Foaming of Bioplastics:

Technologies, Challenges and Future Directions

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Introduction

Why are the VITAL project partners interested in foamed materials? This technology offers many benefits and unique features, including (but not limited to) lighter weight parts, thermal insulation, sound insulation, increased compliance/comfort, impact absorption, liquid absorption (or, conversely, buoyancy), reduction in material usage, and increase in fracture resistance. Some of these features are essential for circular economy development: adding air reduces the quantity of material needed for a product and the associated lighter weight of these components reduces the environmental footprint of its transport.

Properties of the foamed material can be controlled via several factors:

- Properties of the parent polymer and whether it's a "thermoplastic" or "thermoset" material (see definitions box)
- The internal volume of the bubbles (known as "cells")
- Whether the foam is "open cell" or "closed cell" (see definitions box)
- Even the gas within the bubbles may have an influence.

By controlling these properties, a variety of foam types can be created to suit a diverse range of applications, including food packaging, insulation for homes and white goods (e.g. fridges, freezers), pads and cushions in seating, crash helmets, floristry, protective packing, shoe soles, soundproofing, gap filling, filtration and separation (e.g. oil spill cleanup), medical devices, and electromagnetic shielding[1–4].

Thermoplastic foams are of particular importance in the circular economy as the nature of thermoplastic materials is such that they can potentially be melted and re-molded several times before they need to be disposed of. This gives us 2 "R's" of the circular economy: **reduce**, reuse, repair/refurbish, **recycle**, recover (energy, chemical resources)[6]. Project VITAL aims to additionally use biobased thermoplastics, which could ideally be recycled or biodegraded at the end of their useful life.

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DEFINITIONS
In **closed cell foams** the cells are sealed and are not interconnected. These foams are impermeable to liquids. They have excellent thermal insulation, higher mechanical strength (than open cell foams) and find uses in buoyancy, lightweight structural parts, thermal insulation and impact resistance (***Figure 1a***).
Open cell foams consist of interconnected cells. Air and other fluids can flow freely through the structure. These materials are flexible, softer and more breathable than closed cell foams. They find uses in cushioning, sound absorption, filtration, cell scaffolds, and cleaning sponges (***Figure 1b***).
Thermoplastic – a polymer that can be melted and reshaped multiple times.
Thermoset – a chemically crosslinked polymer that cannot be melted and reshaped.

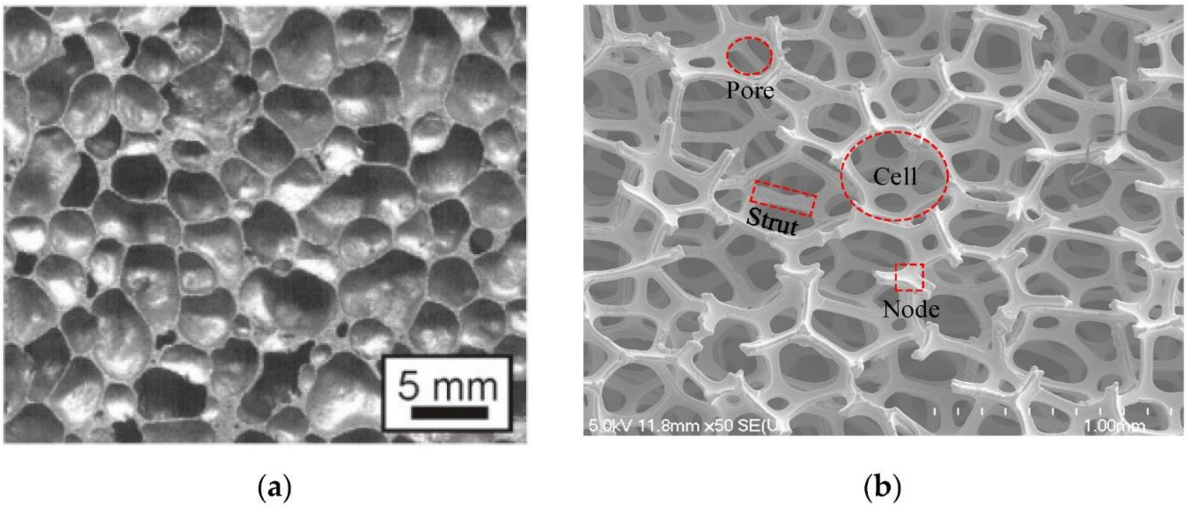

Figure 1. Examples of the microscopic appearance of a) closed cell foam, and b) open cell foam. Reproduced from Yang et al[5] under Creative Commons CC-BY license.

The basic steps of foaming a thermoplastic material are shown in ***Figure 2***.[1,7] Firstly, a mixture of molten polymer and foaming (blowing) agent is created. The blowing agent is dissolved in the molten polymer at this point. Next, a rapid change in conditions (e.g. heat increase, pressure reduction) starts the bubble formation ("nucleation"). Bubbles grow until the plastic either sets under cooling, or the growth is physically constrained.

Next, we look at some specific foaming technologies that are relevant to project VITAL. As in our earlier article, we prioritise research and applications relating to foaming of poly(lactic acid) (PLA), as this is the thermoplastic of main interest to our project. Firstly, we consider the types of foaming agent used in the production of thermoplastic foams, secondly some foam manufacturing techniques and finally we look at some of the challenges of foaming biobased thermoplastics, and how we are working to solve those issues.

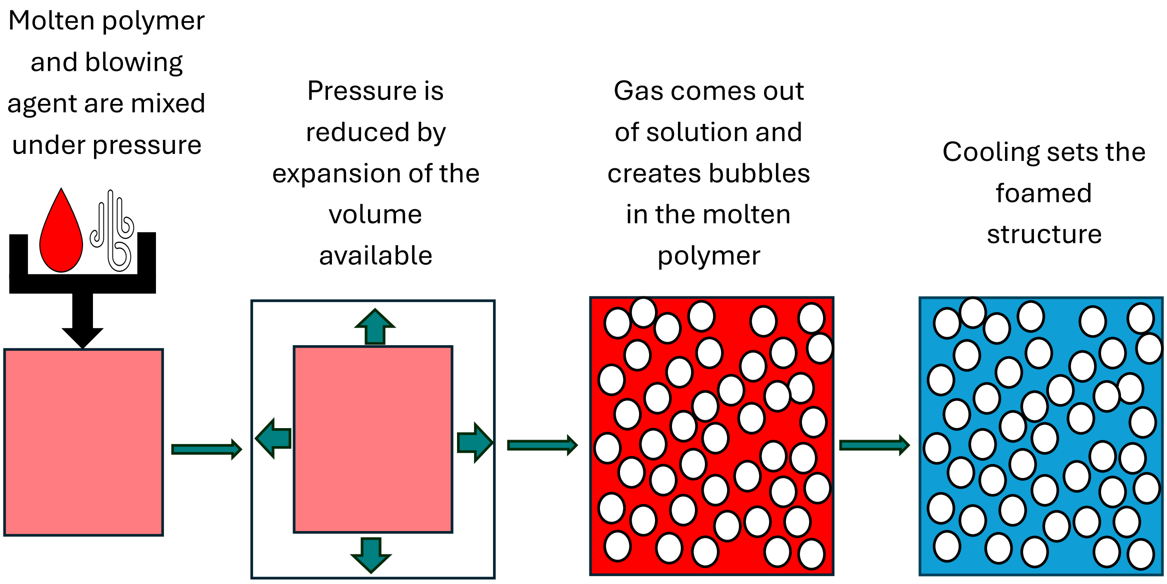

Figure 2. General method of the production of a foamed thermoplastic.

Physical Blowing Agents

Physical blowing agents (PBAs) are either gases or volatile liquids[2]. Their highly volatile nature means that no residues are left in the material after foaming, which is helpful for certain applications (e.g. medical devices). However, specialist modifications to extrusion equipment (direct gas injection into the barrel) are often required to allow use of PBA's[8].

Older PBAs included CFCs, due to their low flammability. They have since been phased out due to their impact on the ozone layer. Current blowing agents include:

- Hydrocarbons (e.g. pentane)
- Atmospheric gases (e.g. CO_2, N_2)
- Water
- Supercritical fluids[9]

Chemical Blowing Agents

Chemical blowing agents (CBA's) generate gases through chemical reactions of added ingredients. Thermal decomposition reactions are most common, however in some cases the chemical reaction of 2 added components can be used[2,3,8]. CBA's can be directly used in most typical extruders without modification, since they are typically added as solid powders or granules[8]. However, they often leave residual by-products behind in the foamed material, which may prevent use in certain applications.

Examples of CBAs include:

- Inorganic carbonates, in combination with citric acid
- Azo compounds (e.g. azodicarbonamide, usually used in combination with an activator)
- Nitroso compounds
- Acyl hydrazides
- Water (reaction with isocyanates in polyurethane thermosets)

Manufacturing Foamed Materials

Foam Extrusion

Foam extrusion is a continuous manufacturing process suited to the production of simple shaped products, such as insulation boards. Polymer pellets are fed from a hopper into an extrusion barrel. The blowing agent can be added to the hopper (CBA) or injected into the extruder barrel (PBA) where it is mixed into the polymer melt at high pressure. As the polymer melt leaves the extruder barrel through a shaping die, it experiences a pressure drop, and expansion occurs[2,7,10]. As the expansion of the material is unconstrained, low density materials can be achieved for insulation, packaging and impact absorption. This method is not used in project VITAL, as we need to create parts with specific shapes.

Foam Injection Moulding

Like the foam extrusion process, foam injection moulding starts with using an extruder barrel to melt and mix the polymer with the blowing agent. Rather than extrusion to ambient conditions, the melt is injected into a mould where the foaming takes place to expand the polymer melt into the desired component shape[2,7,10]. The pressure drop required for bubble nucleation and expansion can either come from underfilling the mould (“short shot” or “low pressure”) and allowing the expansion of the foam to fill it, or from fully filling the mould and then partially opening it to increase its volume (“breathing mould”, “high pressure” or “full shot”). A schematic of the breathing mould method can be seen in ***Figure 3***. Either way, more complex shapes can be created than in the simple foam extrusion process. Densities of foams produced in this way tend to be higher than the extrusion process due to the constraint applied to the expansion stage: this tends to produce stronger materials that are useful for structural applications. This is a key process in use in project VITAL, to produce lightweight, structural, closed-cell foam parts for use in cars and domestic fridges.

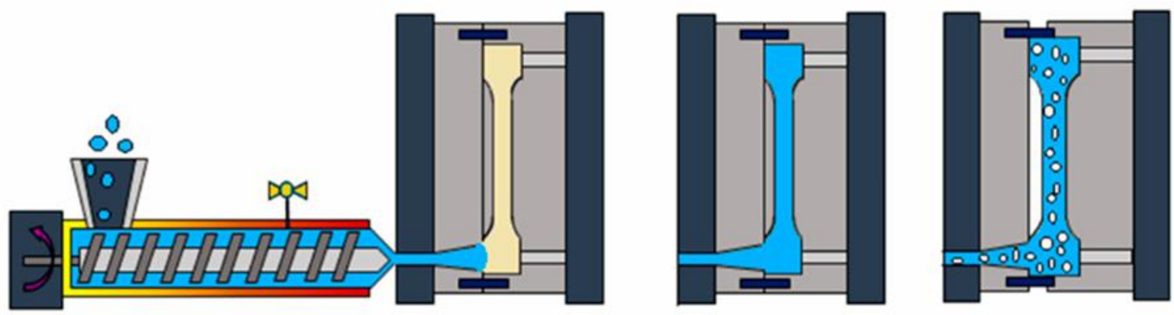

Figure 3. Schematic of the breathing mould method for foam injection moulding of test specimens. Adapted from Villamil Jiminéz et al under Creative Commons CC-BY license [11].

Bead Foaming

The classic example of a bead foamed material is expanded polystyrene (EPS), used in packaging, insulation and cycle helmets. This process is suitable for manufacturing high volume products with complex shapes and very low densities. It requires several steps:

1. Preparation of polymer beads
2. Impregnation with blowing agent
3. Pre-foaming of the beads
4. Final foam expansion and bead fusion within a mould

Classically, steam is used to achieve the final foam expansion and bead fusion, but since many biobased polymers are polyesters, this can have a negative effect on their molecular weight and mechanical properties by causing hydrolysis reactions [7,10,12].

In project VITAL, bead foaming is being used to create seat cushions for high volume automotive seat cushioning applications.

Additive Manufacturing

One of the challenges of the previously described manufacturing routes is that they all require access to expensive tooling/moulds to create the required shape. These approaches are excellent for high volume manufacturing, where large numbers of copies of a part are needed, as the cost of the mould can be offset against the large number of parts that will be created. However, the cost of moulds can be prohibitive for small production runs.

Additive manufacturing provides an alternative technique that can build complex part shapes without requiring the production of expensive tooling. It is efficient in terms of material use and can create more complex shapes than can be achieved via mould-based techniques. However, it can be slow, so it is often less suited for high volume manufacturing. Production of large components also needs similarly large printers!

There are many types of additive manufacturing, but the one of interest for project VITAL project is the thermoplastic extrusion type, which is most familiar to people as “3D printing”.

The combination of 3D printing and foaming technology is not yet well established, but is a subject of intense interest[7,13,14]. Porosity can be introduced to the printed part using a blowing agent within the polymer, as we already discussed, or voids can be printed into the part in defined geometries.

In project VITAL, 3D printing is being used to prepare short-run, custom interior cladding designs to use in cruise ship interiors.

Challenges of Foaming Biobased Thermoplastics

As in our earlier article on biobased polymer recycling, there are several characteristic properties of biomaterials that make achieving our goal of lightweight, biobased products challenging to achieve.

Not just bioplastics, but many thermoplastics suffer from low melt strength, which results in a narrow processing window and cell collapse during the foaming process[1,10,12]. Additionally, certain blowing agents can act as plasticisers, reducing melt viscosity and strength as their concentration in the thermoplastic is increased[10].

PBAs may have poor solubility in the molten biobased thermoplastic, which limits the amount of blowing agent incorporated, reduces the degree of foaming that can be achieved and can cause defects. This issue can be particularly challenging for semi-crystalline polymers, as the solubility of the blowing agent is lower in crystalline than amorphous regions of the polymer. On the other hand, the presence of crystallinity can increase melt strength of the polymer, so a balance must be found.

As already mentioned, CBAs leave behind chemical residues that limit the application of the final foam due to health effects such as irritation and allergic reactions (e.g. in medical applications), and some have exothermic gas-release reactions make the foaming process conditions difficult to control[15]. Project VITAL researchers are trialing both PBAs and CBAs for different processes and applications, and our products have less critical requirements for foaming agent residues than some applications.

Lastly, as in biobased polymer recycling, the water sensitivity of polyester-type biobased polymers can be challenging in bead foaming processes where steam is used to provide heating for expansion of the foam structure. Project VITAL researchers are working with alternative methods of energy input for the final bead expansion stage to avoid the possibility of PLA hydrolysis (which reduces the strength of the produced parts) and also to reduce the energy demand of the process, therefore improving its cost and environmental impact.

Innovations & Future Perspectives

A wide range of additives are under investigation to improve foaming in biobased materials, such as inorganic fillers, lignin, cellulose, graphene, and many others. Additives such as these tend to increase melt strength, accelerate crystallization in suitable polymers and promote bubble nucleation[1,9]. However, nano-fillers in particular can be difficult to disperse effectively in the polymer melt, which makes it hard to reach their full potential in terms of property enhancement.

Blending approaches to improved foaming of thermoplastics can have some interesting results. Blending of miscible polymers can often produce thermoplastics with customized properties intermediate between the individual ingredients, or sometimes synergistic property enhancements can be achieved. Alternatively, blending immiscible polymers can create in-situ reinforcement phases under certain conditions[1,9]. The disadvantage of polymer blending approaches is that they can lead to difficulties in mechanical recycling, as the blended materials would need to be collected and recycled separately from pure materials, and this is not often economically feasible.

Additive manufacturing (3D printing) of foamed materials is an area of significant interest for future customized production of lightweight flexible and rigid materials for new applications such as medical devices, footwear and aerospace industries[4]. The possibilities of combining conventional foaming processes with production of printed void structures are numerous. This is an area of particular interest for project VITAL.

NewWave Replacement of toxic, fossil-based raw materials (e.g. phenolics, isocyanates) with bio-based alternatives is a key target for many researchers. For example, our Biomatters partner project, New Wave is creating new polyurethane foams, and construction materials based on these, from wood waste via a novel pyrolysis process[16].

Conclusions

A variety of technologies are available for foaming bioplastics, some of which need modification to avoid known bioplastic challenges. The technology used for foaming the bioplastic, along with the type of foaming agent should be thoughtfully chosen according to the requirements of the market as some are better for high volume production than others. The use of 3D printing to produce foamed structures is a relatively new development that has high potential in lower volume production environments with high customization needs.

Careful selection of raw material grades and blending with appropriate additives is still needed to mitigate some of the bioplastic challenges and prevent foam collapse during or after production.

Project VITAL is investigating all these elements and is on the way to producing real, foamed bioplastic parts for durable market applications in the coming months.

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