mold walls simultaneously, as this would make opening the mold cavity impossible. These rods would serve to mimic the complex lattice structure of CLIP printings. EVA would solidify around the rods and, upon the rod removal, retain a macroscopic lattice structure. A major question is: how intricate could such a mold redesign be? Even if this method does not match the quality of CLIP printings, ***NIKE*** could pair it with the other alternative strategies we have proposed. The midsoles' mechanical properties could benefit from a hierarchical structure–having structural features on multiple length scales. ***NIKE*** would also need to investigate the durability of these thin rods, as they would be subjected to cyclical loading and varied stresses. Perhaps the rods could use Nitinol, a nickel titanium alloy with shape memory effects.

Additionally, the mold manufacturing method is uncertain. Some of the methods ***NIKE*** currently employs, such as computer numerical control (CNC), casting, and electrical discharge machining (EDM) can produce millimeter scale structures (29). ***NIKE*** could consider metallic additive manufacturing methods, of which there are many. Each has associated hazards, sometimes using highly flammable metallic powders, but these molds are also reusable. Unlike CLIP, adjusting mold fabrication does not introduce constantly cycled hazards into midsole manufacturing.

3.3.2 Health and Environmental Hazard Assessment

Common name	Group I Human Endpoints			Group II Human Endpoints				Physical Hazard	Ecotoxicity	Fate	
	Carcinogenicity/ Mutagenicity	Developmental/ Reproductive Toxicity	Endocrine Activity	Acute Toxicity	Systemic Toxicity	Neuro-toxicity	Skin, Eye, Respiratory Irritation / Sensitization	Flammability	Aquatic Toxicity	Persistence	Bio-accumulation
Ethylene	**M**			L	**M**			**vH to H**	M		
Vinyl acetate	**vH to H**	**M**	**M**	**M**	**M**	M	**vH to H**	**vH to H**	vH to H		
Ethylene-vinyl acetate (EVA)	L			*M*				H to M		vH to H	pC
Acrylic acid	L			M	*H to M*		**vH to H**	**M**	**vH to H**		
Urethane	**vH to H**	*H to M*		*M*	*M*						
Diphenyl (2,4,6-trimethyl-benzoyl) phosphine oxide		**M**					*H to M*		*pC*		
2,5-Bis(5-tert-butyl-2-benzoxazolyl)thiophene	*L*	*L*		*L*			*L*		*L*	*vH to H*	*vH to H*
Tetrahydrofuran (THF)	vH to H	*M*	**M**	*pC*	**M**	*pC*	**vH to H**	**vH to H**			

Figure 23. Hazard table for Additive Manufacturing foaming process.

In examining the additive manufacturing strategy, significant preliminary hazards requiring attention have been identified. As shown in Figure 23, both monomers ethylene and vinyl acetate demonstrate high-confidence hazard levels across all Group I health endpoints. Notably, vinyl acetate's bolded high hazard for skin/eye irritation and sensitization raises concerns about a substantial impact on workers.

Shifting focus to the polymer groups, the urethane subgroup stands out with a bolded high carcinogenic hazard. It is crucial to address endocrine activity, as well as hazards related to skin/eye irritation, sensitization, and flammability for the remaining additives, given that these

hazards are bolded. Furthermore, recognizing that an extended list would likely reveal more hazard concerns, considering the known issues associated with specific chemicals in this novel process.

4. Summary of Health & Environmental Assessment

4.1 Comparative Health and Environmental Assessment

Strategy	Common name	Group I Human Endpoints			Group II Human Endpoints				Physical Hazard	Ecotoxicity	Fate	
		Carcino-genicity/ Mutagenicity	Developmental / Reproductive Toxicity	Endocrine Activity	Acute Toxicity	Systemic Toxicity	Neuro-toxicity	Skin, Eye, Respiratory Irri./ Sens.	Flammability	Aquatic Toxicity	Persistence	Bio-accumulation
Existing Strategy	ADCA		*M*					vH to H	vH to H	M		pC
	Carbon monoxide		vH to H		vH to H	vH to H			L		L	
	Ammonia		*pC*	vH to H	vH to H	*vH to H*		vH to H	L	L	L	L
	Formamide	M	vH to H	vH to H		M		*L*				
	Formaldehyde	vH to H	M	M	vH to H	vH to H		H to M	vH to H	vH to H	L	
Inorganic Carbonates	Sodium bicarbonate*~	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	L	*L*
	Maltodextrin*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	*L*	L	*L*	*L*
	Beeswax*	*L*	*L*	*L*	*pC*	*L*	*L*	*pC*	*L*	*L*	*L*	*L*
	Fumaric acid	*L*	*L*	*L*	L	*L*	*L*	M		pC	*pC*	
	Carbon dioxide~	*L*	*L*	*L*	L	M	*L*	*L*	L	*L*	L	*L*
	Sodium carbonate*~	*L*	*L*	*L*	pC	*L*	*L*	M	*L*	*L*	L	*L*
	Zinc Carbonate	pC						*M*		M	L	
Supercritical Foaming	Carbon dioxide	*L*	*L*	*L*	L	M	*L*	*L*	L	*L*	L	*L*
	Nitrogen	*L*	*L*	*L*	L	*L*	*L*	L	L	*L*	*L*	*L*
Additive Manu-facturing	Ethylene	M			L	M			vH to H	M		
	Vinyl Acetate	vH to H	M	M	M	M	M	vH to H	vH to H	vH to H		
	Acrylic Acid	L			M	*H to M*		vH to H	M	vH to H		
	Urethane	vH to H	*H to M*		*M*	*M*						
	Tetrahydrofuran	vH to H	*M*	M	*pC*	M	*pC*	vH to H	vH to H			

Figure 24. Comparative hazard table including existing and proposed strategies.

The comparative health hazard table in Figure 24 outlines the high-potency concerns associated with each strategy introduced. The table indicates that the current ADCA foaming agent strategy stands out, displaying the most bolded high hazard levels across all health endpoint groups. Gas byproducts, notably formaldehyde, ammonia, and formamide, reveal very high to high hazards with high confidence levels for carcinogenicity, developmental/reproductive toxicity, and endocrine activity. Additionally, these chemicals exhibit very high to high acute toxicity with high confidence levels. This consideration is vital, as these gas byproducts pose a potential risk of exposure to workers during the manufacturing process.

In the additive manufacturing strategy, bolded high hazards for group I and II health endpoints are particularly evident. Specifically, solvents like vinyl acetate and urethane present very high to high bolded hazards for carcinogenicity, potentially causing a significant impact on workers. Another important observation is the prevalence of moderate hazards with high confidence levels within the additive manufacturing strategy. Given that these solvents carry substantial hazards, implementing effective safety controls becomes imperative to mitigate the risk of exposure.

Conversely, both the drop-in replacement and supercritical foaming strategies demonstrate a noteworthy abundance of low hazards. The incorporation of inorganic carbonates in the drop-in replacement, comprising edible chemicals, contributes to these lower hazard levels. Additionally, the supercritical foaming strategies distinguish themselves by avoiding hazardous gas byproducts.

In summary, the health hazard analysis (Figure 24) highlights significant concerns across various manufacturing strategies. The ADCA foaming agent strategy raises alarms with elevated

hazard levels, especially concerning gas byproducts like formaldehyde, ammonia, and formamide. The additive manufacturing strategy underscores the need for stringent safety controls, given bolded high hazards, particularly in solvents like vinyl acetate and urethane. Conversely, the drop-in replacement and supercritical foaming strategies present favorable profiles with a notable abundance of low hazards. These findings emphasize the importance of informed decision-making and robust safety measures for minimizing health risks in manufacturing processes.

4.2 Additional Considerations: Life Cycle Analysis, Carbon Footprint, and Limited Knowledge

4.2.1 Life Cycle Analysis (LCA) and Carbon Footprint Assessment Overview

Figure 25. Life Cycle Production Model.

In addition to our human and environmental health screening, we sought to supplement our assessment by considering additional environmental impacts beyond health endpoints (Figure 25). This allowed us to consider other industry sustainability parameters and create a holistic approach in our recommendations. We have decided to take in LCA and carbon footprint data along with the environmental hazard endpoints in our hazard assessment table. This allows us to compare existing data of the current process for these two metrics to our prospective alternatives. For LCA, we will draw from the typical linear production model, seen in Figure 25, and focus primarily on production, end of use, and waste treatment or recovery.

-	Negative/worse than baseline
0	No impact on current process/baseline
+	Positive/improvement to baseline

Figure 26. LCA and Carbon Footprint Ranking

The aim of this process is to highlight key differences between the standing process for ***NIKE*** versus an alternative strategy and not reinvent the wheel for every aspect of our partner's process. Therefore, we ranked a '-', or negative/worse than baseline, if a strategy's LCA or carbon footprint would have a negative environmental impact on ***NIKE***'s current strategy. A '0', or no impact on current process/baseline, represents the baseline strategy. A '+', or positive/improvement to baseline, was given if a strategy's LCA or carbon footprint would have a positive environmental impact on ***NIKE***'s current strategy. This ranking is a weighted off of industry knowledge and an intensive literature review, which is not consistent for each strategy. However, it allows us to have a general idea if a strategy is worse than ***NIKE***'s baseline, has no impact on the current process, or provides an improvement.

$$CO_2 emissions = estimated\ energy\ consumption\ \ x\ 628\ \ (tCO_2\ /\ GWh)$$

Figure 27. Carbon Footprint Equation

If possible, we ranked strategies' carbon footprint quantitatively given values provided from articles and other publications. To calculate carbon footprint, we take into account estimated energy usage multiplied by a country's emission grid factor to convert to an estimated CO_2 emission value. For the context of energy consumption, it was recommended by our partner to use Vietnam as a relative measurement because much of ***NIKE***'s footwear is produced there. Based on the International Renewable Energy Agency (IREA), Vietnam's CO_2 emission value is 628 tCO_2 / GWh (Figure 27) (37). Overall, this assessment offers deeper insights into potential environmental impact and implementations for ***NIKE***, which are summarized in Figure 27.

Strategy	Life Cycle Analysis	Carbon Footprint
ADCA	0	0
Inorganic Carbonates	-	0
Supercritical foaming	+	-
Additive Manufacturing	-	-

Figure 28. Final LCA and Carbon Footprint Ranking for Strategies

4.2.2 Existing Strategy

While it is known that EVA is difficult to recycle, ***NIKE*** has an existing program to promote EVA recycling and reuse that should be taken into account. This advantage helps ***NIKE*** with waste reduction and can be taken into consideration for both the current ADCA process and any other strategy that utilizes EVA. There is no current documentation on specifications of midsole waste treatment but Hoskins reports that EVA can last up to 1,000 years in the landfill. In addition,

there is some evidence that ADCA presents a potential bioaccumulation hazard (38). As seen in our hazard assessment, ammonia and formaldehyde all are high hazards for ecotoxicity endpoints. In addition, carbon monoxide and formamide are both high hazards for Fate endpoints. This suggests that the ADCA hazard's may persist and potentially the high hazard byproducts may as well.

While the exact carbon footprint value is unknown, we are aware that the required baseline machinery is the Powder Metal Injection Molding (PMIM or MIM). This process of EVA injection typically requires between 0.20 to 0.35 kWh/kg (39). This variation is typically from the fluctuating temperature conditions in the process. Therefore, the estimated CO_2 emission values range from 1.256e-4 to 2.196e-4 tCO_2 * kg/ GWh.

4.2.3 Drop-In Replacements

Among the drop-in replacement strategies, the research suggests that ADCA can be relatively easily replaced by ADCA. Since the machinery does not need to be changed and the general process does not call for the addition or removal of steps, we consider a drop in replacement equivalent to the existing strategy. Therefore, the carbon footprint and expected life cycle would remain the same. However, for the Solvay "functionalized bicarbonate", additional polymers, such as PVA, are currently used. Given that ***NIKE***'s recycling strategy may not be compatible with PVA, we caution that this could negatively affect the waste stream. This allows us to give drop in replacements a "-" for LCA and a "0" for carbon footprint.

4.2.4 Mechanical Foaming

Supercritical foaming has been a desired replacement for solvents due its low human and environmental health hazards in various settings, such as to remove caffeine in coffee to replace water or steam in the concentrated solar power process. For supercritical foaming hazard assessment, there were low hazards for persistence and bioaccumulation. In addition, we expect an easier separation between the polymer from the unreacted monomers and catalysts. As stated prior, it would require altered instruments, require more energy, and increase carbon footprint.

Internal conventional wisdom at ***NIKE*** has shown that the current supercritical foaming process tested, which its specifications cannot be disclosed to us, is six times the energy usage than the traditional process described in above sections. However, the critical point of CO_2 is 304.28K, similar to the current temperature requirement of ~400K for the melting and crosslinking process of EVA. With this in mind, we believe supercritical CO_2 may be achieved within the current temperature required and not increase energy needs from this capacity. Instead, the high-pressure requirements are likely the main factor for increased energy consumption. Therefore, we maintain the stance that it may have a negative impact on carbon footprint. This allows us to give drop in replacements a "+" for LCA and a "-" for carbon footprint.

4.2.5 Additive Manufacturing

For additive manufacturing, there is a lot of conflicting evidence for its end of use, waste treatment, and estimated energy use. We caution the mixed literature surrounding the implementation of this method (40). While some authors rave about the potential waste

improvements, there are also competing studies suggesting the opposite. Kumar suggests an increased recyclability for 3D printed PLA, ABS & PETG materials (41). Furthermore, Enemuoh highlights the optimization potential of 3D printed materials (42). This article suggests an estimated CO_2 emission values range of 0.1896-0.2080 tCO_2 * kg/ GWh. On the other hand, the process is noted as an overall variable and brings a lot of uncertainty to our carbon footprint parameter. In addition, EVA has not been a noted polymer tested in this injection molding process. Therefore, ***NIKE***'s EVA recycling program cannot be used. This is overall negative and brings a lot of uncertainty around the strategy's LCA and carbon footprint, which leads us to give additive manufacturing a "-" for LCA and a "-" for carbon footprint.

4.2.6 Knowledge Gaps and Limitations

Throughout our hazard assessment and additional considerations, there are some limitations to our findings. Due to the nature of some chemical matter (i.e., evolved gasses), some chemical compositions are unknown and were extrapolated from the strategies' mechanism. There were also limitations in some metrics due to gaps in literature. At times, we estimated hazards within the context of benchtop use or as a food additive. Nevertheless our extensive research and thought for each chemical gives us confidence in our rankings.

5. Recommendation & Future Directions

5.1 Summary & Recommendation

The goal of this project was to identify and evaluate feasible alternatives to the blowing agent ADCA for applications in midsole foams. We have identified three strategies, ranging from direct drop-in replacements using inorganic carbonates, to supercritical foaming, in which the foaming process is changed from a chemical to a mechanical one, and finally to additive manufacturing in which foaming is omitted entirely. To summarize, the advantages and disadvantages are outlined in Figure 28.

The ease of implementation is one major consideration for ***NIKE*** in replacing ADCA. Ideally, a single drop-in replacement can be employed in current manufacturing processes, and mitigate the use of ADCA while still maintaining the mechanical properties of the midsole that yield high-performance footwear. However, our research has shown that will not likely be the case and that there is a reason that ADCA is so well-established. Therefore, we recommend that ***NIKE*** pursue a multi-strategy approach in the phase out of ADCA. Inorganic carbonates, especially sodium carbonate, can be used as a blowing agent on a large-scale, but the formulation of the EVA foam needs to be re-optimized to account for the lower decomposition temperature and coaster foam. We foresee this strategy to be employed for most of ***NIKE***'s high-production scale, basic-tier footwear. Simultaneously, we recommend ***NIKE*** slowly begin adapting manufacturing instrumentation to accommodate supercritical foaming - arguably the greenest solution. We believe that midsoles for higher-tier footwear can be manufactured with

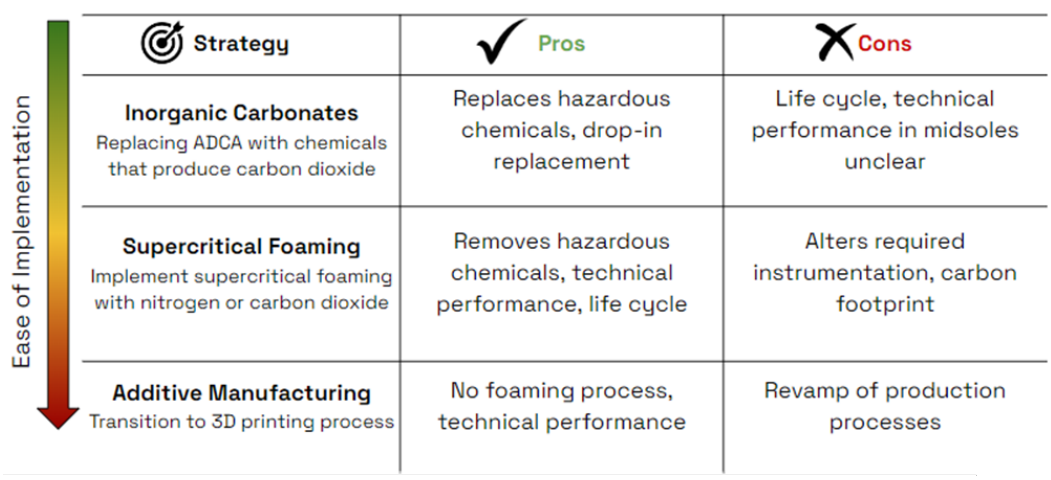


Figure 28. Weighing of ADCA-replacement strategies for midsole foams.

this technology. Finally, as additive manufacturing technology scales and continues to become mainstream, we believe that this strategy can also find broader application within ***NIKE*** manufacturing. We encourage ***NIKE*** to begin laying the groundwork for this strategy sooner rather than later, for example by seeking out industry collaborations. Clearly, the synergistic

implementation of all strategies will be most effective in phasing out ADCA and will ensure ***NIKE*** remains a competitive, innovative leader in the footwear industry.

5.2 Additional Considerations Beyond the Blowing Agent

At this point it is worth reiterating that beyond the blowing agent ADCA there are other parameters that contribute to manufacturing the optimal midsole foam. These include the polymer material and composition, additives and fillers as well as processing parameters and will have to be re-evaluated with the phasing out of ADCA. In terms of the classic injection molding process for example various factors can be adapted to account for an inorganic carbonate blowing agent. The screw chamber temperature can be changed to correct for changes in polymer melt viscosity. The mold cavity size and form can be corrected for changes in midsole expansion or densification. Finally, the mold heat soak time can be varied to account for kinetic differences in gas evolution between N_2 and CO_2 (29). Also, we wanted to mention a new polymer material that has found application in the footwear industry as a greener alternative to EVA. Polyether block amide (PEBA) are bio-based polymer granules derived from castor beans. This polymer has been commercialized as PEBAX in high-performance footwear. Unfoamed PEBAX has a compression set of 43% compared to ***NIKE***'s EVA value of 60% (43). As ***NIKE*** phases out ADCA, we recommend they also think about finding greener alternatives to other components of their midsoles–the polymer material being the largest constituent of the midsole.

6. Conclusion

We have evaluated three feasible strategies that, when employed simultaneously to ***NIKE***'s manufacturing of midsoles, can lead to the phase-out of ADCA. We developed a human and environmental hazard screening process following the criteria outlined by Green Screen for Safer Chemicals. We added life cycle analysis and carbon footprint as additional considerations in our evaluation. Comparing each of our strategies to the baseline chemicals associated with ADCA, we were able to provide strategies that eliminate bad actor chemicals from the midsole foaming process. For all of our strategies, we have also provided commercialized examples, showing that the industry is already clearly moving away from large-scale use of ADCA. Our three strategies can be implemented but with varying levels of ease, thus we recommend a multi-strategy phase-out of ADCA.

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