Rapid Prototyping of Green Composites

by Nadya Peek

B.Sc. University of Amsterdam 2008

Submitted to the Program in Media Arts and Sciences,
School of Architecture and Planning,
in partial fulfilment of the requirements for the degree of
Master of Science
at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY
September 2010

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ABSTRACT

Rapid prototyping employs digital fabrication techniques to quickly manufacture parts. However, the available materials are not yet suitable for making strong, large or durable objects.

Composites are materials which are very strong and lightweight, combining the tensile strength of a fibre and the compressive strength of a resin matrix. Unfortunately, tooling for composite parts is currently expensive, slow to make, and therefore out of reach for many small-scale projects. Furthermore, popular composites are toxic to the environment and the people who work with them.

Green-, eco- or bio- composites employ natural fibres in conjunction with biodegradable, renewably sourced or less toxic (in use and in manufacturing) matrices. Benefits of using natural fibre composites are that besides being light, strong and less toxic, they are also cheaper, of lower density, easier to work with and more environmentally friendly than carbon– or glass-fibre composites. The latest techniques and efforts on green composites however remain firmly in the lab– the resources evaluated are not readily accessible for manufacturing in the field.

Local specialised projects now can use digital fabrication tools to realise structures previously considered prohibitively expensive to manufacture without an economy of scale. But because of the cost, difficulty and potential health hazards of composites, they have not yet been explored as a material for small scale local manufacturing.

Digitally fabricated tooling introduces composite manufacturing as a rapid prototyping method. Green composites enable worker-safe manufacturing with environmentally friendly materials. Together, digitally fabricated tooling and green composite workflows allow faster, cheaper, stronger and less toxic large-scale prototyping in the field.

I present an evaluation of green(er) composite materials which can be sourced and made in the field using low-cost digitally fabricated tooling. This includes case studies in medical devices, vehicles and housing.

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Nadya Peek

CONTENTS

1. INTRODUCTION: FAST, LIGHT AND CHEAP MATERIALS WITHOUT SACRIFICING PERSONAL OR ENVIRONMENTAL HEALTH

The Industrial Revolution provided us with the mechanisation of production facilities, allowing more reliable, cheaper, and higher quality products. Most of the products that surround us now are mass-produced, harnessing cheap transport as access to an economy of scale for the vast quantities produced. Manufacturing costs have gone down so far that it has become cheaper to replace products than to repair them.

Sometimes there are products and tools that we need or want but simply cannot find. A cellphone that has a built in long-range directional antenna that you can point to where you know there is a cell tower. A prosthetic limb that besides looking like your other real limbs, also can do more for you like charge your cell phone or computer. A small UAV that can carry medical samples swiftly from rural areas to large hospitals for testing.

More often, there are products or objects that are so much more abundant, fast or cheap that it doesn't make sense for us to make our own personalised solution. It is easier to donate hundreds of pre-fab FEMA trailers for emergency housing than to try to build personalised houses for a community displaced by disaster. But given time, the one-size-fits-all solution is rejected and replaced with something more suitable.

It is not a sustainable model for us to keep producing more ill-fitting solutions and throwing them away without looking at the supply of resources or where the waste ends up. Manufacturing must come up to speed with the society we now live in. If the whole world is to live and work together, with all humans given equal opportunity, then we must start working on rapid personalised fabrication. Mass produced items used to be the way to make things that would otherwise be prohibitively expensive. Now however, they are simply used to create fat profit margins. Digital fabrication tools enable the low-cost production of products in small runs, and can be used to empower the consumer, the user and the individual to make what they need, when they need it.

Around the world, there are FabLabs, which stands for Fabrication Laboratory. In the FabLabs there are computer-controlled machines that can be used by novices for personal fabrication. Most of these FabLabs are not in fancy universities or the R&D labs of large companies: they are in *the field*, where they are being used by locals to solve local problems. A lab in an agricultural area of India might try to make tools to test for milk adulteration. A lab in Afghanistan may make replacement communication systems while waiting for country-wide infrastructure to return.

In the field it remains difficult to make lightweight, strong structures such as airplane wings or solar collectors. However, there is still a need personalised, lightweight and strong items. A rodeo kayaker in Maine may want to design a special paddle for low water. Young amputees in India may want a prosthetic limb that allows running, swimming and climbing trees.

In this thesis I will consider the possibilities using making strong, lightweight materials in the field for personal fabrication. High-performance composite materials were invented by for military defence purpose. Is it viable to use manufacturing techniques and materials that were invented for defence missiles and spaceships on a small scale? How can digital fabrication be employed to make these slow, expensive processes cheaper and more accessible? Is is safe for novices to work with composites? What could green composites offer as materials and workflows to a small scale user? What are the available green composite materials and how to work with them?

PLASTICS

Plastics are one of the cheapest materials to mass produce products with, but they do not last well in their functional form– the pieces snap, bend, deform. The rendered useless plastic material lasts lifetimes in landfills without degrading.

Waste production has steadily increased by approximately a kilo per person per day since the 1960s, for a total of a 68% increase today [50]. In that time, waste recycling has only increased a total of 33%, and this increase has slowed significantly in the last 10 years. This is an unsustainable discrepancy for the environment. Current production rates are already revealing the limitations of the planet's energy resources and raw materials, not to mention the effects on the earth's biosphere and ecosystems.

Plastics are currently a very inexpensive and diverse material, easily moulded or extruded into mass produced items. They are mostly produced by polymerising monomers extracted from crude oil. As the price of oil goes up, the cost of making common plastics will also steadily increase. Although many types of plastic are readily recyclable, it can be difficult to sort waste according to plastic type for processing. The amount of plastic which ultimately is recycled remains low.

In response to the increase in oil cost and a drive to be more sustainable, many companies have started developing plastics using vegetable oils and other non-petroleum derivatives. They derive the monomers from soy or corn oil. There has also been a leap in the development of biodegradable plastics which need not be recycled, made from starch derivatives. This allows the plastic industry to rely on renewable resources such as soybean oil to make plastics they are familiar with, or to replace common plastics with alternative materials which are biodegradable and need not be recycled.

Plastic is abrasion-resistant and durable, but mostly do not have great tensile strength properties. Because of the manufacturing methods commonly employed, it remains difficult to make large-scale objects (4m+) of plastic. When making higher-strength or larger-scale objects which must remain very light, composites are often employed alongside plastics for reinforcement.

COMPOSITES

A composite combines two or more constituent materials to form a hybrid material that displays a combination of the ingredients' mechanical properties. In general, the constituents include a reinforcement material and a matrix material. A historical example of a composite is adobe, a building material that combines mud and straw into bricks through compression. A popular high-performance composite is currently carbon fibre in an epoxy plastic matrix, which has great strength while remaining very light. Carbon fibre is therefore used extensively in demanding technological applications such as aerospace engineering, prosthetics manufacturing and sports equipment. Like plastic, composites can be easily made into an array of shapes and forms. Once joined, it is very hard to separate the constituent materials of a composite, making them bad candidates for recycling.

Besides being difficult to recycle, it is relatively hazardous and difficult to work with high performance composites. Fibreglass and carbon fibre dust pose significant respiratory hazards, and epoxy resins emit noxious fumes while curing. Because of the capital needed for health protection and the machines used for producing high performance composites, as well as the expense of many of the moulding options, composites are still mainly produced in mass-production facilities. This keeps the cost of composite structures high for small production runs, and does not encourage prototyping and innovation with composites.

GREEN COMPOSITES

Environmentally friendly composites are a possible alternative to (reinforced) plastic materials. Instead of using the typical epoxy resins and plastics, they use biodegradable matrices and plant– or animal-based biodegradable fibres. At the time of writing, not all the mechanical properties of the green composites match those of their non-green counterparts, nor do they last as long, but these qualities could also be seen as features. A beneficial side effect would be that the constituent materials are far less hazardous to work with, and could enable individuals and companies with small production runs to use high strength and low weight materials.

There has already been extensive research in green composites, especially with regard to their biodegradability and environmental impact in comparison to other materials [28, 3]. Green composites are also already used in various industrial applications such as automotive and building parts [16]. However, there has not yet been an extensive evaluation of how green composites could be used on a small scale, and what they could be made of. Sourcing fibres and resins can be challenging on a small scale, especially in rural areas.

Lifecycle analysis

Even though green composites sound appealing in their material choice, more characteristics should be taken into account when choosing the right material for a product. A lifecycle analysis (or lifecycle assessment, or LCA) studies the phases the product goes through– raw material production, manufacturing, distribution, usage, disposal and all of the transport required between the different stages [31]. This information is used to form a methodical analysis of the environmental impact of a product. A full lifecycle analysis of a given product could take several years, and without strict standards, the information obtained through the LCA could be misleading [21].

For green composites, many factors come into consideration with the growing, harvesting and preparing of the fibres and the extraction and preparation of the resins. For composites like glass– and carbon-reinforced epoxy resins, several decades have gone by in which manufacturers could streamline their processes. Their methods have become very efficient in cost, waste and labour in comparison to the early 60s. With wide-scale adoption of green composites, cost, waste and labour can also be expected to decrease.

With small scale green composite development, the actual cost of producing prototypes may not reflect the true cost of material and development. Without executing a full lifecycle analysis, I will attempt to provide an accurate idea of how different green composites could be used. In some cases, the use of biodegradable materials is not as efficient as fully recycling a material into new products. In others, a part might be so specialised it can not be recycled or reused.

Thesis overview

In this thesis I will consider the possibilities of field fabrication of green composites for specialised projects. It includes an outline of composites in general in chapter 2. It continues with an overview of green composites already developed in academia and industry research institutes, an overview of green composites currently in use in industry, and an evaluation of the mechanical properties of selected green composite combinations in Chapters 3 and 4.

Chapter 5 details tools developed for more efficient (in energy and cost) high performance composite manufacturing. These include methods for making intelligent moulds that heat the parts internally, and embedding temperature sensors into moulds to be able to sense the cure cycles of the curing resins.

In Chaper 6 I briefly outline possible recycling practices and possibilities for different types of composite materials and propose methods of manufacturing composite materials that can be reused over and over in different products.

Chapter 7 looks at some case studies of green composite development and use, including data from a development and design session on lower limb prosthetics in collaboration with BMVSS and the Jaipur Foot Organisation in Rajasthan, India.

A summary and outline of possible future research and goals is included in Chapter 8.

2. BACKGROUND

Composite materials are gaining popularity as lightweight, strong materials. High-performance composites are made through a range of specialised techniques such as vacuum moulding or pultrusion. This chapter gives an overview of contemporary composite applications and techniques, and can be skipped if the reader already has familiarity with the subject.

2.1. COMPOSITE TYPES

The term composites nowadays generally refers to high-performance composites, extremely strong and light materials. The most popular is to use woven carbon fibre or fibreglass cloth injected with epoxy resin. Carbon fibres are around 2 to 5 times as strong in tension as glass fibres, and about half as strong as a corresponding part made in steel (although much lighter). Aramid fibres (including Kevlar and Nomex) are more flexible than carbon fibres, although more difficult to process. The final part made with a woven fibre cloth will not be homogenous in its stress distributions, the direction of the weave of the fibre will influence the strength of the material. Aligning the fibres in the direction where tensile strength is required is key to maximising the strength of the material.

Carbon fibres are made by taking other fibres, such as polyacrylonitrile or rayon, and incinerating them at extremely high temperature in an inert environment. Different types of carbon fibre result in different mechanical properties: fibres heated to 2000°C have high tensile strength, but fibres heated to 3000°C will have a higher modulus of elasticity. Depending on the heat and the original fibre, the resulting carbon strand can be anywhere between 40 and 95 percent carbon, and between 4 and 10 micrometers wide. This is only one-tenth of the width of a common human hair, and cause for concern in working with carbon fibre– the fibres are small enough that when breathed in, they can not be expelled from the lungs and may cause a range of respiratory diseases.

Glass fibres are made by extruding heated glass into fibres. Different glass types will result in different mechanical properties in the fibres. The most commonly used is e-glass, but other types such as s-glass will be used for parts that require higher tensile strength. The width of glass fibres is comparable to the width of carbon fibres (glass fibres being around 8 to 30 μm in diameter and carbon fibres being 5–8 μm), and there are similar health hazards associated with working with glass fibre.

Aramid fibres such as Kevlar are extruded through a spinarette, similar to nylon. The resulting fibres are anisotropic, their long polymer chains along the fibre give it much more axial than transverse strength. Unlike carbon and glass fibres, aramid fibres are thicker and less of a health hazard when working with them, but require special tools to cut and sand due to their toughness. Kevlar is often used in combination with glass fibre to combine the mechanical properties of both materials.

Fibres for composite lay-up are mostly bought in fabric or ribbon form. Different weaves of fabrics for composite lay-up include satin, twill and plain. Satin and twill weaves are easier to form to curves, although there is more fibre slippage than in plain weave fabrics. Fabrics can also come in non-woven forms, such as matted fabrics. Matted fibreglass is common in hull manufacturing, as it is one of the easier materials to quickly form into a mould.

Chopped fibres can also be added to a plastic to increase its tensile strength properties. The fibre must be long enough for the fibres to break before they are pulled out of the matrix material. Chopped fibres added while the resin has already started curing can introduce many voids, therefore chopped fibre composites are often mostly used in injection and pressure moulding.

The most common type of matrix for composite materials is currently epoxy resin. Epoxy resin consists of a resin and a hardener. Combining the two results in an exothermic reaction in which covalent bonds are formed between the resin and the hardener [41]. The amounts of resin and hardener are optimised for a full reaction, resulting in an inert, strong, and rigid material. To start the reaction, the epoxy may need to be heated to an activation temperature.

Epoxy resin are molecules that contain one or more *epoxide* groups. The epoxide equivalent weight is one of the key features of epoxies, along with the molecular weight of course, and the viscosity.

The most common type of epoxy resin is a glycidyl epoxy, and the most commonly used glycidyl epoxy is the Diglycidyl Ether of Bisphenol-A (DGEBA). The properties of DGEBA depend on the number of repeating units there are on the molecule, and the resulting molecular weight. The repeating units in commercially available epoxies range from between 1 and 25 repeats. The longer the polymer chains in the epoxy, the more rigid the fully cured material will be, but also the more difficult it will be to ensure a complete reaction. Hardening agents for epoxy contain an active hydrogen atom, which breaks free the double-bonded oxygen atom in the epoxide group. This is an exothermic reaction.

The most common types of curing agents are amine-based. The primary and secondary amines react strongly with the epoxide groups, whereas the tertiary amines act as a catalyst for the reaction. Other common curing agents include anhydrides and phenolics.

Working with epoxy has many health hazards associated with it. The most common problem is a sensitisation to the hardeners, which can cause allergic reactions in humans that work with the material over long periods. Working with epoxies has been the leading cause of occupational asthma. Some epoxy hardeners are also known endocrine disruptors, and the damaging effects of working with too much epoxy could be shown generations later.

2.2. CURRENT COMPOSITE PRACTICES

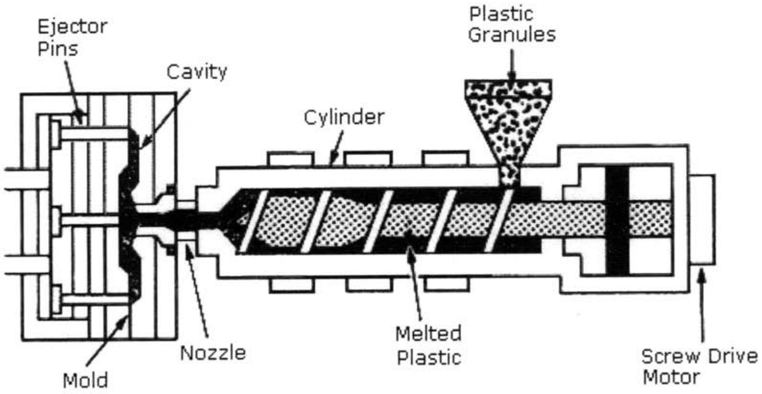
Since the introduction of composites to automotive and aerospace applications in the 1960s, composites are now also used in structural earthquake reinforcements in buildings, compressed natural gas tanks, surfboards, boat hulls, race bicycle components and medical devices. Any application where both strength and weight are important factors are good candidates for composite techniques and materials. Composites are also good for applications which need better acoustic damping properties than metal can provide.

Composites will last a very long time– unlike metals, there is for instance no cyclical loading limit for carbon reinforced plastics. However, once the composite parts have reached the end of their useful life, they remain difficult to break down. Unlike metal, they cannot be melted. Instead, they can be shredded and reused as chopped fibre, or they may be decomposed by hydrous pyrolysis after which the fibres and monomers may be extracted and recycled. However, this process is not cost effective at most scales, and has yet to be implemented widely.

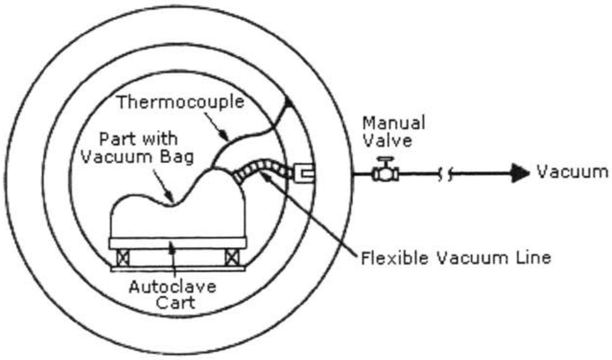
On a small scale, high performance composites are used by hobbyists interested in building their own custom sports gear (surfboards, kayaks) and by prostheticists making stiff, light, custom sockets for their patients.

COMPOSITE LAY-UP TECHNIQUES

Depending on how many of the same part must be made, how big it is, its shape and the materials you will be using, different composite manufacturing techniques are preferable. Composite techniques are often developed specifically with a part in mind. In the following figures, common methods for composite manufacturing are described.

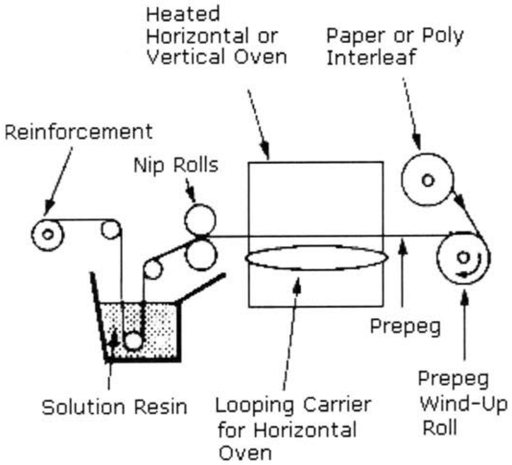


(a) Injection moulding: an extremely common method for making parts, injection moulding uses thermoplastic granules which are heated and injected through a screw barrel into a mould. The process is easily automated, but the moulds are expensive to make, being generally precision-milled from aluminium. Therefore, injection moulding is mostly used in large runs. Because fibres are damaged in the injection process, it is unpopular for many composites.

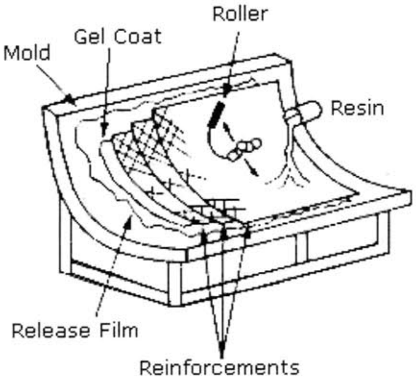


(b) Vacuum bagging and autoclave curing: pressure is exerted on a part by drawing a vacuum on a surrounding bag. The part is covered with a release film, and then with a bleeder mat which will absorb the excess resin, and placed into the bag. A vacuum is drawn on the bag, drawing out air bubbles and excess resin. The entire bag can be placed into an autoclave for heating and curing. Vacuum bagging is a popular technique for large parts that are produced in small runs.

Figure 2.1: *Injection moulding and vacuum bagging. Images from United States Department of Labour OSHA Technical Manual, section III chapter 1*

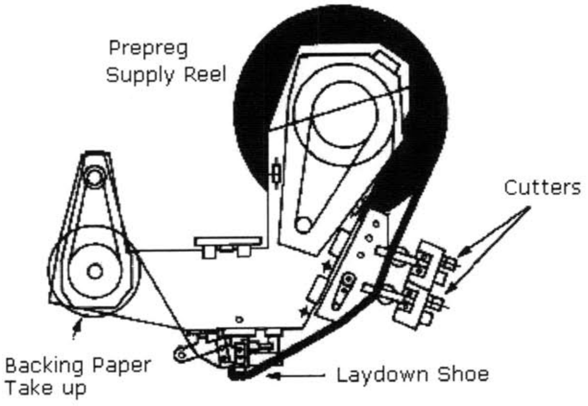


(a) Solution pre-pregging: fibre mats are pre-impregnated with resin before lay-up. One method for impregnation is submersing the fabric into resin. Another method is hot-melt pre-pregging, which impregnates the fabric through heat and pressure. Pre-preg material is used with resins with a curing temperature which is much higher than atmospheric temperature, and pre-preg material is generally stored in coolers.

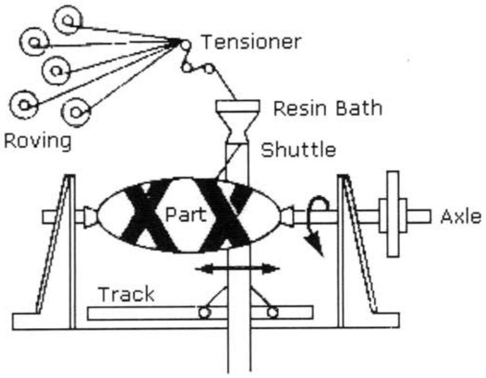


(b) Hand lay-up of prepreg: a mould is prepared with a desired degree of surface finish. Sheets of pre-preg are rolled onto a part, as many layers are required. While rolling the fabric on, the direction of the fibre can be alternated. The part can later be vacuum bagged and/or placed in an autoclave for heat and pressure.

Figure 2.2: *Pre-preg composite. Images from United States Department of Labour OSHA Technical Manual, section III chapter 1*

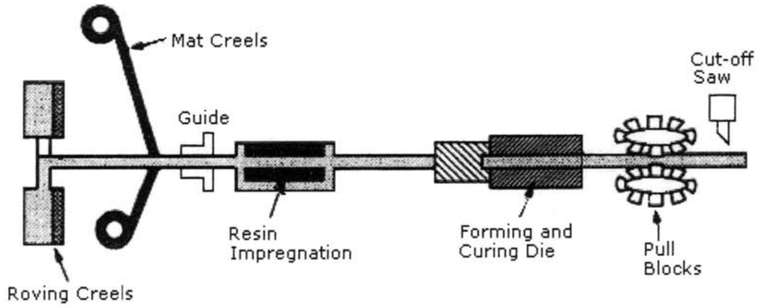


(a) Automated tape lay-up: a robot automatically covers the surface required with pre-preg tape. This process is only used on relatively simple surfaces and with large runs.

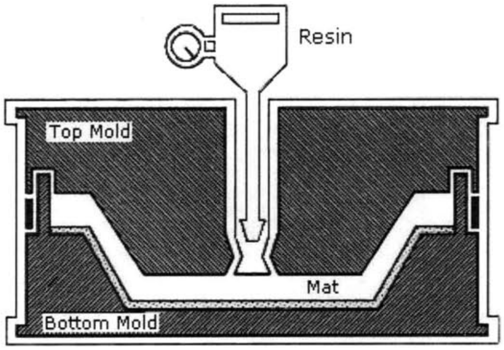


(b) Wet filament winding: a highly precise way of orienting the fibres, and therefore the strength axes, of a composite part. A robot soaks roving in resin and winds it directly over the part. This method is used for parts where strength and weight are extremely critical.

Figure 2.3: *Automated lay-up methods. Images from United States Department of Labour OSHA Technical Manual, section III chapter 1*



(a) Pultrusion: is similar to the extrusion process– roving is directly formed and cured into a part which is then cut to appropriate length. This method is mostly used for bars and rods.



(b) Resin transfer moulding: fibre matting is placed into the mould, later resin is poured or injected in. This process is similar in concept to injection moulding, however, the part will still need curing and the fibre mat placement is not automated. It is therefore a much slower way of making parts.

Figure 2.4: *Pultrusion and resin transfer moulding. Images from United States Department of Labour OSHA Technical Manual, section III chapter 1*

3. GREEN COMPOSITES

Due to the health hazards and difficulties with recycling of contemporary composites, and also the dependency on the petroleum industry for the ingredients for epoxy resins and common plastics, researchers are turning more and more to materials which are come from renewable sources, can easily be recycled or can biodegrade. The terms *green composites, biocomposites, ecocomposites* all broadly refer to materials that occupy this space. They are inclusive: they are used to describe any combination of these materials, whether natural fibres in a synthetic matrix, natural fibres in a renewable synthetic matrix, synthetic fibres in a biodegradable matrix, synthetic fibres in a renewable synthetic matirx, natural fibres in a natural matrix, etc.

Even though the ecologically responsible choice seems clear when choosing between natural and man-made fibres, one must take the full process of growing, treating, manufacturing, usage and degrading or burning into account when comparing the two materials. If the farming, chemical treatment and manufacturing are done poorly, this can make the natural fibres a less responsible choice.

For matrices, biodegradable options will not be explored by industry unless they can be shown to be cost effective. As the cost of raw materials for epoxy resins and synthetic plastics rises, matrices sourced from increasingly cheaper renewable materials becomes more interesting.

This chapter is an analysis of current research in renewable, biodegradable, non-toxic composite materials. I will begin with a consideration of natural fibres: how they are harvested, prepared and processed, and what their mechanical properties are. Then I will consider types of biodegradable matrices: mechanical properties, how they degrade and what they can be used for.

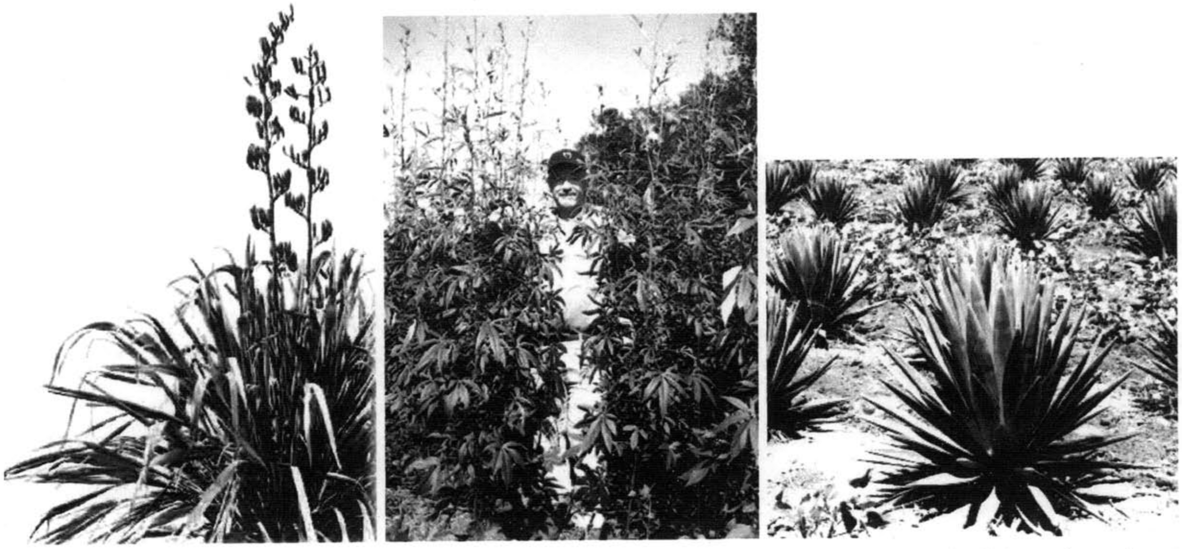
Wood is an excellent example of a biocomposite material: it contains long oriented cellulose fibres set in a lignin matrix. Both constituent materials are biodegradable. The cellulose provides tensile strength while the lignin provides compressive strength and hydrophobicity. However, wood takes a long time to make and cannot always be formed into any shape desired. The end of the chapter is a consideration of different types of natural fibre-reinforced composites.

3.1. NATURAL FIBRES

Natural fibres can loosely be divided into vegetable, animal and mineral categories. The first contains fibres like cotton, hemp and sisal, whilst the second contains silks and hairs, and the final contains materials like asbestos. Vegetable fibres are mostly made of structural polysaccharides like cellulose, whereas animal fibres largely consist of polypeptides. Mineral fibres will not be considered in this chapter.

3.1.1. ANIMAL FIBRES

Animal fibres such as wool, silk and feathers are harvested for fabric production all over the world. Specialty fibres such as spider silk are used for technical applications such as body armour and bullet-proof vests. Animal fibres have many beneficial properties– they are strong, thin, do not collect odours and are effective at managing temperature.



(a) Flax plant. Flax is grown to make both linen, a fabric made from the bast fibres of the flax plant, and linseed oil. Linseed oil has polymer-like properties, and is therefore commonly used in varnishes, paints and resins. Image from alibrown.co.nz

(b) Kenaf plants. The fibres will be extracted from the stalky stems of plants. Kenaf can grow up to 3m in height in only 90 days, making it a very good alternative to wood pulp for cellulose. Image from vtcarpets.com

(c) Sisal plants. Sisal is a robust desert plant, related to agave. Its crop requires no pesticides and is relatively low maintenance. Image from examiner.com

Figure 3.1: *Fibre crop plants: Flax, Kenaf and Sisal.*

In composites, using animal fibres is less researched than vegetable fibres due to the high cost and therefore lower application potential of animal fibres. However, the incredible strength and mechanical properties of different silks has been of academic interest for quite some time. Silk fibroin, the structural of the two proteins that make up silk, is made of antiparallel pleated-beta-sheet structures which in rest are contracted 5.6 % from their full elongation [48]. This gives silk a high tensile strength and its elasticity. The other silk protein, sericin, is the sticky material that surrounds the fibroin. More mechanical properties of silks and other fibres can be seen in table 3.1.

Silk's mechanical properties decrease when the fibres are soaked in liquid, making silk less ideal for thermoset resin composite applications [37].

Chitosan is the material that makes up shells in exoskeletal animals such as crabs and lobsters. It is a crystalline polysaccharide, and can be used both as a resin and as a reinforcement material. Some experiments have been done using both silk and chitosan as implantable scaffolds for tissue regeneration [5]. Usage in biomedical applications mandates low toxicity and full biodegradability without microorbial activity, both of which are achieved by silk-chitosan composites.

3.1.2. VEGETABLE FIBRES

Within the realm of vegetable fibres, one can distinguish between fibres harvested from different types of and different parts of plants. Cotton, kapok and baobab are hairs of plants, that grow in bolls around their seeds. The hairs are picked, then combed, spun and woven into fabrics. Cotton makes up a large portion of the apparel fabric industry, along with artificial fibres like nylon and polyester.

Kenaf, flax (linen), ramie, hemp, jute, wisteria, rattan and papyrus all are bast fibres, which are collected from the inner bark of the stem of certain plants. To harvest the fibres, they must be separated from the woody core and the outer skin of the plant, a process known as retting. Bast fibres are becoming more

Table 3.1: *Characteristic properties of selected natural and synthetic fibres. Adapted from Bismarck et al. in [7] with additional data from [2, 10, 38].*

Fiber	Density (g/cm^3)	Diameter (μm)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elogation at Failure (%)	Microfibril angle (θ)
Spider silk	1.3		1300 – 2000	30	28 – 30	
B. Mori silk	1.3 – 1.38		650 – 750	16	18 – 200	
Flax	1.5	40 – 600	345 – 1500	27.6	2.7 – 3.2	5
Hemp	1.47	25 – 500	690	70	1.6	6.2
Jute	1.3-1.49	25 – 200	393 – 800	13 – 26.5	1.16 – 1.5	8.1
Kenaf	1.2		295 – 1191	53	1.6	
Ramie	1.55		400 – 938	61.4 – 128	1.2 – 3.8	
Sisal	1.45	50 – 200	468 – 700	9.4 – 22	3 – 7	10 – 22
Cotton	1.5 – 1.6	12 – 38	287 – 800	5.5 – 12.6	7 – 8	20 – 30
Coir	1.15 – 1.46	100 – 460	131 – 220	4 – 6	15 – 40	39 – 49
E-glass	2.55	<17	3400	73	2.5	
Kevlar	1.44		3000	60	2.5 – 3.7	
Carbon (mesophase)	1.78	5 – 7	3400	425	1.4 – 1.8	
Carbon (turbostratic)	1.78	5 – 7	4800	240	1.4 – 1.8	

popular as a fast growing and low cost source of cellulose for paper production. Kenaf absorbs one and half times its weight in atmospheric CO_2 in its growth, making it an attractive carbon offset crop as well. Bast fibre plants are hardy, and require minimal insecticides and fertilisers.

Sisal, abaca, raffia and pineapple leaf fibres are harvested from the cores of leaves of plants. To extract the fibres from the leaves, they are decorticated. This is a mechanical process where the leaves are crushed and rinsed in rotating drums until only the fibres remain. The fibres are dried and combed and used in twines, ropes and carpets. These fibres are generally harder than bast fibres, with slightly higher tensile strength.

Coir is a fibre that is removed from the fruit of a coconut plant. It is the fibre that is in between the outer husk and the inner flesh of the coconut. These are shorter, curved fibres, making them less appealing for some purposes, but coir has some redeeming qualities due to the elastic structure of its cellulose and its high lignin content. Coir also is highly rot-resistant, does not degrade in water but absorbs a lot of moisture. Because of this coir sacks and netting are often used in horticultural applications.

Bamboo, bagasse and corn stalks are cane fibres. The latter two are particularly appealing because they are byproducts of large industries: sugarcane and corn. Such 'agri-waste' can typically be cheaply obtained. However, there is the risk that the subsidy of these agricultures will cease and the processes developed to use the materials will no longer be economically viable.

Recently, there has been a rise in labelling clothing and fabrics as 'bamboo'. These however, are not generally made directly from bamboo fibres. Instead, the cellulose from bamboo is extracted and used to make artificial threads. These threads are mainly cellulose-based, and thus not completely synthetic like nylon or acrylic, but they still require a large amount of chemical processing. Regenerated cellulose fibre based fabrics are also known as viscose, rayon, modal, cupra and tencel. The US Federal Trade Commission has since prohibited the labelling of regenerated cellulose fabrics as bamboo. Anecdotally, the first carbon fibres were made by incinerating regenerated cellulose fibres.

Each of these vegetable fibres has in common that its main strength is received from its cellulose content. Each individual fibre consists of several layers of oriented cellulose, a diagram detailing them is in figure 3.3. Microfibrils of cellulose make up elementary fibres, which are grouped together and held in place with

Figure 3.2: *Decorticated sisal fibres from Reynolds Advanced Materials, Boston MA. Even within a single sisal fibre (which is a bundle of elementary fibres) there is a variation in width of up to 200%. The different part of the leaves produce different qualities of fibre, and this must be taken into account when producing parts with sisal.*

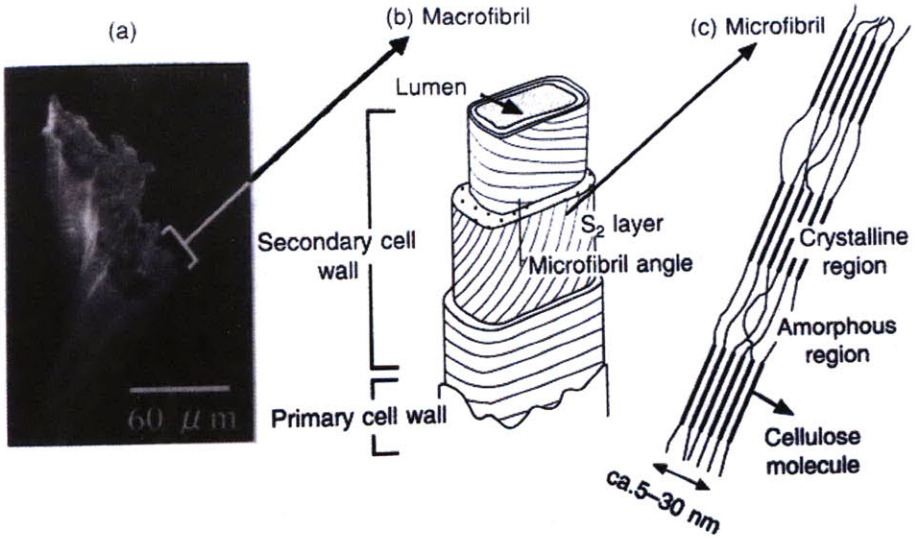


Figure 3.3: *(a) Scanning electron micrograph of kenaf bark fibre. (b) Schematic representation of an elementary fibre with two layers of fibres depicted. More layers can grow in a counter spiral. The primary cell wall will contain haphazard cellulose fibres, while the inner layers of cellulose will be helically arranged at an angle particular to the type of plant. (c) A microfibril of cellulose, with the crystalline and amorphous regions. Images from [33].*

pectin, hemicellulose and lignin. Hemicellulose is made up of branched polysaccharides, while lignin is a large polymer that cross-links both hemicellulose and cellulose, making it more impermeable to water.

Cellulose is a long polysaccharide chain that is linked in a crystalline structure. Unlike hemicellulose or starch, cellulose does not branch in its structure. There are several different crystalline structures known which correspond to different bonds within and between the molecules. The naturally occurring type of cellulose is cellulose I, regenerated cellulose fibres are known as cellulose II. Cellulose III and IV are obtainable through chemical and mechanical processes, and not widely used. Once cellulose has been converted to cellulose II, it can no longer be converted back to cellulose I.

Within the macrofibrils, the microfibrils of cellulose in the secondary cell walls is aligned at a certain angle. The more parallel the microfibrils are to the direction of the macrofibril, the more tensile strength the macrofibril will have. The larger the angle that microfibril is aligned at, the more flexible the fibres will be. Sisal and coir have relatively high microfibrillar angles (30 – 40 degrees) whereas flax, hemp, kenaf and jute have microfibrillar angles of under 10 degrees [7].

3.1.3. FIBRE EXTRACTION AND PROCESSING

To separate the fibres from the leaf tissue or woody core tissue of the stalks, the fibre crop must be retted. There are many different methods of retting, each with its own disadvantages. Traditionally, fibres were extracted through field–, stand– or water-retting.

Field retting leaves the cut fibre crop in the field to begin decay. Microorganisms separate the fibres from the core, due to the preferential consumption of the carbohydrate-rich woody core. To uniformly field ret the crop, it must be turned over in the field during the process. The decaying plants can produce fibres of varying quality depending on the weather and water damage sustained during retting.

Stand-retting is similar to field-retting, but instead of cutting the crops, the plants are killed by an open gas flame aimed at the base of the plant. After incineration, the plant is left to stand in the field for retting, but is less susceptible to water damage than field retting. It requires more energy than field-retting, and due to weather still produces variable quality fibres.

Fibres can be separated from the plants by soaking the plants in warm or cold water for a matter of days for digestion with anaerobic bacteria. However, this process produces a lot of wastewater with fermentation and also creates a large amount of gases. Because of the environmental impact, malodorous gasses and dangers with storing gas in water tanks, water retting is now mostly prohibited in Europe.

Figure 3.4: *Left: Raw hemp fibres from Hemp Traders ltd. in Santa Monica, CA, Right: Washed kenaf fibres, FK100 DSAT 50mm fibres from Bast Fibres LLC New Jersey.*

The above methods are traditional, and although simple, provide fibres without much consistency. To be able to extract fibres with consistent mechanical properties at a low cost, the retting process must become more refined. Methods developed for this include ultrasound retting, steam explosion retting, enzyme retting and chemical retting [7]. All of these retting processes take place in water.

Ultrasound retting submerges raw plant straw into a hot (70°C) bath of alkali surfactants and then submits the straw to 40kHz ultrasound. The fibres are separated, and the water and waste can be used as fuel. This process requires more energy than traditional methods, but produces technical-quality fibres.

With steam explosion retting, the raw straw is penetrated by steam and hot water. It mechanically separates the fibres from the woody stem. The resulting fibres are quite fine, but require some degumming before they can be used in fabric applications.

Enzyme retting targets pectin in particular. Removing pectin removes the waxy adhesive between the fibres and the woody material, allowing easy fibre extraction. The raw straw is often fractured before being placed into the enzyme bath to improve absorption.

Chemical and surfactant retting uses acids to separate the pectin, woody core and fibres. It produces very high quality fibres but also produces more waste than any other retting process. The water must be separately processed before it can go to a water treatment plant.

After retting, fibres are modified to provide better resin/matrix adhesion. Gummed fibres will not bond well and therefore slip in a resin matrix, and not provide structural reinforcement. To prepare the fibres for embedding in a resin, all non-cellulose material must be dissolved. This is typically done by washing the fibres, submerging them in an alkali (mercerisation) bath or boiling the fibres in a hydroxide salt. The processes for improving interfacial shear strength between the fibre and the matrix can be categorised as

Figure 3.5: *Chemically retted hemp fibres from Hemp Traders ltd. in Santa Monica, CA*

mechanical, micro-mechanical and chemical [8].

Cellulose fibres are inherently hydrophilic due many hydroxyl groups that are at the molecule's surface which can form hydrogen bonds with water molecules. The lignin helps the plants resist water absorption. However, once it is removed from the plant fibre, the cellulose fibres will easily absorb water and swell in the process, causing mechanical failure in the composite materials the fibres are embedded in.

The most common fibre treatment is mercerisation, bathing the fibres in a NaOH bath [14]. Different durations, concentrations and temperatures will affect the fibres in different ways.

Another common chemical treatment for the surface of the fibres is a silane treatment. Silane molecules form a siloxane bridge with the cellulose molecules and then also have a organofunctional group which can bind to polymers. This greatly improves the interfacial shear strength of the fibre/matrix interface [13].

Physically, the fibres' surfaces can be modified using discharge treatments: low-temperature plasma, sputtering and corona discharge [4]. The structurally modified surfaces have different matrix adhesion properties that can result in much higher tensile strength of the composite.

The retting and preparation process used affects the mechanical properties of the final fibre product. More chemical/mechanical processing can affect the structural integrity of the fibres as well as their water absorption potential. Even if the fibres are structurally affected by the retting process, the most important thing is to have predictable material properties. The best fibres for use in green composites are homogenous, evenly de-gummed and separated into similar elementary fibres.

For use in composite manufacturing techniques, fibres must be prepared into woven or felted cloth, tapes or evenly chopped. Finding technical natural fibres in these states is still uncommon and much of the preparatory fibre work must be done by the manufacturer or the composite part. Storing natural fibres mandates low humidity and controlled temperatures to prevent degradation.

3.2. MATRICES

The matrices used for composite materials that are classified as 'green' are not always biodegradable. Some composites are made with resins that are sourced from renewable resources instead of petroleum, but are not biodegradable [52]. Some include 'normal' resins and plastics that are combined with natural fibres, such as polypropylene-kenaf composites or sisal-epoxy resin composites. Biodegradable resins can be synthetic, i.e. synthesised from a raw material that is not already a resin, or natural, i.e. extracted from a plant, or bacteria already in its resin form.

In this section, I will examine possibilities of biodegradable resins in particular. I will examine synthetic resins derived from proteins, starches and sugars, natural resins made by bacteria and resins extracted from plants.

3.2.1. POLYLACTIDE (PLA)

Use of polylactide biodegradable plastics is on the rise. Its products are clear, thermoplastic, and depending on the mixtures of different repeating units in the polymer, they behave similar to polystyrene, polypropylene or polyethylene. Polylactide is derived from lactic acid, which occurs naturally in many plants and animals. To acquire large enough quantities of lactic acid, industry has taken to fermenting sugars and starches from crops such as sugarcane, corn or potatoes. Because of this, packaging made with PLA is often marketed as 'corn plastic' or 'starch plastic'.

The most common form of lactic acid is $L(-)$-lactic acid, but $D(+)$-lactic acid is also common. When the two stereoisomers are mixed, the resulting plastic behaves much like a copolymer. Polylactide made with repeating units of the L-stereoisomer is called poly(L)lactide (PLLA), whereas polylactide made with the D-steroisomer is known as PDLA. Combining the two is officially known as PDLLA, but when the combinations of the stereoisomers is unknown, the plastic is also often referred to as polylactide or PLA [18]. The name 'polylactic acid' instead of 'polylactide is falling out of favour, because the plastic referred to is not actually an acid.

The fermentation of starches and sugars into lactic acid is done by bacteria. These bacteria only operate within a narrow pH range, so to keep the pH neutral while acidification is ongoing, salts must be added to the starch solution. These salts later become a significant waste product: about a 1 to 1 ratio in weight of produced lactic acid and produced salt.

PLA has a very low glass transition temperature, which makes it unsuitable for use in any application with operating temperatures over 80°C. However, its low glass transition and melting temperature also make it more suitable for using with natural fibres, because its low processing temperatures do not damage the fibres [39]. Its melting temperature is around 170°C depending on the ratios of different stereoisomers, which means that it can still be used in most conventional vacuum moulding, extrusion and blow moulding machinery. Due to its brittle qualities, to use PLA for films and blow moulding, a plasticiser must be added.

Until recently, PLA was not an economically viable alternative to petroleum-derived plastic, due to low cost of raw oil and the relatively high cost of sugar and starch crops, and the difficulties in fermenting sugars and starches into very pure quantities of lactic acid. However, cost of petroleum has steadily been increasing, and as the demand for PLA increases, its manufacturing process is made more efficient and economical as well. The hope is that prices of PLA will continue to decrease as its quality improves and its mechanical properties in green composites become better known.

3.2.2. BACTERIAL POLYESTER RESINS

Certain types of bacteria convert sugars into polyesters to store the carbon and energy. This type of polyester is known as polyhydroxyalkanoates (PHA). The two main types of PHA are poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxyvalerate) (PHV) [20]. Copolymers of PHB and PHV biodegrade at a similar rate to PLA, and also by means of hydrolysis. On its own, PHB is very brittle and has low impact resistance.

PHB degrades at temperatures higher than 170°C, but its melting temperature is only 10 degrees above that. This makes processing the polymer very tricky, and makes it unsuitable for applications that operate at a range higher than 160°C. PHB can be blended with PHV to decrease melting temperature, but this also decreases the glass transition temperature and flexibility of the material, making it pliable at room temperature. Attempts have been made to blend polyhydroxyalkanoates with synthetic polymers to decrease their melting temperature without changing its tensile strength or elongation at break.

Using a plasticiser, PHAs can be used in typical injection moulding equipment. However, using PHAs is still uncommon due to the high cost involved with producing PHAs and their limited availability. The amount of energy required to produce PHB is still higher than that required by conventional polymers [20]. Currently PHAs are not a viable option for large scale green composites, although they are finding some application in the medical implants sector.

3.2.3. STARCH-BASED RESINS

Starch-rich crops are grown worldwide on a large scale. Crop processing and starch extraction is already well studied by the food industry. Using cereals, tubers or roots as a source for renewable polymers would be a great step forward for sustainable materials.

Different types of starch are characterised by the amount of amylose and amylopectin they contain. The ratio between the two can vary from 1:4 to 3:1 in naturally occurring crops to 1:99 in genetically modified crops [9]. Amylose is a linear chain, whereas amylopectin is branched. Different crops will also produce starches with different amounts of proteins, particulates and other internal cell matter like lipids in them. Lipids and fats will effect the mechanical properties of plastics produced from the starches.

The glass transition temperature and the melting temperature of starch are above the degradation temperature [32]. Because of this the gelatinisation of starch must occur with a plasticiser such as water or glycerol. Using only one or the other is generally not desirable, because the water will evaporate too quickly, leaving the final plastic brittle and prone to shattering, whereas oils will evaporate too slowly and not result in a plastic with good compressive strength.

Starch products remain highly moisture sensitive due to their hydrophilic constituent molecules. Even without further processing, gelatinised starch can be used to make films. Kept dry, the starch films become very brittle, when exposed to water they quickly degrade. Starch products can be improved by cross linking the starch molecules by means of chemicals such as formaldehyde or acids, making the resulting products stronger but still susceptible to water.

Starch has been used in PHBV plastics as a low cost filler for the otherwise high-cost material. These compound materials have mechanical properties similar to common polyolefins and easily degrade in water [44]. Starch has also been blended with a hydrolysis product of poly(vinyl acetate), PVOH. These blends have been marketed as water-soluble films for bags and liners. The life of the blend is not long enough to use for products with a usage time of more than a few weeks.

Starch-based resins are cheaper and easier to make than bacterial polyester or polylactide plastics, but because of their poor mechanical properties and sensitivity to water, they are still of only limited use for composite applications. They require heat curing and drying, making them unsuitable for injection moulding and extrusion. For foam packaging, agricultural and medical applications, starch resin research is continuing rapidly and will hopefully produce stronger resins in the near future.

3.2.4. PROTEIN-BASED RESINS

Proteins are large molecules made of peptides. They can be heated or exposed to variable pH levels to denature the protein molecule. Denaturation causes non-covalent change within the molecules, unfolding the peptide chains. By modifying the protein molecules to cross-link into aggregates, resins can be formed.

Soy beans are one of the United States largest crops, with a farm value of 30 billion US dollars. This leaves them second to only corn in the US, at almost 40 billion US dollars. After the beans are hulled (a process which only removes about one-tenth of the weight of the bean), they can be ground to make fatty flours. The flours can be defatted either chemically or mechanically, after which they contain at least 50 percent protein in weight. Carbohydrates and soluble proteins are removed to make soy protein isolate, which must contain at least 90 percent protein in dry weight. S.P.I. is relatively inexpensive (on the retail market, about 5 US dollars a pound) and can be used to produce soy bean resins.

By plasticising SPI with glycerol, polyethylene glycol, propylene glycerol, sorghum wax, sorbitol or butanediol, soy protein plastics with a range of mechanical properties can be produced [29]. Cross-linking agents such as formaldehyde can be added to improve mechanical properties like in starch-based resins. The mechanical properties and water sensitivity still limit the applicability of soy protein resins.

It has been attempted to improve soy protein plastics by combining the plastics with other biodegradable polymers. Starch and protein polymers can be cross linked to form compound polymers with better mechanical properties and water resistance than the two resins can achieve alone [36].

Like with starch-based resins, protein-based resins remain too sensitive to moisture and too weak to be integrated into industry on a wide scale just yet. However, with american agricultural research agencies highly keen on finding new applications for soy bean crops, research is set to improve in the future.

3.2.5. CASHEW NUT SHELL LIQUID RESIN

Cashew nut shell liquid is a phenol, naturally occurring in the green husk around the cashew nut. It is extracted from the cashew when the kernel is being removed from the nut, either mechanically, chemically or by heat. The liquid obtained from the shell is mostly anacardic acids, which causes a rash upon skin contact. It is modified to increase the amounts of cardanol, which besides uses in resin can also be used to make curing agents for epoxies. The CNSL can then be polymerised in a variety of ways, most commonly using a method analogous to how Bakelite was made. This involves polymerising the cardanol and cross linking it with formaldehyde to make cardanol-formaldehyde resin. Formaldehyde is classified as a class 3 carcinogen, and in combination with the irritant status of CNSL makes CNSL resins less appealing even though they are fully biodegradable.

Fully biodegradable matrices show promise in achieving similar mechanical properties to petroleum-derived non-biodegradable matrices in the near future. However, it will require improved manufacturing methods to make biodegradable resins cost competitive with their non-renewable counterparts. As petroleum prices rise and more policy is implemented restricting the use of common plastics, biopolymers will become more and more attractive as replacements.

3.3. SELECTED RESIN/MATRIX COMBINATIONS

Many studies have been done testing the mechanical properties of both natural fibres in synthetic matrices and natural fibres in biodegradable matrices [26, 40, 28, 6, 2]. With so many options in both natural fibres and matrices, it is difficult to quantify the choice of one composite over another, especially considering the variability in sources for natural fibres and biopolymers.

The 'greeness' of a composite can vary from non-toxic, to recyclable, to renewable, to reusable. Polyurethane is already a less toxic plastic than epoxy resin, and polypropylene can be melted down, separated from fibres and reused. Renewable resins do not rely on petroleum or fossil fuels, and reusable materials allow full recycling without decay in the process.

Selecting the correct green composite for an application depends on what fibres in what weaves are locally available, what tensile strength in required, what resins are locally available, the manufacturing methods that are possible for making this part, the composite part's exposure to water in its intended purpose, how long the part should last and how it should degrade, amongst many other factors. The 'greeness' is often considered a secondary aspect best maximised, but important enough to make or break the project.

Using synthetic thermoset polyester resins and epoxies in conjunction with natural fibres has been shown to exhibit good mechanical properties, good sound-proofing and low cost [40]. However, due to the hydrophilic nature of the natural fibres, composite parts lose their dimensional stability when exposed to water, even though the resin does not degrade. Water present in the fibres before they are processed into a composite leads to quicker degradation within the composites even if no external moisture is introduced.

Epoxy resins which produce high temperatures (up to 200°C) during the exothermic reaction of their cure cycle can damage the structural integrity of the natural fibres being set in the matrix. Caustic or acidic resins can degrade the cellulose in the fibres. Moisture in the fibres can also cause inconsistencies in the curing of polyurethane or epoxy resin.

Furthermore, the variability in natural fibres makes it difficult to produce reliably reproducible figures for biocomposites. With regards to these concerns I will include some studies on properties of natural fibre composites here.

3.3.1. Kenaf-PLA composites

Kenaf is a popular, fast growing crop that fixates a large amount of CO_2 during growth. This makes it particularly green to companies interested in improving their corporate image. PLA is brittle and deforms at low temperature. With the addition of kenaf, PLA will exhibit more heat resistance and have enhances crystallisation [42]. The tensile strength of kenaf degrades at 180°C, so manufacturing of kenaf-PLA composites is best done at the lowest temperature possible. Successful manufacturing with conventional moulding techniques has been done at 160°C [34]. Serizawa et al. have found the mechanical properties of kenaf-PLA composite to be comparable to that of fibreglass reinforced ABS [42].

3.3.2. Sisal-CNSL composites

CNSL resin is an inexpensive natural resin which has been tested as a matrix for sisal-CNSL composite roofing. It has been found to have poor mechanical properties in comparison to sisal-epoxy and sisal-polyester composites, but these properties are still adequate for roofing applications [35]. Bisanda et al. report tensile strengths of 24.5 MPa and a Young's modulus of 8.8 GPa for corrugated sisal-CNSL composites [6]. Their UV radiation tests demonstrate degradation in the sisal fibres after prolonged exposure, and further cross-linking in the matrix.

3.3.3. Soy protein composites

In an extensive mechanical analysis, Lodha et. al report on ramie-soy protein isolate composites a tensile strength of 81 MPa and a Young's modulus of 200 MPa when the protein is plasticised with 30 percent weight content of glycerol [26]. Increasing the fibre content in the composite led to higher fracture stress and Young's moduli, and lower failure strain percentages.

Lu et al. report tensile strength of 26 MPa and a Young's modulus of 158 MPa for soy protein isolate polymer reinforced with chitin whiskers as a nanocomposite. Their tests kept the samples at a fixed 43 percent relative humidity, although they also report that adding chitin reduces the water sensitivity of the soy protein isolate polymer [27].

3.4. Green composite research

Green composite research is driven in part by the academic community, researching the possibilities of materials and crops, and in part by industry seeking cheaper alternatives to current practices. The largest user of composite materials is by far the automotive industry, followed by aeronautics and civil engineering, who together account for almost 80 percent of all composite production. Both parties are motivated to wean production off of using petroleum and fossil fuel industry by-products and moving towards more sustainable practices.

Especially since the great rise in cost of oil, peaking in 2008 at 160 US dollars a barrel vs. less than 20 US dollars in 1999, finding alternatives for petroleum-based resins and plastics had an economic incentive besides an environmental one. Exploring low cost or subsidised crops such as soy beans and corn as possible petroleum alternatives for manufacturing epoxies and plastics is gaining momentum in the field [52, 22].

Simultaneously, laws are being introduced that regulate the amount of waste products may contain, and these laws are based on current material practices. Automobiles may, for instance, only have 5 percent of their material incinerated or sent to landfills in the European Union [12], which is based on the toxicity of burning epoxy resins and other common current composites. Because of this, using biodegradable materials is again discouraged, even though they could quickly degrade in landfills or be incinerated without producing toxic gases. To be able to promote research in green composites, policy must be adopted to reflect possibilities of biodegradation as a route for waste, and to recognise differences between bio-composites and synthetic composites.

Using natural vegetable fibres still has the benefit of being low-cost, having a green image and having low-density fibres which are non-abrasive and do not require strict health regulations for the staff working with them. This is already enough for natural fibres to be adopted into many applications in industry. However, natural vegetable fibres still have too much variation, are difficult to source reliably and have poor performance in water. If usage of natural green fibres is to rival synthetic fibres, these production line problems must be addressed.

Using biodegradable matrices is a limited option for parts that require resistance to heat and water. PLA and PHA and its derivatives still do not rival completely synthetic polyesters in mechanical properties or price. CNSL, although promising, is restricted in its applications by its irritant nature. Chitosan and other animal-derived polysaccharides are widely used for medical applications, but the production does not yet address making large-scale parts.

As techniques for production, manufacturing and storage improve for green composites, they become more viable for application in production. Reliably sourcing homogenous fibres and resins is a challenge for manufacturers making small runs. However, as green composites research continues, the price of the materials will drop, and the efficiency of the manufacturing processes will increase.

4. APPLICATIONS OF GREEN COMPOSITES

In industry, there has been a trend of 'green' marketing, where companies can improve their corporate image by including buzzwords such as *sustainable, bio, green, eco* and *organic* in their products. Biocomposites are similarly plagued by ill-defined delimitations between stages of 'bio', and marketed as made from biocomposites may refer to fully biodegradable composites such as kenaf-reinforced PLA, or only semi-degradable composites such as hemp in an epoxy resin matrix. Even if the driving force for incorporating more green materials into products is only better marketability, it promotes research in green composites. In this chapter I will have a look at some of the green composite products that are being offered or presented to the market.

4.1. PACKAGING AND CASING

Bioplastics are being used more and more in the packaging industry. PLA is food-safe, relatively low-cost and appealing to consumers because of its green image. Because of the volume of demand for PLA and even PHA, manufacturing plants are growing in their capacity and able to provide high-quality bioplastics for use in composite materials as well.

Figure 4.1: *PLA used for disposable drinking cups by GreenWorks and Mountain Mist Eco-craft stuffing and batting products. Photos from their respective manufacturers.*

PLA is widely used for medical purposes. Companies like Mastbiosurgery, Parietex and Permacol market sutures, screws and films for use in reconstructive surgery. The grade of PLA used must be very high to not contaminate the implant site. The benefit is that the PLA pieces do not need to be removed like titanium screws and plates would.

The largest PLA production plant is owned by NatureWorks and is located in Blair, Nebraska, USA. It currently produces about 3 million pounds of PLA per year. The PURAC plant in the Netherlands used to be the largest producer of PLA, but produced low quantities of high-grade PLA for medical purposes. PURAC has planned an expansion that should rival the NatureWorks plant. The Futerro plant in Belgium recently started production, and are currently offering PLA for internal evaluation, and plan on manufacturing at least 3 million pounds of PLA by the end of 2010.

Many of these PLA-only products have opened the PLA market for composites. PLA has a low glass-transition temperature, and therefore cannot be used to hold hot beverages. However, this makes it easier to use as a thermoplast to mix with fibres. The low glass transition and melting temperatures ensure that the fibres are not damaged by excessive heat while moulding.

Figure 4.2: *NEC and NTT DoMoCo released a phone, NEC N701i ECO, with a casing made of kenaf-reinforced PLA. The phone was set to be more expensive than its non-ECO counterpart. NEC has also released laptops with cases made of PLA. Images from NEC and slashphone.com*

Figure 4.3: *Fibrolon is a wood-reinforced PLA composite. FKUR manufactures Fibrolon along with BioFlex and Biograde, extrusion and injection moulding plastics, in their biodegradable range. These products are shown for demonstration purposes on their website. Their more popular products are the PLA-based plastics Bio-Flex and Biograde. Images from fkur.com.*

In the packaging and casing industry, the use of natural-fibre reinforced plastics has been low. Packaging and casing does not require the increased strength provided by fibre reinforcement. Manufacturing composite sheets and films requires more specialised manufacturing techniques. As the bio-plastic packaging market grows, there will surely be packaging requirements that warrant fibre composites.

4.2. AUTOMOTIVE INDUSTRY

The leading user for natural fibre composite materials is currently the automotive industry. The automotive industry is already one of the largest users of composite materials in general, so expanding to green composites is a natural extension of their manufacturing interests.

Unlike for packaging and electronics casing, the larger components of cars need reinforcement and shape maintenance. Using a reinforcing fibre increases the tensile strength of the component. Natural fibres are attractive to the automotive industry because of their low density, low cost, and non-abrasive qualities. However, they remain less strong than their synthetic counterparts, and susceptible to water logging and damage. Therefore, green composites are currently only used for indoor structural components.

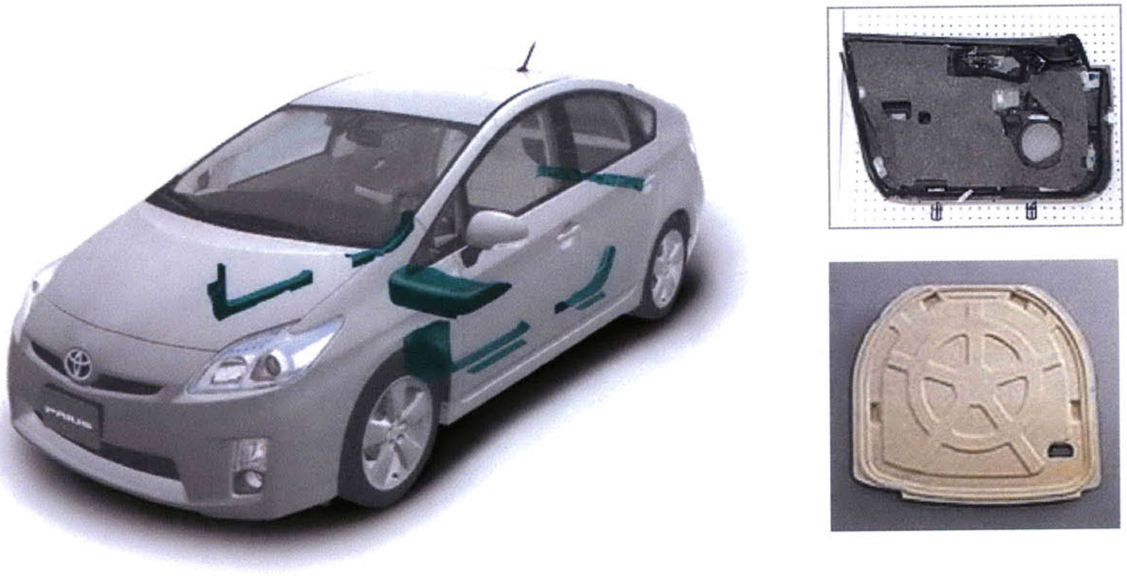


Figure 4.4: *In the Toyota Prius, several interior components are now made with kenaf/ramie reinforced PLA. On the right the parts of the interior that are made with green composite are shown in green. On the left is a side door cover and a spare tire cover made with kenaf reinforced polypropylene. Images from toyota.co.jp.*

Toyota recently (2009) released concept car renderings of vehicles entirely made of bioplastic composite [49]. However, much of the work on applications of green composites in automotive industries has historically been done by car manufacturers in Germany [47]. In 2000, Audi released the first mass-produced all-aluminium body car. To match the interior to its lightweight exterior, the internal panels were made with flax/sisal reinforced polyurethane. By 2005, the automotive companies that would ship cars with some components made from natural fibres included Audi, BMW, DaimlerChrysler, Fit, Ford, Peugeot, Renault, Rover, Saab, Seat, Volkswagen and Volvo (see table 7.4 in [47]). Many of the natural fibre composites did not use biodegradable matrices.

The leading reason to use natural fibres is their low weight and low cost. Even with the variability of the natural fibres, reducing the weight by up to 100% in comparison to glass fibres makes natural fibres an attractive option. The European Commission's end of life vehicle directive is already of great influence to what materials are being used in car manufacturing [12, 15]. Policy decisions that require manufacturers to innovate their materials are a strong driver for further research in green composites.

Robert Boyer and Henry Ford with the Soybean Car.

Figure 4.5: *Already in 1941, Henry Ford showed a so-called 'Soybean Car' at a Dearborn Michigan community festival. The exact construction of that car is actually unknown and little documentation exists of it. However, Lowell E. Overly, one of the engineers who worked on the car, state in a 1951 interview with V8 Times that it was made of 'soybean fiber in a phenolic resin with formaldehyde used in the impregnation' [11]. Unfortunately, soon after the unveiling of the Soybean Car, World War II broke out and all research efforts were redirected. The Soybean Car was not revisited afterwards. Image from* `http://www.thehenryford.org/research/soybeancar.aspx`

4.3. BUILDING AND RESIDENTIAL APPLICATIONS

Composites have been used for millennia in building applications. Adobe, a clay and brick composite, was used in almost all ancient tropical civilisations. Bricks varying in size from several inches to several feet are baked of mud, clay, straw and grass. Abode has good thermal regulation properties and can also last a very long time. Some surviving adobe buildings are over 2000 years old (see figure 4.6). Adobe construction is now still popular in the stucco architecture in New Mexico and Utah.

Figure 4.6: *Citadel of Arg-é Bam: the oldest adobe structure in the world, located in Iran and built before 500 BC. Photo by Ales Kocourek.*

For more rapidly deployable composite materials in buildings, new types of green composites are on the rise. Especially in countries where wood is difficult to source and maintain due to humidity and lack of local wood sources, composite building materials are on the rise. Green composite materials can be engineered to be dimensionally stable and not warp with humidity and heat the way wood often does.

Figure 4.7: *Paperstone is a trademarked composite made with recycled paper fibres and a blend of resins including cashew nut shell liquid. Here are countertops and knife handles made with paperstone. Photos from paperstoneproducts.com and buckknives.com.*

Fully green composites such as Paperstone are being used for indoor applications such as countertops, windowsills and door threshholds. Paperstone contains recycled paper fibres set in a phenolic resin matrix made with predominately cashew nutshell liquid. The composite can be acquired in different varieties ranging from fully recycled paper fibres to new fibres, if different colours are desired. It is marketed for many applications, such as countertops and knife handles (see figure 4.7).

Other composite indoor materials include jute-reinforced phenolic resin, used for doors, window shutters and door frames. Hessian cloth was used to produce shutters and door frames that were tested for their mechanical durability in India [46]

To analyse the applicability of different green composites in outdoor building applications, many weathering studies have been performed, exposing the composites to humidity, acidity and UV light [46, 45]. Natural fibre with polyester resin samples predictably degrade faster (losing half of their tensile strength in the time it takes for a glass composite to lose only 10 percent [46]). The natural fibres absorb water, swelling and causing rotting within the composite. Also, the residual lignin from the fibres further decays, leading to so-called fibre blooming– separation of fibre strands. To prevent rotting and water absorption, natural composite materials should be coated with a layer of UV– and water-resistant resin– for instance polyurethane.

Figure 4.8: *Corrugated Asphalt Roofing Sheets (ARS) made with natural fibres and hot paving grade asphalt. Images from BASIN pamphlet on roofing, Shelter Forum, Nairobi, Kenya.*

(Semi) green composites are also suitable for use in roofing applications in low-cost (developing world) housing. Corrugated metal roofs are expensive, have difficult thermal conductance properties and can quickly corrode in many humid environments. To address these issues, some developing countries started manufacturing asphalt and cement tiles (sometimes reinforced with natural fibres like sisal). Although cheaper, the concrete tiles are still very heavy. Asphalt tiles exhibit warping after some time in hot tropical climites (see figure 4.8). Using cashew nutshell liquid and sisal composite has been showing promising results in developing lightweight, strong and cheap roofing tiles, although these have not made a widespread entrance in the field yet. Although the natural fibres degrade in sunlight, it has been shown that sunlight might even improve the mechanical properties of CNSL resins [6].

4.4. FUTURE APPLICATIONS

Although some of the examples listed in this chapter are cursory attempts from manufacturers to produce green composite products to improve their corporate rating, others are genuine attempts to incorporate green composites into their respective markets. As green composite materials mature, the ability to reliably source homogenous natural fibres and resins improves and petroleum-based products fall more and more out of favour, we will see more and more applications of green composites.

5. TOOLS FOR COMPOSITE MANUFACTURING

Current composite manufacturing techniques can be quite unwieldy, and not particularly energy efficient. For advanced high-temperature epoxies used in aeroplanes, the methods for curing and testing wings are scaled up versions of methods used on much smaller parts. The industry to make A380 and 787 wings was based around airplane-sized autoclaves. A significant amount of energy can be saved by locally heating the parts that need to be cured instead of building larger and larger autoclaves. This chapter describes a tool developed for heating and curing composites in place, while sensing their cure cycles. Heating modules and temperature sensors are embedded in the mould itself, running closed-loop temperature control. The smart mould uses calorimetry to determine the end of an exothermic cure.

5.1. SMART MOULDS

High-performance composites are often made with two-part epoxy resins. The curing process of epoxy resins is an exothermic reaction that can be regulated by varying the surrounding temperature and the ratios of the hardener and resin. Current practice for monitoring epoxy curing are either imprecise or very expensive. In this section I describe a system of distributed heat regulation and cure monitoring embedded directly into the composite mould itself. The mould becomes the new smart tool for composite fabrication.

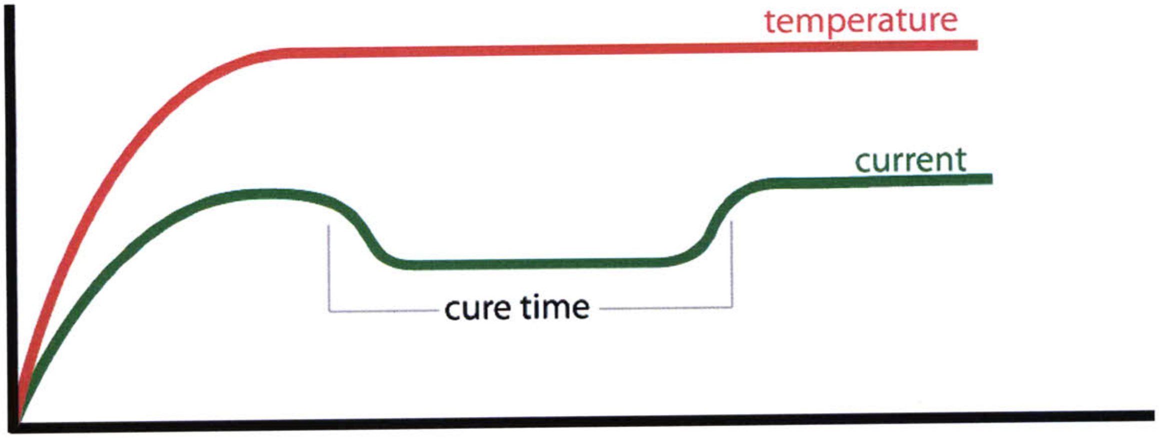


Figure 5.1: *With a closed loop temperature controller maintaining the mould at a fixed temperature, the excursion in input current needed indicates another energy source providing heat within the mould. In this case, the exothermic epoxy reaction.*

Current common practice for testing whether the epoxy has finished curing is to check a jar of epoxy curing outside the mould. The assumption is, if the jar of epoxy is cured, the part curing in the mould must be cured as well. This is not always accurate, and some more sophisticated methods are also in use. These include monitoring the optical qualities of the resin, checking for a change in opacity in the cured part, or monitoring the dialectric constant of the curing part, waiting for the constant to cross some threshold [25, 23]. These require specialised sensors specifically for the epoxy resins being used, and need to be tuned for each curing process.

Some attempts have been made to use differential scanning calorimetry to check for the end of the exothermic epoxy curing reaction [41]. Checking for the end of an exothermic reaction would eliminate the need for specialised sensors. These cure sensing attempts remain limited however, for they employ use of an autoclave to heat the mould and component– not an easily scalable process.

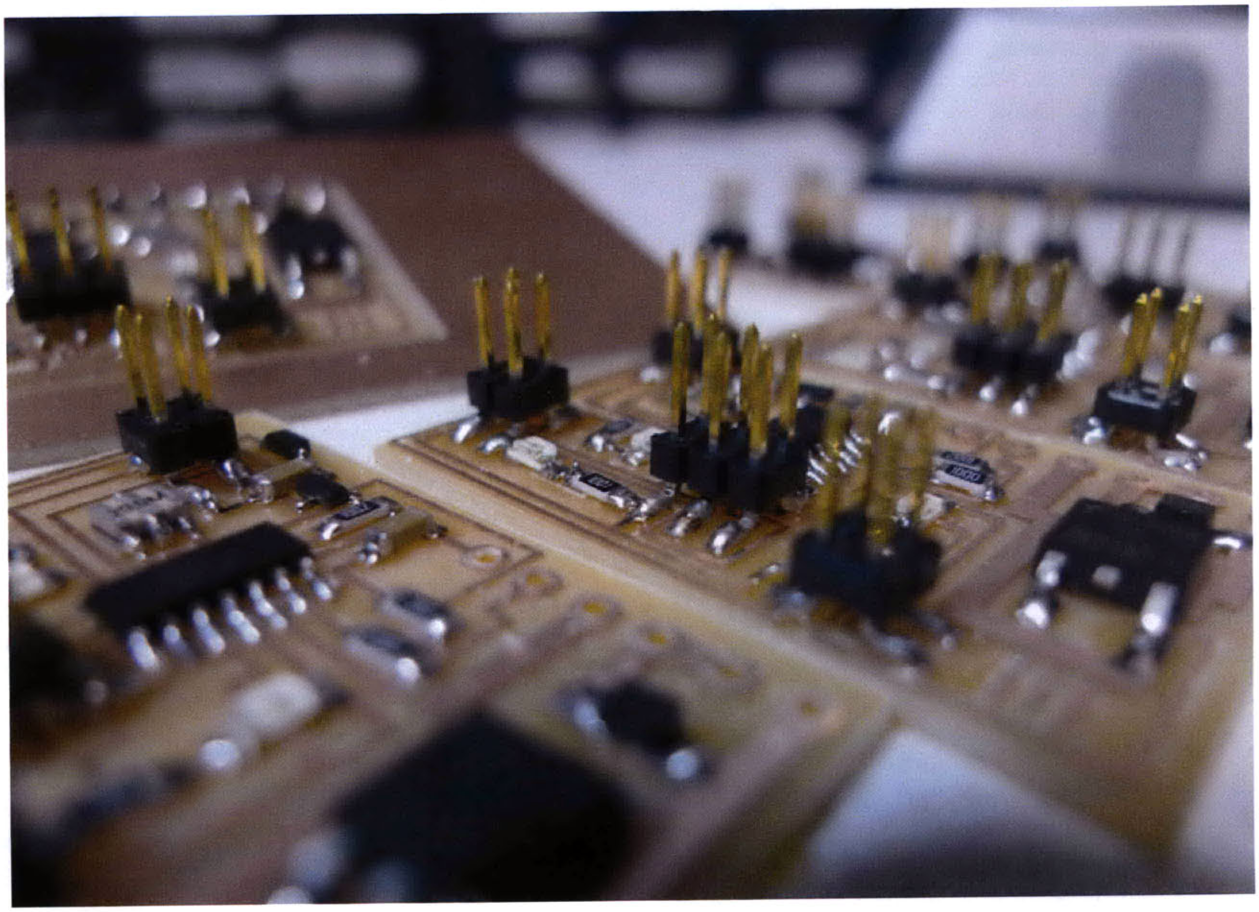


Figure 5.2: *Epoxy heat cure sensor boards made on a Roland Modela milling machine with an Atmel AVR ATTINY45 to control PWM of NiCr heating wire and read a large-range (4-400°C) glass bead thermistor. The boards pass their data through a serial conversion bridge board to a GUI written in Python wxWidgets.*

To sense the curing of epoxy in a mould, one can use calorimetry to monitor the amount of heat produced in the chemical reaction. If an exothermic reaction is taking place, the amount of current needed to keep the mould at a constant temperature will be less (see figure 5.1). If the temperature in a mould is kept constant and there is no exothermic reaction going on, the amount of energy required would remain constant. If there is an exothermic reaction taking place within the mould, the amount of energy required to keep the mould at a constant temperature should be less. To be able to sense this, closed-loop control must be implemented for the temperature levels in the mould, maintained along with a log of the current (and therefore energy) used to heat the mould.

To test a heated mould with calorimetry for cure sensing, we built a system that controls a network of nodes, each equipped with a temperature sensor (glass thermistor) and a heating element (NiCr wires). The nodes perform closed loop temperature control and can be set to different temperature profiles that can correspond to the thickness of the part at that location in the mould. The nodes communicate through Asynchronous Packet Automata, a communication protocol developed at the MIT Center for Bits and Atoms in collaboration with Spirit Aerosystems, where the geometry of the node's connections determines how to address them. The nodes are controlled with a series of simple commands, including current up, current down and read temperature.

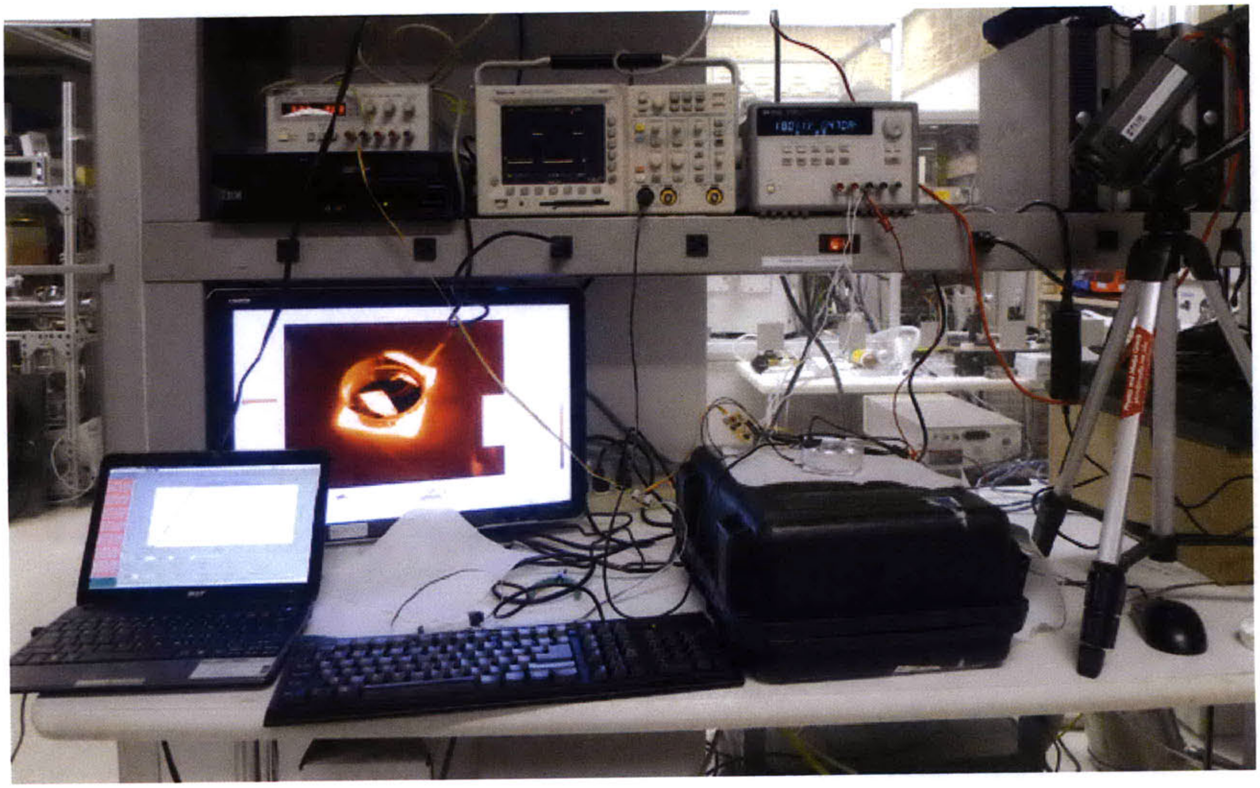


Figure 5.3: *An evolved heat experiment set-up: separate power supplies (that share ground) power the microcontrollers and the heating pads. In an aluminium cup, 2 part polyurethane is curing. The netbook is running the cure sensing software, while the desktop computer is displaying the infrared image of the setup. The oscilloscope is monitoring the PWM of the heater pads. In this set up, only one node is connected to the interface (because the part I am curing is only a small cup of urethane).*

I set out to cure a polymer on the test tool to determine whether we would be able to see the excursion in input current as a result of the exothermic curing reaction. I have done an experiment with two part polyurethane, of which the setup is detailed in figure 5.3 and the results are shown in figure 5.4.

This preliminary experiment demonstrates the possibilities of in-place heating and cure sensing of composite parts. It shows closed-loop temperature control which can be used in calorimetry for cure sensing. To further develop this research, curing profiles of many different resins could be characterised so the control software could automatically detect the cure of a part.

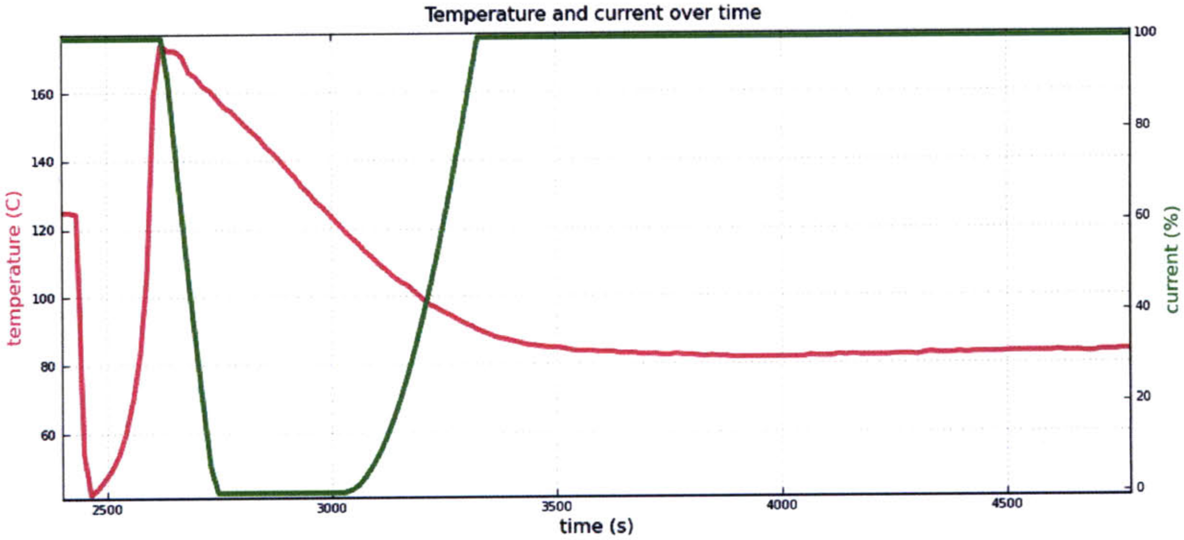


Figure 5.4: *This is the resulting plot of an experiment where the sample cup was initially held at 120°C. The 2 part polyurethane was introduced at t=2450, after which the exothermic reaction begun and the sample began producing its own heat. The current decreases to maintain the temperature, later increasing again to maintain temperature after the end of the exothermic reaction and also the end of the cure. At t=3300s, we can say that the part has finished curing and can be removed from the mould.*

6. CRADLE TO CRADLE COMPOSITES

Plastic waste fills landfills, streets and oceans. Policy and precautions are being introduced to reduce plastic waste and to increase recycling efforts– here in Jaipur, India, at the time of writing, plastic bags have just become illegal for vendors to distribute. However, plastic remains used in many other products besides packaging. To be able to promote a healthier life cycle for plastics, more care must be given to understand the future of a product after it has served its intended purpose.

Recycling plastic waste can be mean two things. The discarded plastic can be melted down to create post-consumer plastic material that can be reprocessed in conventional ways. Or the plastic products can be reused– for instance in the refilling of soda bottles. Either option does not offer enough change in the world's current plastic consumption. Unlike its name implies, in any recycling process there is a degradation of material. Melted PET cannot indefinitely be made into new plastic products, as the plastic is degraded and more foreign substances are introduced.

One option for further reducing plastic waste is to invent new methods of degrading large synthetic polymers into short polymer chains that can be absorbed by the environment. Another, largely the topic of this thesis, is to create easily biodegradable polymers sourced from renewable materials to replace current plastics. Unfortunately this research is not far enough along to warrant fully abandoning conventional plastics.

Composites form an extra burden upon waste and recycling, because the research that was first done to make fibre-matrix adhesion as strong as possible must now be undone to recycle the materials. For thermoset resins, this has been attempted by means of grinding the composites to separate the fibres and matrix, and then reusing the fibres in new composite materials. This messy process produces recycled fibres which are not of the same quality as virgin fibres, and conventional lay-up techniques cannot be used.

Instead of extracting materials for reuse, composites can be shredded or granulated and then incorporated into injection and compression moulded products for reinforcement [17]. This does not rival the strength of the original composites, but it uses conventional manufacturing technology and processes and a market already exists for the materials. However, because a German legislation was introduced in 1995 dictating that 80% of composite waste should be recycled, research is still ongoing on methods for fibre and matrix reuse [1].

6.1. GRINDING

The grinding process for the reuse of composite materials begins with the shredding of the discarded products in shredders which operate with very high torque to overcome the strength of the composite materials. The shredded composite is then fed through hammer mills which reduce the size of the composite further. Both the shredders and hammer mills which exhibit extreme wear and tear when recycling composites like carbon fibre [19]. The recyclate will have shorter fibres but also more homogenous properties with each added pass through the hammer mill. Making composite recyclate with predictable sizes of thermoset residue and little moisture or contaminants provides a valuable filler and reinforcing material for polymers.

6.2. CHEMICAL DEGRADATION

Polymers can be selectively degraded through the addition of solvents like ethanol, potassium hydroxide and amines. However, the solvents also adversely affect glass fibres, and the process is done at 450°F, making it unsuitable as an extraction method for natural fibres [19]. Viability studies are being conducted for plants chemically extracting glass fibres by means of chemical degradation of the polymer matrix. Carbon fibre extraction is also being studied, although no plants for its extraction already exist.

6.3. PYROLYSIS

Pyrolysis degrades materials at high temperatures without the presence of oxygen. It is used to produce carbon fibre, charcoal and PVC, amongst other things. Because of the selective degradation of materials at different temperatures, it can be used to extract fibres from thermoplastic matrices. The extracted degraded polymers can be used as liquid fuel.

Leeds University has been researching using pyrolysis for the selective degradation of matrices specifically for recycling automotive parts [19]. Using a drum carder machine, they can carefully separate glass fibres from their matrix. The resulting fibres are blackened in the process, but can be cleaned again using low-temperature oxidisation.

6.4. PHOTOLYSIS

UV light will cleave large polymers and speed up the plastic degradation process. At the same time, it is difficult to expose polymers to UV light without exposing them to oxygen, so both the cleaving and oxygenation processes will be in conflict. Because most landfill waste is buried, it is not exposed to constant UV light, making this process difficult to implement in practice.

6.5. SNAP TOGETHER COMPOSITES

Instead of trying to extract separate fibres and matrix derivatives, researchers at the MIT Center for Bits and Atoms have been exploring the idea of using composite snap together parts to make the composite products desired [51]. This way, after their useful life the composites can be disassembled and snapped together into a new configuration. The geometry of how the parts would snap together is crucial, as the efficiency of force transfer between the parts would determine the overall strength of the part. If the force is being distributed well through the aggregate, this method for reuse could provide and alternative to recycling methods.

7. ADAPTING GREEN COMPOSITES FOR SMALL-SCALE FIELD USE

The properties of green composites are widely researched, and large-scale industries have begun manufacturing products with green composite components. However, small scale usage of green composites for personal fabrication remains limited. Even though the non-green alternatives can be hazardous to work with, with glass- and carbon fibre being known to cause severe respiratory illness, and epoxy resins being known endocrine disruptors, natural fibre composites have yet to make an entrance for individual use.

This chapter details my exploration of rapid prototyping with green- and semi-green composites. With it I have analysed the feasibility of rapid prototyping with green composites for personal fabrication. Using materials available in small quantities and rapidly prototyped moulds, I have tried making parts for marine, medical and artistic applications.

The first part of making your own green composites is sourcing the material. This proves to be no simple task– unlike glass fibre, natural fibres are not readily available in pre-woven mats for use in composite lay-up. Even acquiring unwoven or matted retted and mercerised fibres is complicated. When searching for technical fibre sources, many vendors would require minimum orders of 1000 kg or more, or would decline to share the details of the fibre treatment process. Like explained in chapter 3, the extraction process after being harvested is of great influence on the mechanical properties of the resulting natural fibres. Without a data sheet or list of mechanical properties, it is unclear whether any of the experiments conducted would later be reproducible.

The raw fibres I eventually acquired included caustically treated uncombed kenaf fibres, uncut decorticated sisal fibres, raw hemp fibres and mercerised hemp fibres. I tested other fibres by purchasing apparel fabrics made of jute, hemp, cotton, flax and rayon. Apparel fabrics are suboptimal for experimentation because the individual fibre has been highly treated and it is unlikely that one can reproduce the exact mechanical properties of the resulting composite.

Moulds for many types of composite manufacturing using thermoplast resins must be made of metal or a highly temperature resistant material. Because of the high cost and labour required to make blow moulds, extrusion moulds and injection moulds, I did not do many experiments with PLA, polyhydroxyalkanoates or commercially available biodegradable thermoplast polymers such as cereplast. Instead I experimented with making resins from protein powders and starches available at a small scale that I could use in hand-lay up and film layering processes.

These fully green resins do not possess very good mechanical properties. They are very hydrophilic and will easily decompose in water in a matter of hours. Because of this, I started using more not-green polymers like polyurethane in my composite applications. In the future, using fully green resins which one later coats with a coating of for instance polyurethane could be a good possibility for making more sustainable versions of the composite parts described in this chapter.

7.1. RAPID PROTOTYPING OF TOOLING FOR COMPOSITE LAY-UP

Making moulds is often the most time-consuming part of making composite parts. Classic moulds and dies are often made of machined aluminium or steel. Making these moulds requires specialised machining equipment and skill. The materials that the dies are made with are expensive– a die for a part with a volume of .5 litres could cost around 2000 US dollars.

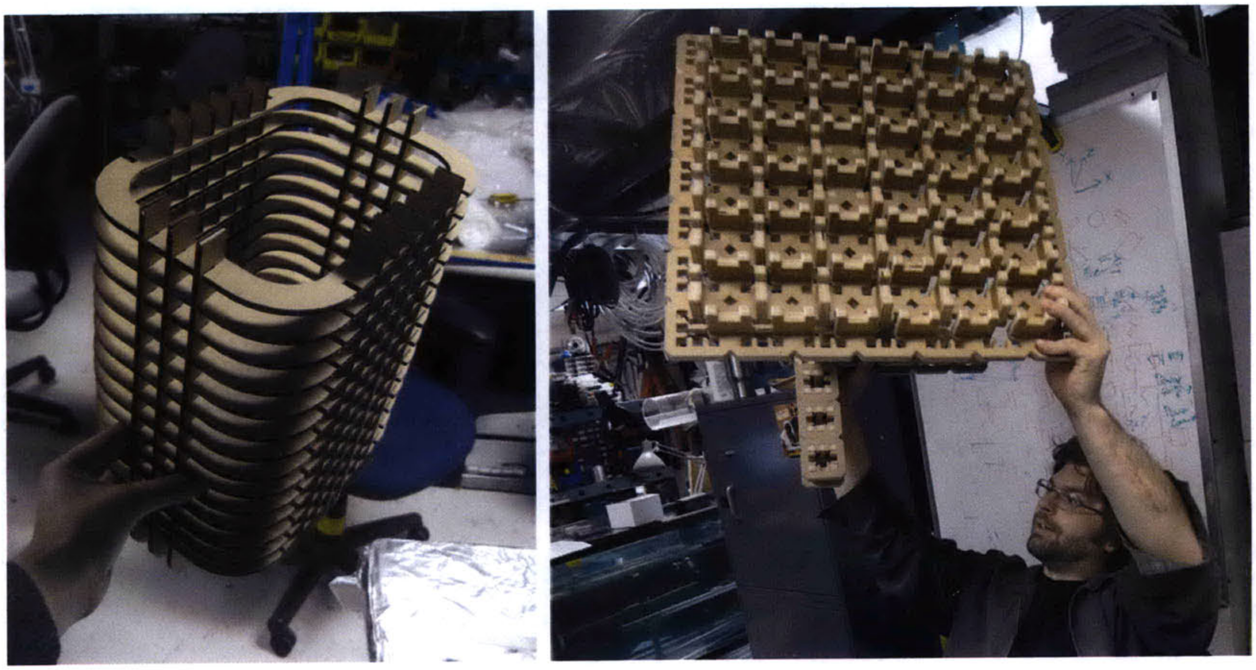


Figure 7.1: *Using 2D tools to make 3D jigs for fibre lay-up methods. On the left a laser-cut press-fit cardboard mould which was later coated in a rayon-epoxy composite. On the right Jonathan Ward's digital assembly kit, made of pieces of plywood cut on a ShopBot CNC mill. See also [51].*

Instead of machining metal blanks for composite tools, I've been using snap-together structures that can be made using 2D processes on machines available in FabLabs. Laser cutting cardboard structures, covering them with cling wrap as mould release and removing them after the composite has set is one method I've become fond of. It is cheaper and faster than milling aluminium blanks commonly needed for composite tooling.

Another method which does not require one to design the snap-together mould structure in advance is to use small snap-together components that can be assembled into a mould like Lego. Jonathan Ward has developed a method of hierarchical snap-together components, which allow you to quickly build with large structures, and then snap on smaller components to build with greater resolution [51].

After making the snap-together structure, wet hand lay-up over the mould is possible. To cover the mould adequately, one can use pre-sewn fabrics or lay up strips of fabric impregnated with resin. For better surface finish, the mould can be vacuum-bagged after lay-up with a finishing film of choice.

For making moulds for small-scale parts, a method available in the FabLabs is 3D printing the part needed and using that as a positive to make a silicone or silicone-and-plaster mould. When doing this, care must be taken to ensure the 3D printed part has exactly the right dimensions, as many 3D printers will skew or stretch a part if not calibrated correctly. The direction that the part is printed is also often of importance– there will be less precision in the direction of deposition.

Using silicone and closed moulds has the drawback that many voids can form if fibres are placed into the mould before pouring in the resin. One way to avoid this is to have an open-faced mould and vacuum bag that structure, giving better surface finish to the open face and removing more air and excess resin. Even so, chopped fibres in moulds create difficulties with voids.

7.2. MAKING RESINS

In the paper *Characterization of interfacial and mechanical properties of green composites with soy protein isolate and ramie fiber*, Lodha and Netravali describe a method for making cured soy protein isolate sheets, modified from a method described by Liang et. al [26, 24]. I first tried to replicate this using impure soy protein isolate in the form of protein shake powder, as is commonly available in food supplement stores as a muscle builder. Unfortunately, although the main ingredients of these shake powders are soy or whey protein isolate, they have added ingredients including sugar, which prevents the protein from cross linking properly into a polymer. The final sheets were sticky and not strong at all.

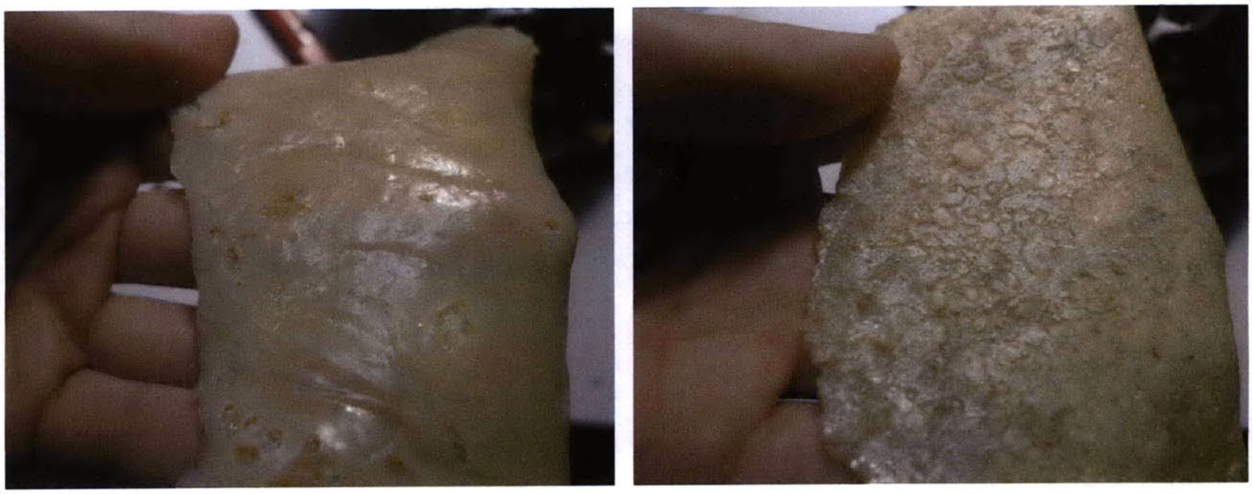


Figure 7.2: *Using soy protein isolate obtained from Barry Food Farms inc., glycerol and deionized water, I made some protein sheets like described in [26]. These first few attempts had trouble with uniform curing, and would result in flakey tops or gel-like bottoms that would later crack.*

I then obtained pure soy protein isolate powder from the health food wholesaler Barry Food Farms Inc. and again attempted to make soy protein polymer. I mixed by weight 3 parts soy protein powder with 1 part industrial grade glycerol and 10 parts distilled water, and hot pressed the resulting granules into a sheet on a t-shirt transfer press heated to 70°C for 2 hours. The resulting sheet had a flakey surface finish as can be seen in figure 7.2.

For better soy protein sheets, I tested different amounts of water and glycerol mixed into the soy protein isolate. Finally I increased the amount of water to 15 parts, and the amount of glycerol to 1.5 parts, which I would hot-press for up to 10 hours to obtain a tough, flexible, leathery sheet of soy polymer, 2 mm thick (see figure 7.3). I hot-pressed the soy protein isolate between sheets of aluminium foil, which resulted a slightly wrinkled surface finish.

Left to dry overnight, the sheets would curl while still drying more, resulting in an undesirable crumpled morphology. If I had not hot-pressed the sheets long enough, they would crack when drying. (Also, there was one small problem where one of the dogs frequently in our lab came and ate all my protein sheets when I wasn't paying attention. Very classic.) To avoid the crumpled drying, I tried drying the sheets between layers of tissue under weights. This worked, but it took up to 72 hours for the protein sheets to reach their final state of dryness.

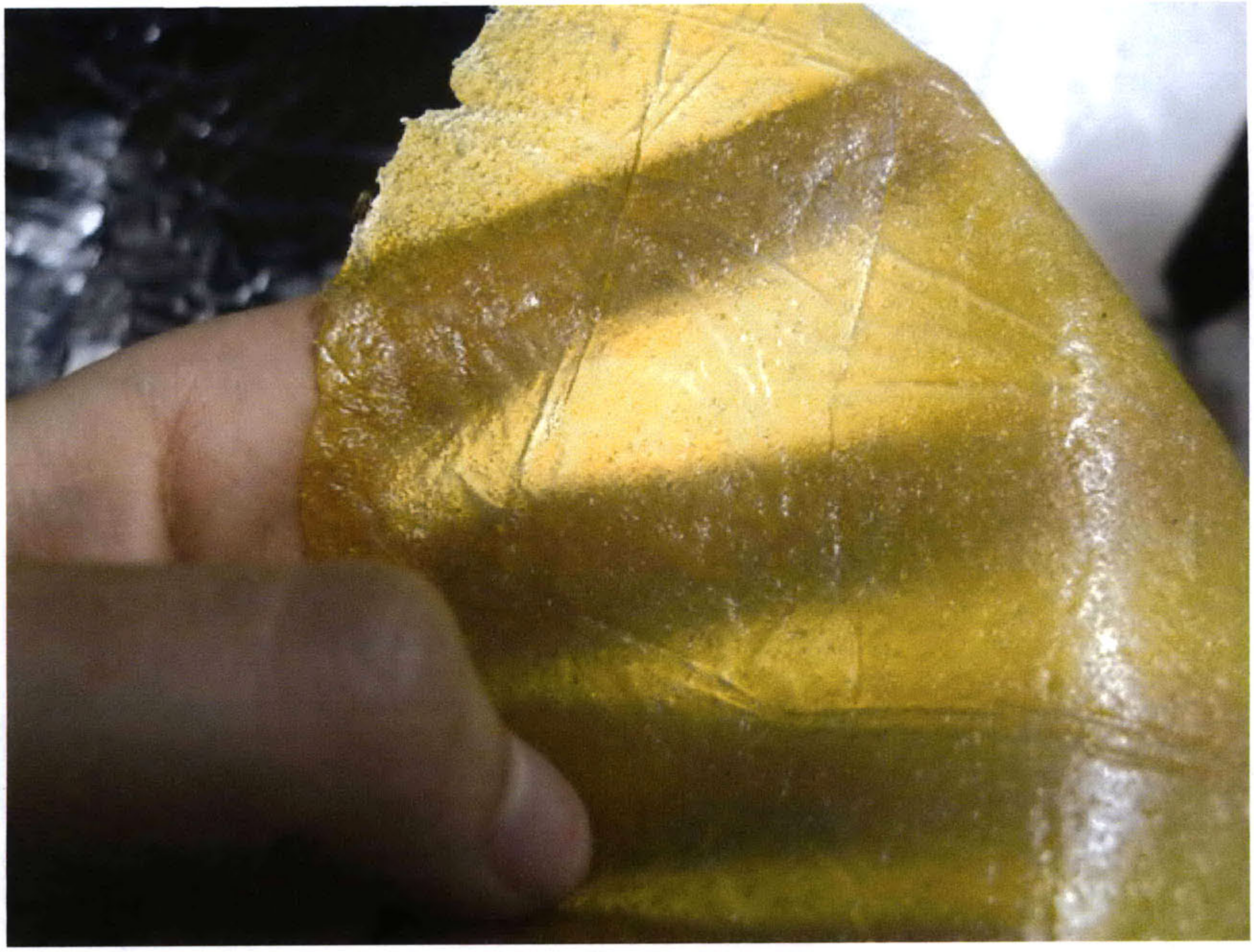


Figure 7.3: *The soy protein polymer sheet was pressed between two sheets of aluminium foil in a hot press. The aluminium foil was slightly wrinkled, which caused the lines and texture.*

I then tried combining the soy protein polymer with chopped sisal fibres of 50 mm in length. The sisal fibres had not been chemically treated after decortication, and I found the fibre-matrix adhesion very poor. Especially with the increased amounts of glycerol, the sisal fibres would slip out of the matrix instead of breaking. Increasing the fibre length made it difficult to obtain a flat 2mm sheet, and my attempts at using longer chopped fibres resulted in thicker sheets with cracking and unevenness.

One thing that was not at all a problem was the disposal of the leftover bits of protein sheet. Once submerged into water the sheets immediately softened, and within 2 hours would no longer hold shape. If left in water for 48 hours, the sheets would entirely dissolve and create a rather smelly solution. Uncured protein granules would begin moulding within one day of being mixed. A demonstration of the decomposing can be seen in figure 7.4.

The process of making protein resin sheets was quite slow, and curing and drying the sheets required a lot of heat, and thus power. Getting the protein sheets to cure into a particular shape that was not a sheet was difficult, the thicker parts would always shrink more and cause the final part to warp. Without milling metal self-heating and drying moulds, I thought the protein resin approach was not working that well.

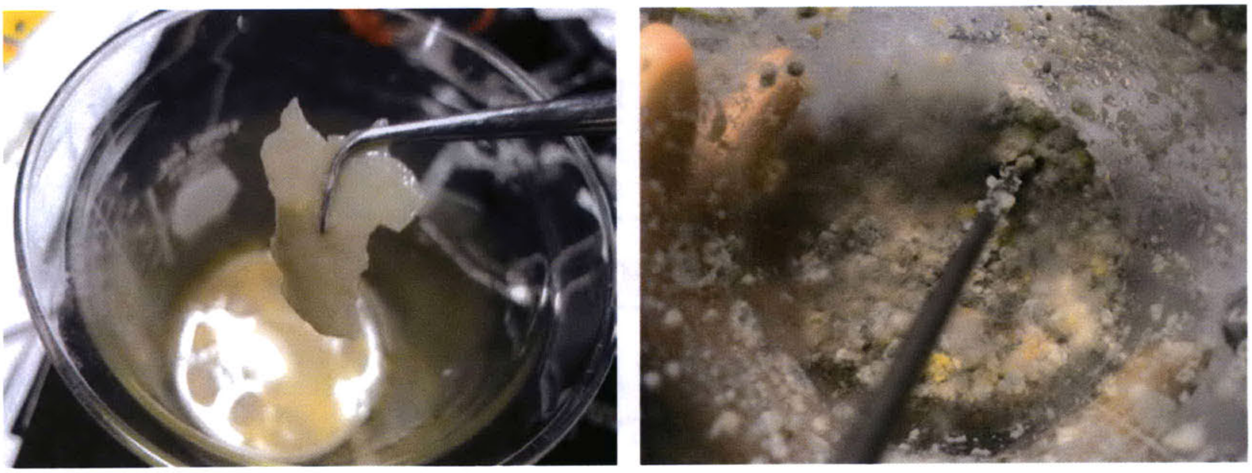


Figure 7.4: *Submerging the protein film into water would cause it to disintegrate within a matter of hours. Uncured protein granules left at my desk for more than 2 days would start moulding abundantly.*

Looking into new options, I went with trying similar method of making sheets, but instead of using protein isolate, using starches as the base. I also started experimenting with using alcohol as a solvent for the resin, so it would evaporate quicker and dry the film faster. I sourced potato and corn starch from Barry Food Farms Inc., although these starches are also readily available in food marts.

I settled on a by-weight combination of 3 parts starch, 12 parts water, 1 part alcohol, 2 parts vinegar and 1 part glycerol. Unlike the protein mix, this does not produce granules to press, but a milky runny suspension. The alcohol and vinegar also help as cross linkers in the polymer. To gelatinise the starch, I heated the mixture on a hot plate to boiling, while stirring vigorously. The mixture becomes thick like custard, and as it thickens, becomes more transparent as well. Upon cooling, the paste sets into a gelatinous mass, so spreading the paste before it sets is often easier, but if it is very hot it will contract significantly while drying and cause cracking.

I used a variety of methods to make resin-only sheets, including spreading over sheets of aluminium foil, spreading over sheets of plexiglass and baking sheets of resin in metal trays. A separated sheet of corn starch can be seen in figure 7.7. After drying the sheets, they can be wetted and spread over fibre lay-up, allowing each ply to dry before applying the next.

Another method for lay-up using the starch sheets is using the undried paste to do slow wet lay-up like illustrated in figure 7.8. Using woven linen fabrics and starch paste that has not yet gelled, one can laminate a mould with plies of starch impregnated fabrics. The resulting structure is very stiff and strong, but will disintegrate quickly in water. In the image I'm using the cardboard mould as a structural element of the part, but you can also mould the starch onto a smooth surface to release it from the mould afterwards.

Starch sheets were slightly more successful than protein sheets, but both remain weak and plagued by their lack of resistance to water. Using them for parts that should last longer than a few months does not yet seem like an option. However, for simple throwaway structures like toys, using easily compostable materials could be great.

Facing these difficulties, I did not entirely rule out non-green resins, but tried to keep using resins and plastics which did not emit high levels of VOCs and were not as irritant on skin contact. I used a lot of the Smooth-on line (`http://smooth-on.com`) of casting plastics, because they are readily available in small package sizes and easy to mix and use.

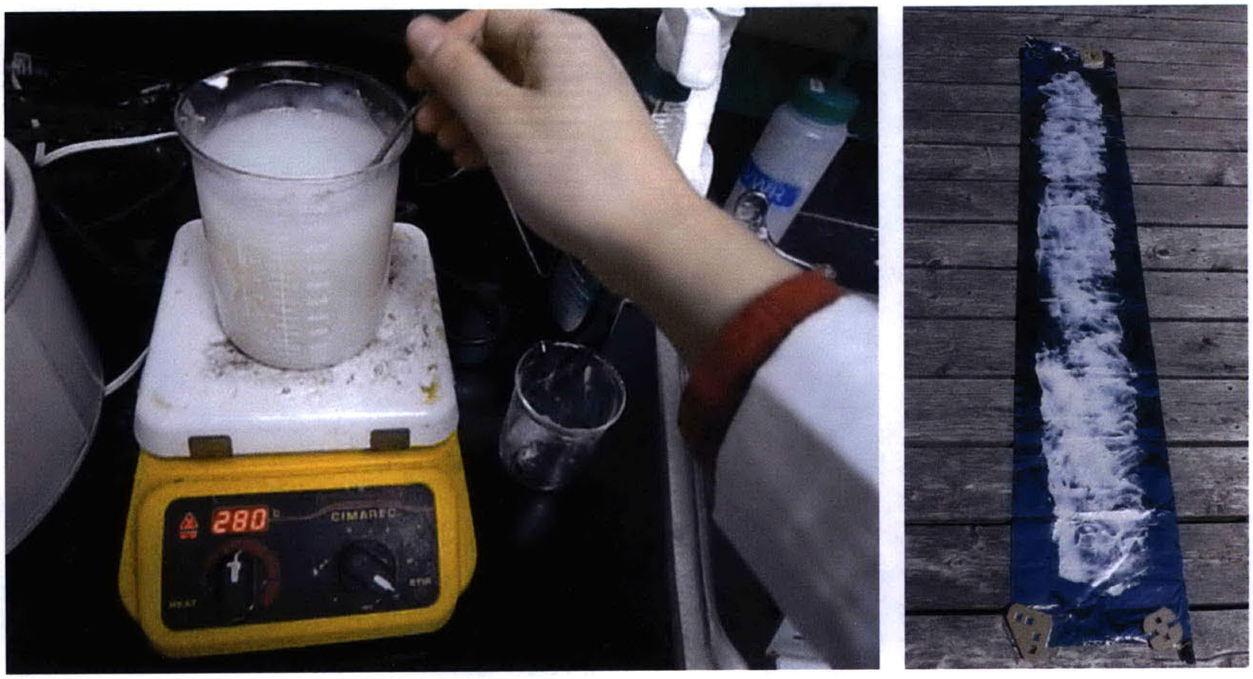


Figure 7.5: *Plasticising corn starch with glycerol, alcohol, white vinegar and water and sun-drying the resulting paste on aluminium foil. Sun drying is faster, but can lead to more cracking and also exposes the film to dust and particles from the outdoors.*

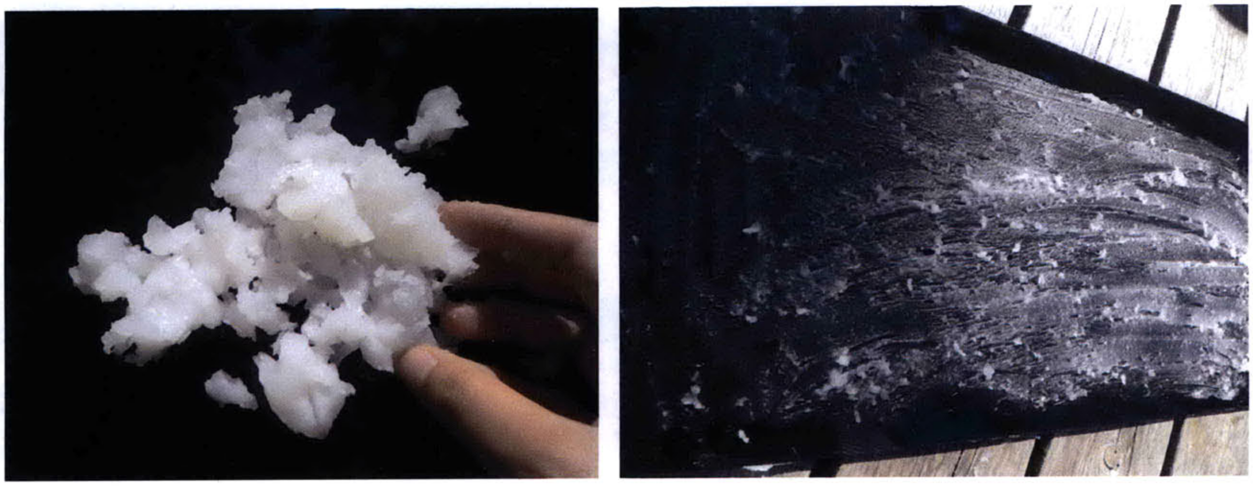


Figure 7.6: *The corn starch paste can be spread either while hot or after it has cooled. If the paste is spread hot, it will shrink considerably while drying. This is a difficulty with making large sheets. If the corn paste is too cool, it will have already set, and it will not spread into a thin film like you can see in the photo on the right.*

Figure 7.7: *A sheet of corn starch film, dried at room temperature on aluminium foil. The film after curing is sensitive to ambient moisture, and can shrivel or crumple if stored with uneven amounts of humidity on either side of the sheet. The tensile strength and elongation at break is highly dependent on the plasticisers used and their ratios.*

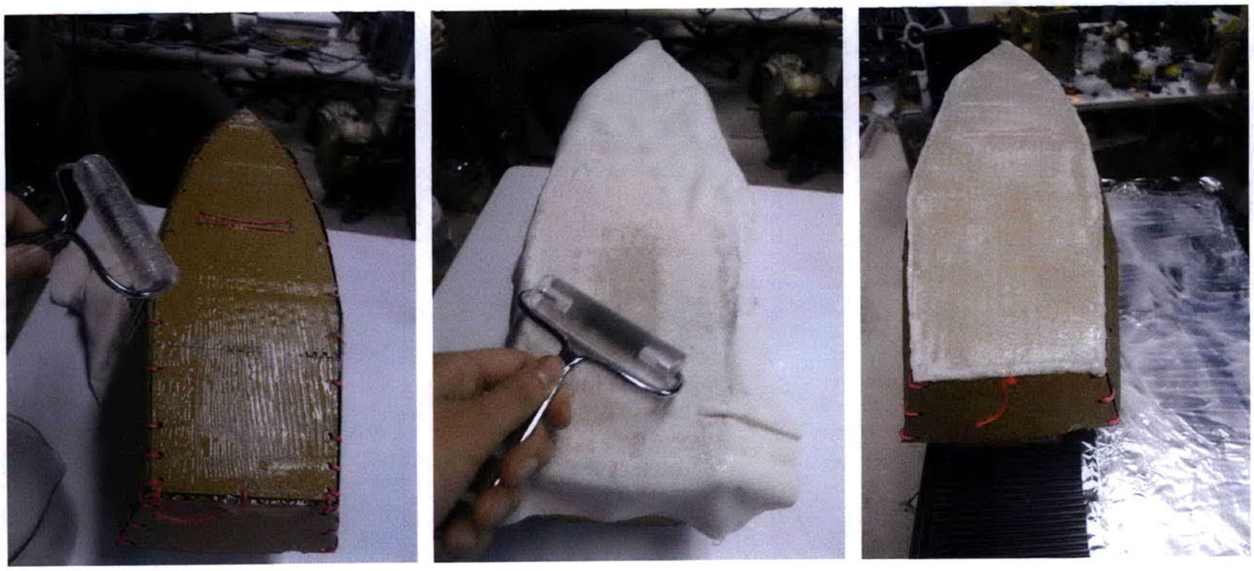


Figure 7.8: *Using wet corn starch paste for linen and cornstarch lay-up. The resulting composite is stiff but very sensitive to moisture. Between each ply the composite must be set to dry completely,*

7.3. Friendly composites in How to Make (Almost) Anything

In the fall semester at MIT Neil Gershenfeld teaches the class *How to make (almost) anything*, an introduction to all kinds of fabrication. Every week in the class is devoted to a different manufacturing process, and one such week was devoted to composites. Instead of guiding the students through the safety precautions required for working with carbon and glass fibres, the students were encouraged to work with non-toxic resins and materials. I tried to supply good fibres and ingredients for green composite experimentation, including linen, cotton and silk cloth, sisal and kenaf fibres, starches and proteins as well as polyurethanes and epoxy resins.

Figure 7.9: *David Robert, David Cranor and Edwina Portocarrero built an inflatable mould which they used to lay up recycled apparel fabric with epoxy resin.*

Using an inflatable dome structure, students were able to very quickly make a temporary mould for a hutch. They laminated the inflatable hutch with cut strips of used clothing bought per pound dipped in epoxy (see figure 7.9. The resulting structure was still somewhat prone to cracking (the varying thickness of the fabric in different places caused extra stress concentrations) but withstood quite a gale while on display outside the lab. Sitting inside, light coming through the different colours of fabric had a stained-glass effect.

Taking inspiration from starched shirts and wallpaper glue, Jean-Baptiste Labrune moulded several stiff bowl shapes with unwoven sisal and one ply of jersey-knit rayon along with gelatinised corn starch (see figure 7.10). Hannah Perner-Wilson started using knit tubes and a gysum and Portland cement mix to mould over inflated balloons. Sarah Reed made a cork granule composite frisbee that lights up when it is thrown by means of an vinyl-cut circuit board that is moulded in place.

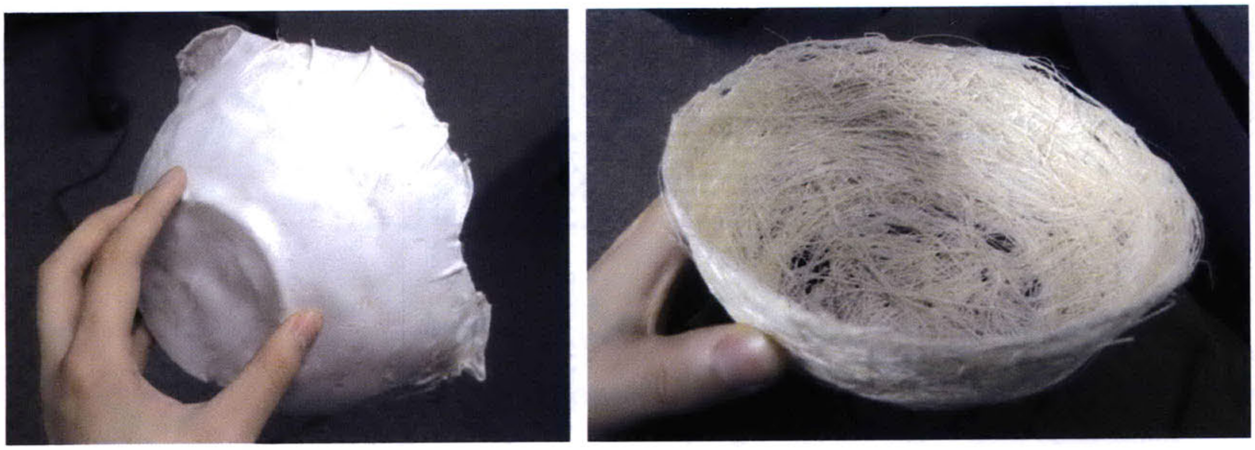


Figure 7.10: *Jean-Baptiste Labrune used boiled corn starch, rayon (left) and sisal (right) to make bowl shapes. Even with only one ply of jersey-knit rayon, he was able to keep the form of the mould. The jersey-knit fabric allows the fibre to conform better to the shape of the mould.*

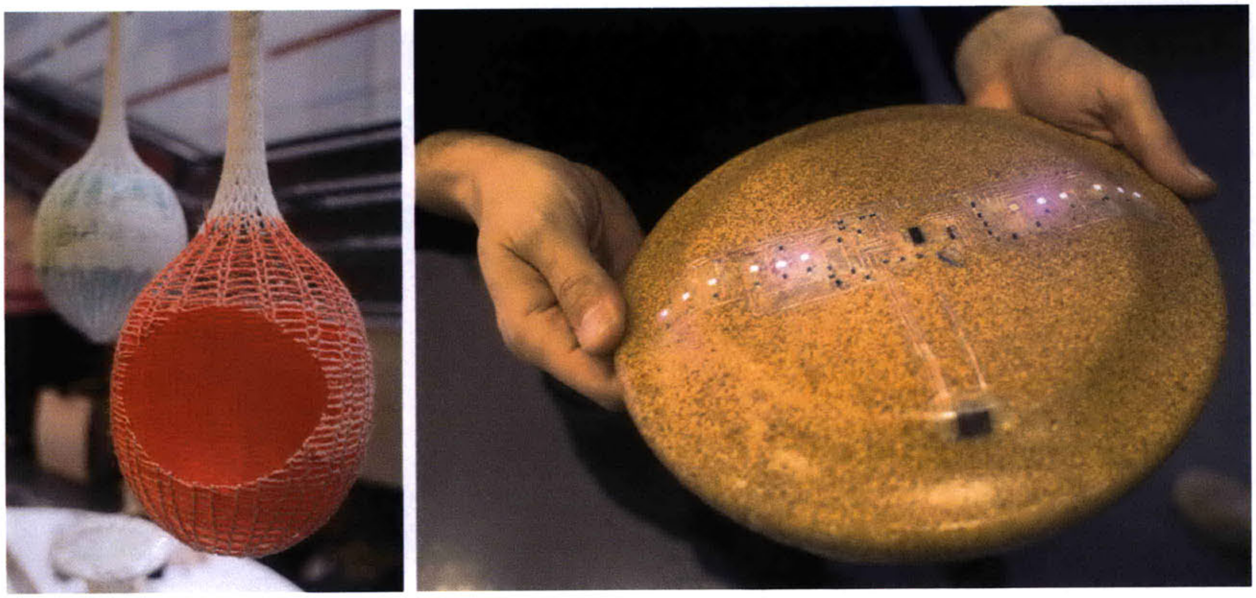


Figure 7.11: *Hannah Perner-Wilson's wool-plaster forms, made from knit tubes and Hydrostone, and Sarah Reed's cork composite frisbee with moulded-in-place light-up circuit.*

7.4. COMPOSITE CRAFT

I was given the opportunity to travel to Haystack Mountain School of Crafts in Deer Isle, ME, to work for 2 weeks with artists, craftspeople and designers there on prototyping processes. Neil Gershenfeld and the FabLab crew (Kenny Cheung, Jonathan Ward and I) were invited to be visiting scientists in an institution which otherwise only uses traditional technologies. Going to Haystack involved me bringing several bales of natural fibres: sisal, cotton, hemp and kenaf; metres of woven fabrics; many gallons of low-VOC emitting polyurethanes; and also some starches and soy protein isolate to try the less durable kind of resin. This paired with the tools available in a FabLab -laser cutters and small- and large-scale CNC routers- allowed the fabrication of tools for rapid prototyping with green and semi-green composites.

Figure 7.12: *Tom Spleth and Juan Torres took to the visiting artists studio deck to try to see what forms would emerge from hand sculpting curing strips of canvas and polyurethane.*

At Haystack, the concentrations include glass blowing, ceramics, fibre arts, enamelling and woodworking. Many of these disciplines have a more intuitive workflow than CAD/CAM, the process is ongoing experimentation and refinement of the material and design in real time. Instead, with the FabLab, prototypes are made in iterations of designs each given explicit form by means of a machine tool path. Finding the overlapping workflows was one of the most interesting aspects of working at Haystack.

Tom Spleth is an artist who works mainly in plaster and ceramics. At Haystack he was teaching slip casting, a method of making porcelain forms by pouring liquid porcelain into plaster forms. The plaster forms are made by working with the plaster while it is curing, forming it with hands and tools until it sets. Tom is interested in working with materials in this semi cured stage, the material changing along with his process. To test some semi-green composite materials, Tom impregnated cotton canvas strips with quick curing urethane and held them in shape as they cured, mirroring his process for plaster. The urethane he used was Smooth-on's Smooth-cast 300.

The canvas fabric is not ideal for wet lay-up better would be a thinner, more loosely woven fabric applied in more plies that can better form curvaceous shapes. However, with the thick cotton canvas, the shapes held in place by hand retain more form and thus the thick canvas is perhaps not such a bad choice for this working method.

A more conventional composite manufacturing technique would be to use a mould to give form to the flexible sheets of fibre as they are being set into a shape. Using cardboard moulds cut on the laser cutter like shown in figure 7.1 or plywood structures cut on the larger CNC mill, one can quickly friction-fit together shapes to use as jigs for fabric-resin layup. Using this technique, Matt Bissett and Leslie Tarp, participating in the woodworking workshop, set out to make the skeleton of a canoe.

(a) wooden boat frame

(b) polyurethane and cotton lay-up

Figure 7.13: *Matt Bissett and Leslie Tharp made a structural boat form of wood, stapled cotton and linen fibre fabrics onto the frame and brushed on polyurethane resin (Smooth-on Smooth-cast 310). They started with 3 layers of fabric, and later added more for better structural integrity. Photo in (b) by Haystack Mountain School of Crafts*

They lined the sides of the canoe with strips of wood, and then laminated cotton canvas with polyurethane plastic (the same materials Tom Spleth was using) onto the form. They used 3 layers of ply over the entire structure, adding the last layer of ply after the maiden voyage when they decided they needed more structural integrity.

The design and manufacturing of the canoe was done in less than 2 days, a good demonstration of how fast a prototype can be made. In future revisions, thinner ply might be used to give a smoother finish to the outside of the boat, and a mould used that can later be removed from the canoe, making the resulting structure lighter.

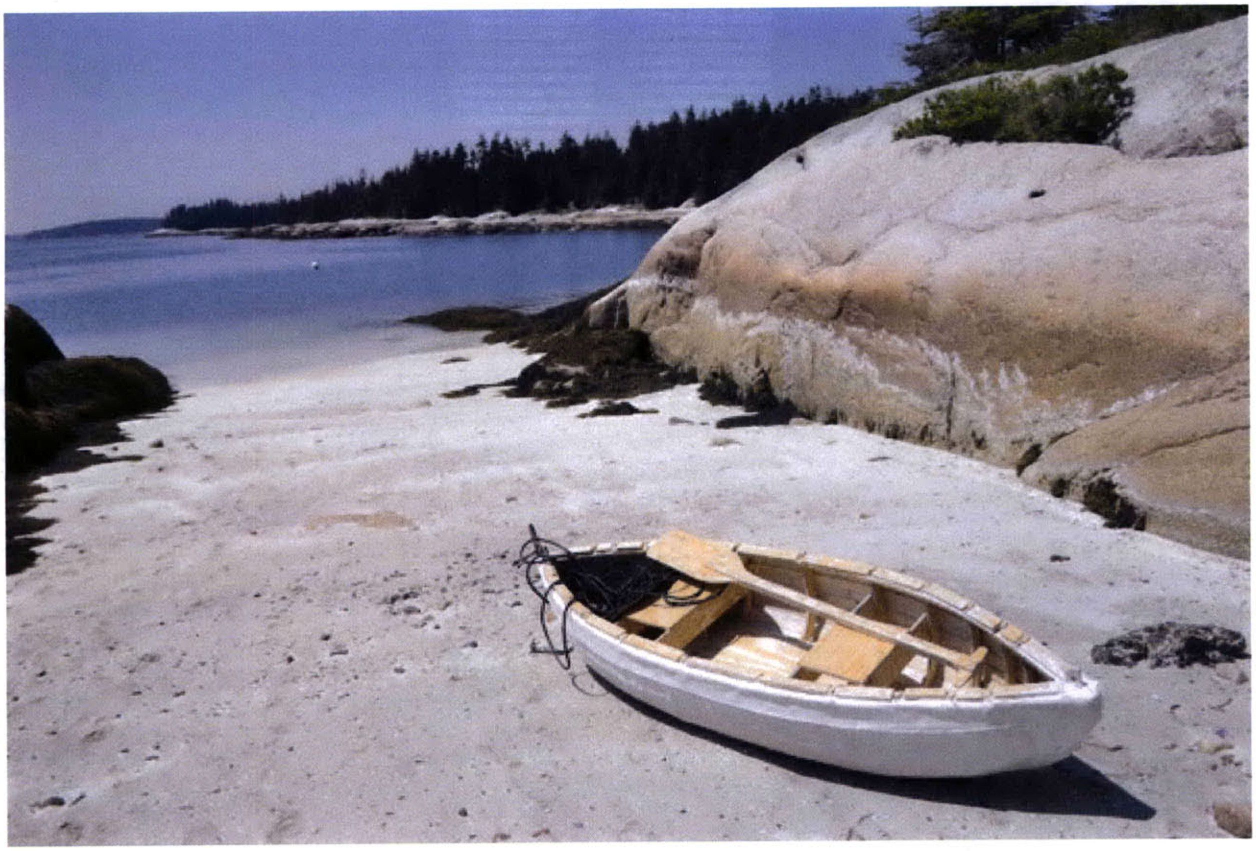


Figure 7.14: *The green-composite boat ready for its maiden voyage at Sandy Beach on Deer Isle, ME. The paddle, support structure and seats are cut out of plywood. Photo by Leslie Tharp.*

Without a hot press at Haystack, there was not much experimentation with soy protein isolate sheeting, but the starch plastic was quite popular. Without using it as any kind of composite, it was set in the small milling machine the laser cutter to see what would happen. Laser cutting the starch polymer smelled a bit like toast, a welcome change from the fumes of cut acrylic.

Without any structural integrity, the starch sheeting was cut only decoratively. Notes and announcements were etched into the sheets which were left around the campus to be discovered before the first rain washed them away.

Figure 7.15: *A laser etched sheet of potato starch film. The potato film was dried outside, which caused the imperfections on the film you see here. Potato starch film can easily be laser etched or cut, although even so the applications remain limited.*

Figure 7.16: *Because of the lack of woven or knit structural natural fibres (like sisal, which in strength is comparable to fibreglass), this was an exercise in getting long sisal fibres into a sheet. The hand-knitted sisal unfortunately did not have uniform stretching properties. However, if knit with more care, knit natural fibres could be useful in making sheets that can attain non-zero Gaussian curvature during composite lay-up.*

7.5. MEDICAL DEVICES

Carbon fibre is used extensively in prosthetics as a strong and lightweight material. In its raw form, it is not even particularly expensive, but the amount of work and technical expertise needed to form the carbon fibre into its final form makes the final prosthetics relatively expensive.

When still so nascent a field, and still without the mechanical properties that rival carbon fibre, it may be unwise to use green composites already for medical devices. If prosthetics and orthotics fail, the patients lose a lot of confidence in their mobility, which is very damaging to their usage. Biodegradable composites might also seem counterintuitive to what you seek in a limb, so it must be certain that green composite prosthetics would not degrade before their end

However, I began a collaboration with Dr. Pooja Mukul, a rehabilitation doctor and prostheticist from the Jaipur Foot Organisation, who has been working on low-cost prosthetics for the past 20 years. She had so many ideas for tools and prototypes she would like to develop for her deserving patients that it was difficult to not try to use the materials I was working with (and many more) for the cause.

7.5.1. BMVSS, THE JAIPUR FOOT ORGANISATION

Figure 7.17: *BMVSS also manufactures hand-powered tricycles, wheelchairs and crutches to the disabled. Here a stack of coir mats, used as padding in the tricycle and wheelchair seats.*

Bhagwan Mahaveer Viklang Sahayata Samiti (Bhagwan Mahaveer Disabled Help Organisation or BMVSS) produces the most low cost lower limb prosthetics in the world, fitting around 100 patients a day with above the knee or below the knee limbs. Their famous Jaipur foot is made of closed cell microfoam and rubber, hand carved and moulded in-house [43]. Together with the fitted leg and knee, each limb comes out to about 30 dollars in cost. I visited their organisation in August 2009 as part of working in India on FabLabs, and returned to Jaipur to start prototyping digitally fabricated prosthetics in 2010.

The shafts of the legs are made from high density polyethylene tubing, a thermoplastic they bake in large precision ovens and then fit around the plaster of Paris mould they have taken of the leg stump. If the technician is making a full contact below knee socket, first a sheet of polyethylene is fitted around the stump, and the shaft is fitted over the polyethylene. The foot is screwed directly into the shaft, without an interior pylon.

For an above knee prosthetic, standardised brims are used to make the socket for the patients. These are all open ended sockets. The patient can be fit with a polycentric endoskeletal knee (such as the Jaipur Knee) or with a locking external knee joint. The pylon extending from the knee joint is screwed directly into the foot. No alignment below the knee can take place, all the positions of the foot, pylon and joint are fixed.

Figure 7.18: *A mould is taken from the patient's stump using plaster of Paris and cotton bandages. A positive cast is created using plaster of Paris. While forming the mould, the technician locates landmarks like the patella tendon and applies pressure and counter pressure to obtain a load bearing ridge there later. After the positive is cured, it is modified with more plaster to relieve pressure on boney prominences and increase pressure on muscles for fit.*

The fitment process takes less than one day, and on average the workers see about 4 to 5 patients a day. The workers who do the fitting are part trained medical staff and part untrained workers who have built up years of skill in the fitting of these low-cost prosthetics. Many of the technicians initially came in as patients, and stay as foot makers or fitters.

In more standard prosthetic clinics, for below-knee amputees, a plaster cast is taken of the patient's stump, in the same way as is done at BMVSS. The plaster is modified and a full contact socket is fit with an EVA or silicone liner. An alignment pyramid is laminated to the socket at to the foot, a connection system that allows alignment of the pylon and foot after the fitting process. Pylons are fit for all patients, and a soft cosmetic cover is fit over the socket, pylon and ankle area.

Figure 7.19: *In an open-ended socket, high-density polyethelene pipes (HDPE) heated to 200°C are hand formed over the modified and extended plaster of Paris positives. This step requires two technicians to deal with the hot HDPE before it cools down so much it can no longer be hand formed. If the patient is given a full-contact socket, polypropylene is first vacuum formed over the non-extended positive, then the polypropylene and PoP positive is extended, and HDPE is hand moulded over both. The plaster is then chiseled out.*

Figure 7.20: *The open ended sockets are cut to size, sanded and finished. There is no foam or silicone liner used, the patient simply wears a pair of cotton socks in the socket.*

Figure 7.21: *The sockets are tested on the patient who is given cotton liner socks to wear with the open-ended socket. If the patient approves the sockets, feet are added, screwing through the bottom of the leg into the wooden ankle-block of the Jaipur foot. The alignment that is done here is mostly by eye by the technician.*

Figure 7.22: *Within hours of taking the first cast, the patient is given the final prosthetic, with leather suspension belts. Some gait training is offered, but due to the massive number of patients waiting, patients are often left to their own resources to learn to walk with their new prosthetics.*

In Jaipur, because the patients come in, are fitted for free and then leave for long journeys to their homes which are often days worth of travel away, there is almost no follow up. Even at the clinic, because of the massive amount of patients and the lack of time, patients are not given hardly any gait training. The alignment of the prostheses is only quickly checked during the fitting.

Because of the time constraints, limited experienced prostheticists and the low-cost requirement, innovating in materials and designs at Jaipur foot is difficult. Limiting the amount of customising necessary for each patient would improve throughput and quality. Improving the technology used in the limbs would improve the overall product. It is with improvement in mind that I set out to work with BMVSS. Luckily, MISTI gave a grant for travel between Jaipur and Cambridge to foster a collaboration between BMVSS and MIT.

Figure 7.23: *Several design iterations for the extension pylon. In the left most photo (a) Cindy Oh on the left, Deema Totah on the right with a recycled aluminium crutch on a Jaipur foot. (b) A stepping design for extension, prototyped out of wood on a bandsaw. (c) A nylon rod cut to be extendable on the waterjet cutter (d) Nylon extension fitted with a 3D printed female pyramid, ready to be used to make a mould.*

At MIT in the spring, the D-lab (D standing for developing, design, dissemination, and other nice D-words) teaches the class Developing World Prosthetics. Ken Endo, PhD candidate in Biomechatronics and the instructor of this class invited me to lead a team of undergraduates working in this class. After discussing with Dr. Pooja Mukul the idea for a prosthetic that could grow with a child, extending the period in which the patient could use a prosthesis without coming back for a fitting, I proposed the project *an adjustable paediatric pylon.* Two lovely mechanical engineering undergraduates signed up: Deema Totah and Cindy Oh. We invited Dr. Mukul to Boston halfway through the semester to evaluate our progress.

7.5.2. ADJUSTABLE PAEDIATRIC PROSTHETIC DESIGN

The design of an adjustable pylon came with the constraints that it should be light, load bearing, durable and not get weaker with extension. It should extend at least 2 inches in maximum .75 inch intervals, and should be compatible with standard feet, pyramids and attachment systems. Besides all this, it should be low-cost and manufacturable in India.

The standard size for a pylon at BMVSS. is 1.5 inches. Common paediatric prostheses will use a narrower aluminium pylon to save on weight and bulk. We started testing with a 1.5 inch pylon to still be able to use the pylons available in Jaipur.

Before settling on the step design you can see in figure 7.23 we experimented with screw designs, hinges and other mechanisms. We rejected any design that had rotational play– the pylon must not suddenly throw the foot 90 degrees to the left or right. We considered reusing crutches and their aluminium locking system, but decided against something with an unreliable supply chain.

At first our plan was to cut the pylon from a pre-extruded composite rod on the water jet cutter. However, cutting our test material, nylon (the left two images in figure 7.23) showed that the 1 mm of material removed would cause the rod to not fit together tightly afterwards. We did not want to use twice the length of rod than was needed in the pylon.

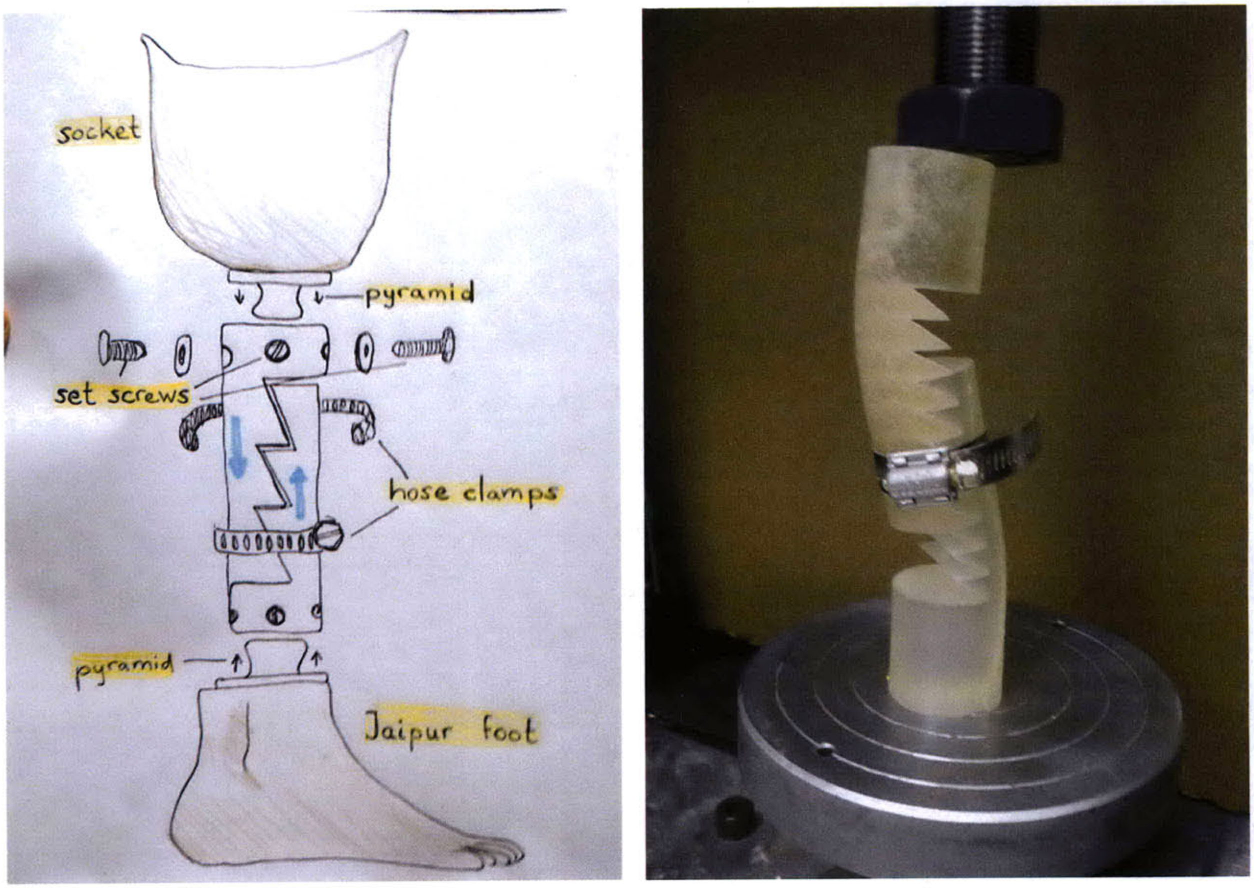


Figure 7.24: *Left: An overview of the components and conceptual structure of the extendable paediatric pylon design. Right: Testing how much load the cast polyurethane pylon could handle. The material failed at 1500 Newtons, but did not crack.*

Instead we decided to make a positive of a prototype that we would cast out of (semi) green composite. To make the mould, we used platinum cure silicone (Smooth-on's Dragon Skin 10) set in a cardboard fitting.

Using green composites without any of the more high-tech lay-up techniques (injection moulding, filament winding or high-pressure resin transfer moulding) was frustrating. The fibres we would include in the polyurethane casts would simply trap air and create voids. The voids would make the piece flexible and unusable as a pylon. More on this problem is in the next section, on pyramid design.

Finally we decided to make our first prototypes out of just cast polyurethane. Even though we hadn't settled on a material yet, we decided to test the first cast cut pylon's strength on a universal testing machine (see figure 7.24). The material failed at 1500 Newtons, but did not crack. The deformation showed that we really did need to include something in the design to avoid the buckling in any given direction. We decided to include filler pieces with the pylons that can be placed in the gaps that come up (see figure 7.25).

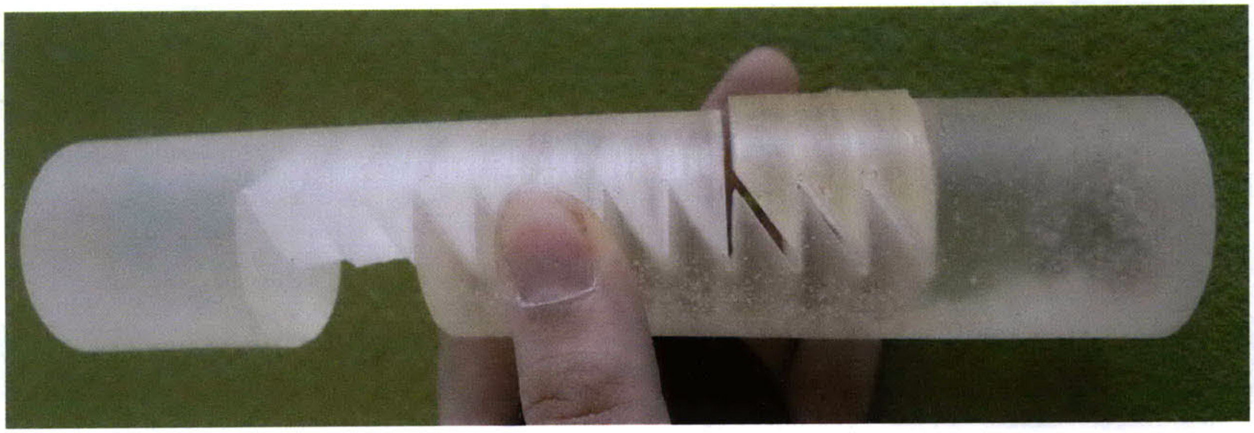


Figure 7.25: *Filler pieces added to the design to prevent excessive deformation under load. In a next revision of the design, the filler pieces and the pylon might include a notch to hold the piece in place.*

The other projects in the DWP class included a redesign of the Jaipur/Stanford knee, a vacuum casting method for making moulds of patient's stumps and a new cosmetic cover for the shape and roll foot. The projects had a varying level of success, mostly due to the limited amount of communication between the engineers, the doctors and the patients. The amount you can learn from dealing directly with the patient in the field is invaluable for the project. Figuring out how to structure the communication between the users and the designers would help this class in the future.

7.5.3. Pyramid alignment system

Prosthetic alignment ensures that the prosthetic foot is placed under the load bearing line from the residual limb. At BMVSS, the prostheses are aligned by eye. After the foot is screwed onto the shaft no more alignment can take place unless new holes are drilled. Because new holes degrade the foot, this is avoided. However, correct alignment of the prosthesis is crucial for natural gait. In less low-tech prosthetics, post-fitting alignment can take place by adjusting the interface between foot, pylon, socket and eventually knee joint. Most commonly this allows rotational medio-lateral and anterior-posterior adjustments, but some also allow the shifting of the entire interface along the plane parallel to the floor. These interface systems have standardised measurements so that male and female alignment parts work across different prosthetic brands.

The rotational alignment system has what is known as a pyramid and a pyramid mate. The pyramid has a rounded surface that matches the rounded surface of its mate. Set screws are set in at an angle, pushing the faces of the pyramid further into the female part. This pushes the rounded surfaces together, creating a strong bond that can be rotationally adjusted at very minute levels.

Most pyramid systems are made from CNC machined metal, and are priced accordingly. A titanium pyramid even without its mate can easily cost \$ 70, more than twice as much as the cost of an entire Jaipur limb. Researching low-cost alternatives for alignment systems could be very helpful for better fitting Jaipur legs. With this in mind I set out to experiment with composite and plastic pyramids.

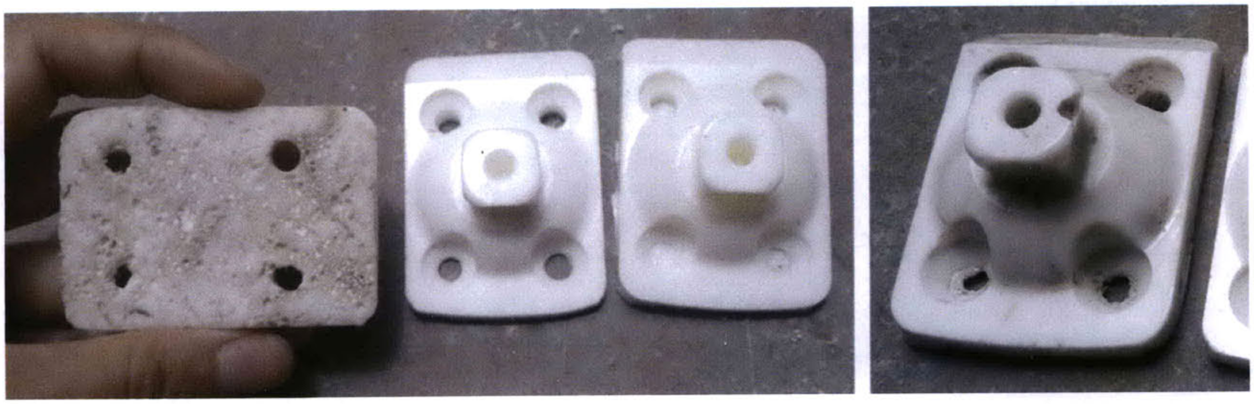


Figure 7.26: *Casting a standard sized pyramid of Smooth-cast 300 polyurethane with kenaf reinforcements, Smooth-cast 300 polyurethane only, and Task 4 polyurethane. All casting resins from Smooth-on. On the right the top view of the kenaf-reinforced polyurethane.*

I casted several different types of pyramids, each first printed on a 3D printer and then used to make a mould. The pyramids can have a varying inclination to better align with the part it is being placed on. Many paediatric patients have congenital deformities which result in residual feet. These result in widely varied angles on the bottoms of sockets, which can be very difficult to attach more standard pyramids to.

Reinforcing the cast pyramids with kenaf fibres with this moulding technique resulted in far too many voids (see figures 7.27 and 7.30). The alkali surface of the kenaf also had some chemical influence on the curing of the polyurethane, resulting in a soft, pliable final material.

Although it is a good method for testing the shapes of pyramids, the cast pyramids are not strong enough even for implementation in paediatric prosthetics. This work will be continued with different moulding techniques, stiffer resins and thinner, technical fibres.

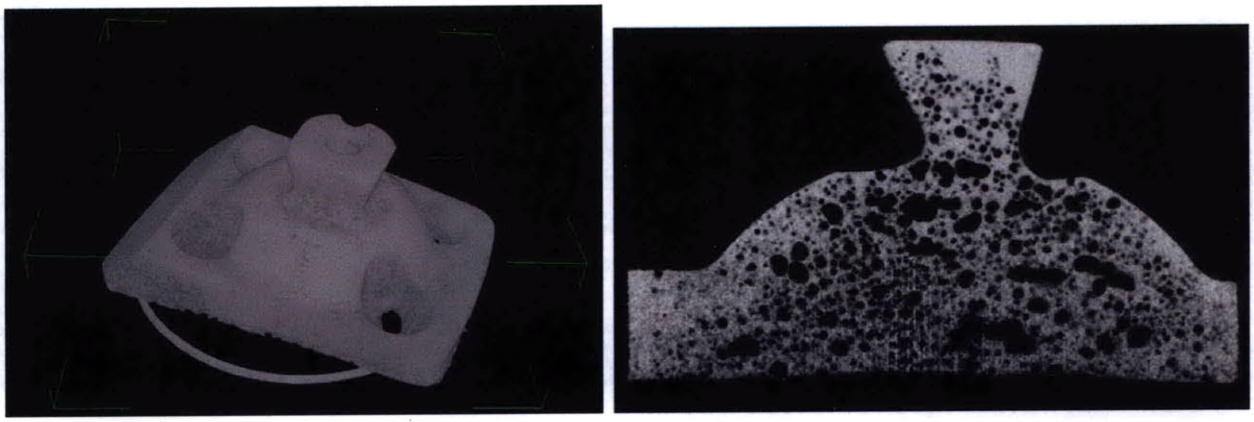


Figure 7.27: *CAT scan of the kenaf-reinforced polyurethane casting of an alignment pyramid. Because of the fibres, many air bubbles are trapped inside the the casting, weakening the structure. On the right a cross section showing the voids.*

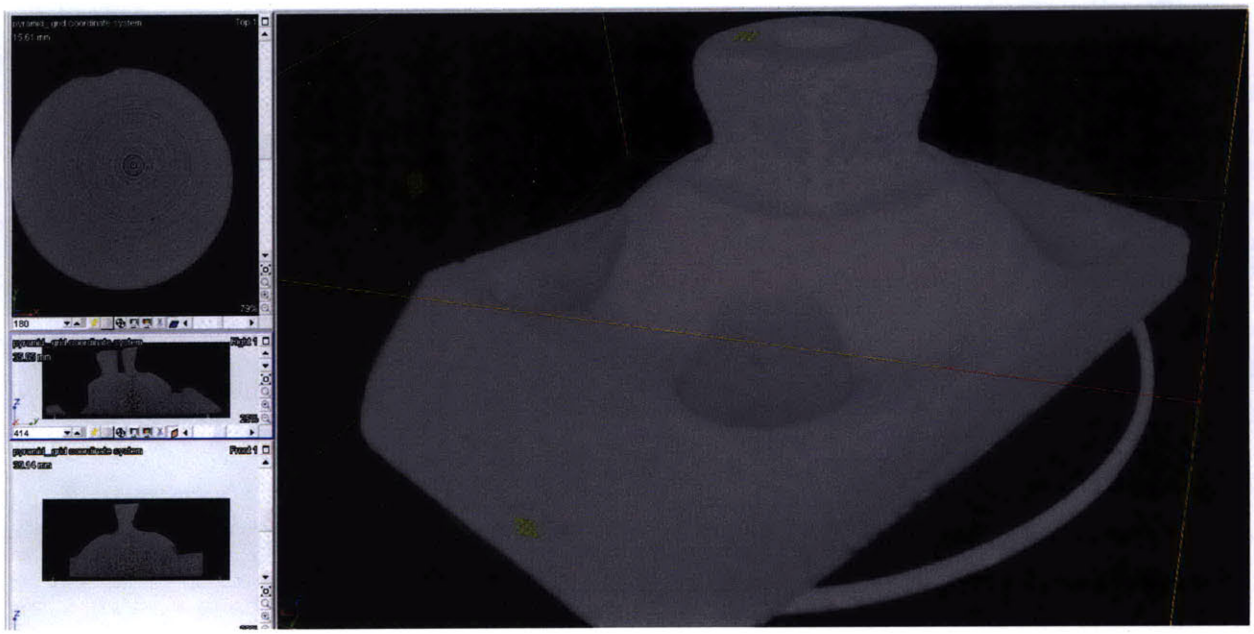


Figure 7.28: *CAT scan of a polyurethane only casting of an alignment pyramid. Without fibres to trap in air, the casting has far less and smaller voids and therefore is stronger. The ring shapes in the cross section on the left are artefacts from the CAT scan. Even so, there are still many voids in the casting, and in the future a different manufacturing technique might be preferable.*

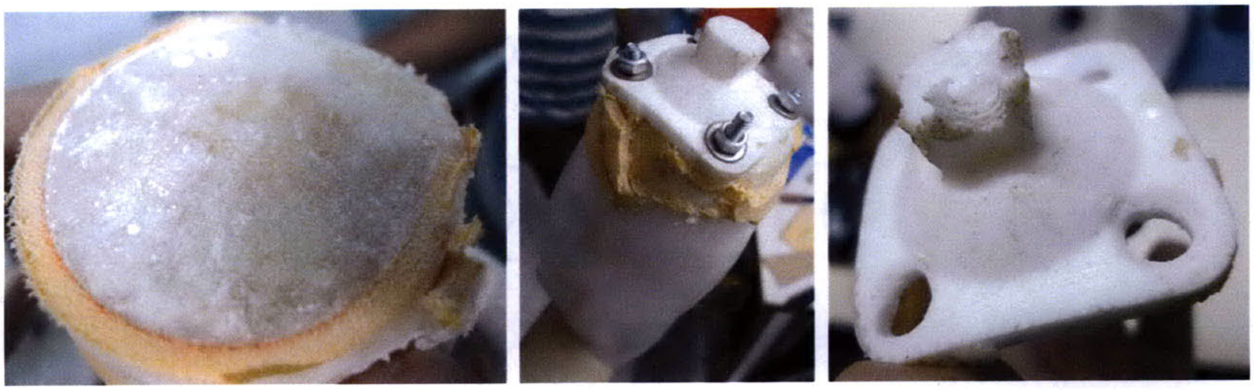


Figure 7.29: *The socket is prepared for bonding with a flat pyramid by building up a layer of hemp-epoxy composite over the curved socket surface. The pyramid is bolted on and the screws are ground down. While attaching the pylon to the pyramid, the set screws damaged the pyramid beyond useful life. The strength of the set screw should be comparable to the strength of the pyramid material if it is to be used while aligning the prosthetic under load.*

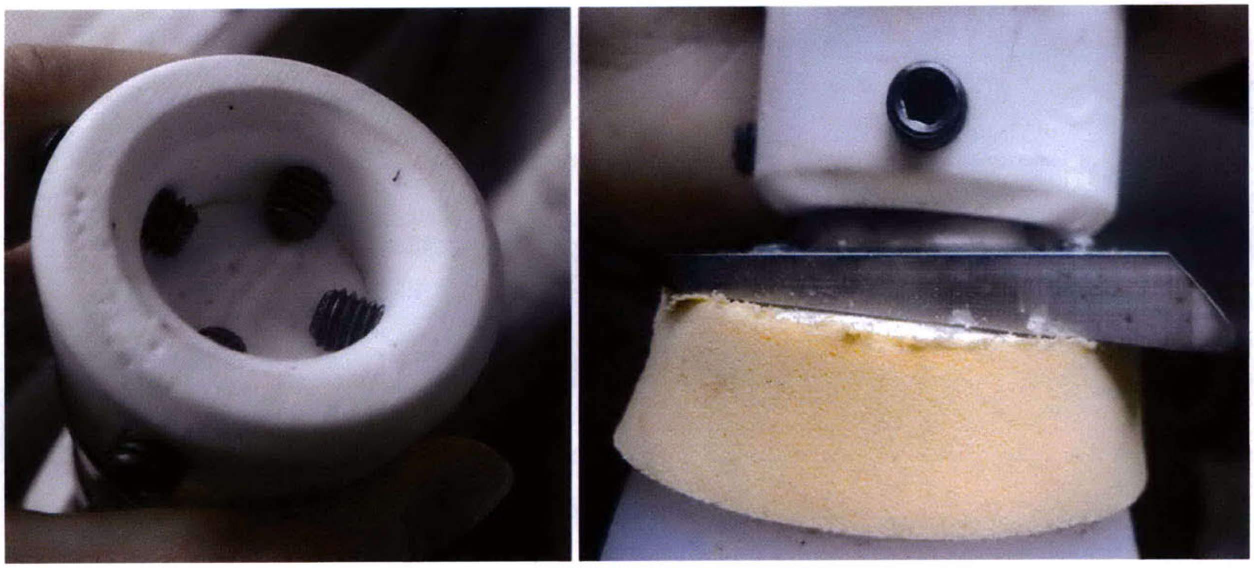


Figure 7.30: *The female part of the pyramid does not have to have the same material strength. As long as the material retains the set screws without slippage and does not crack under normal load, it is strong enough for the female adaptor. On the right the hemp-epoxy flattened socket with a machined titanium male pyramid and a polyurethane female pyramid.*

7.5.4. PATIENT TESTING

Finally, I decided to travel to Jaipur for 4 weeks to speak to the patients and doctors in person and continue work on the extension pylon. Based on our findings during DWP, I modified the design of the extension prostheses to be wider, have smaller ridges, and be easier to mould. The smaller ridges maximise the amount of material at the narrowest part of the continuous pylon, while the wider pylon increases strength without making the overall design larger. A female pyramid for alignment was integrated into the pylon itself.

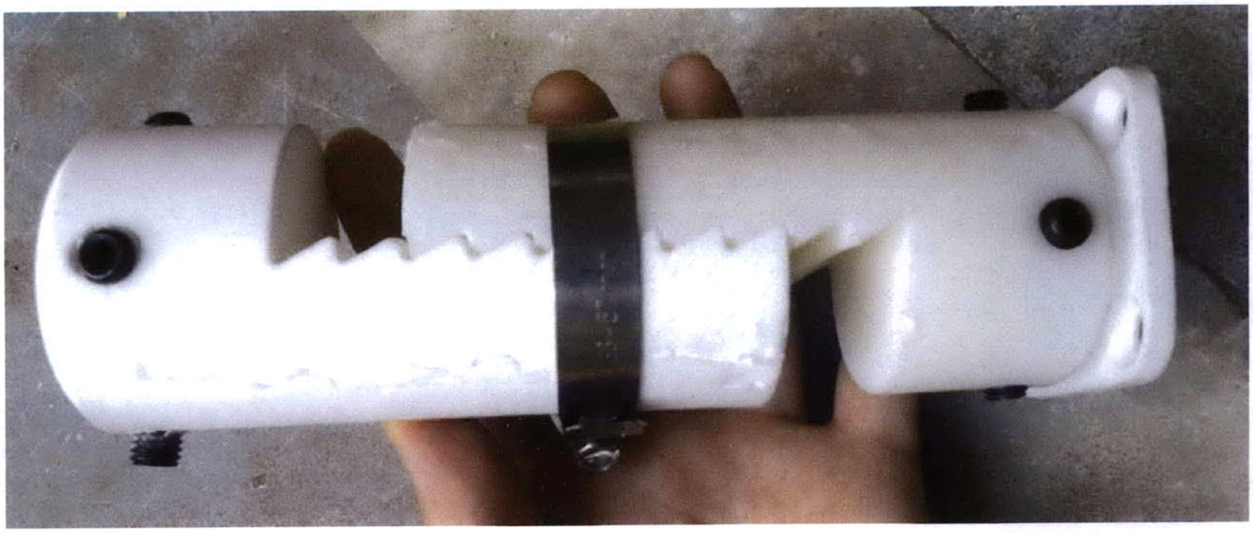


Figure 7.31: *The new design of the extension pylon with integrated female pyramid part. The pylon has smaller, less sharp extension ridges to spread the load, and is wider, to provide more strength. The two parts are hose clamped together, and shown here without the support pieces. The total cost of the hardware is about 60 Indian rupees ($1.25) and the polyurethane is about $4, although that is still sourced in the US in retail quantities. The piece on the left is made of Smooth-cast 305, whereas the piece on the right is made of Task 4 with some embedded sisal fibres.*

The total length of the pylon including the female pyramid parts is 6 inches. The total ridged area is 3 inches. This allows 2 inches of extension while maintaining 2 inches of contact between the separate components. The pylon can be cut to the length required by the patient. Slot pieces for in between the extension and the original are not included in figure 7.31, but are included in the design.

I made the extension pylon parts for testing in the College of Engineering, Pune FabLab in Maharashtra, India. I cast a 3D printed model into Dragon Skin platinum cure silicone, and used the cardboard framed silicone mould to cast polyurethane versions out of Smooth-cast 305 and Task 4. The Task 4 polyurethane is harder and more durable, but takes longer to set and does not machine as well.

The extension pylon was originally intended for paediatric trans-tibial amputees. Non-paediatric patients have no need for extension prostheses, and below-knee amputees are simpler to fit to start out with. We did not test the design on above-knee, not because an extension pylon would be unsuitable for an above-knee amputee, but because we were to begin testing with less possibilities for failure.

An 8 year old trans-tibial patient may need a prosthesis that measures between 5 and 10 inches from their stump to the floor. This depends on their height, and the length of their stump. Unfortunately, in India many amputees are not amputated by an orthopaedic surgeon but by any doctor who is available. Instead of cutting the leg in such a way as to provide best prosthetic fitting, the patient might have an amputation cut very far down at the ankle, or a leg which has been amputated through the knee, leaving the patient without a knee joint and with very little space to fit a new knee. Paediatric patients are typically under 60 kgs in weight and require smaller, lighter components. Simultaneously they tend to have good vascularisation and muscle tone in their stumps, unlike diabetic and elderly patients who often lose sensation in their stumps.

Figure 7.32: *Extension pylon attached to two different paediatric Jaipur feet. The first has a very high ankle block, and the pyramid that is attached to it is too large for ankle. The second has a locally manufactured cast metal pyramid, but that pyramid is only screwed in in the centre, causing rotational play.*

Prosthetic feet come with different sizes of ankle blocks. Some have a high profile, while some end just about where a loafer would. This has to be taken into account when choosing a length of extension pylon– with a 4 inch foot and 5 inches of space from the stump to the floor, only one inch would be left for the pylon, leaving only the female pyramids and no space for the extension ridges.

Figure 7.33: *This patient is 8 years old, 42 kg and has been walking on a prosthesis for the last 2 years. Here I am taking a plaster cast of her stump to make a socket of EVA-lined polypropylene, seen on the right.*

The EVA and polypropylene, both heated to 200°C, are consecutively vacuum formed over the positive with hemp fibres as an interface in between. The EVA is bonded with rubber compound, while the polypropylene is simply melted onto itself and into the hemp. Carbon fibre sockets or sockets with a carbon fibre brim are often fitted to patients in the developed world, mostly to make the prosthesis lighter. The stiffness of the socket feels very different for the patient– a polypropylene socket will flex with normal walking, while carbon fibre will not.

Since it is hardly mixed with the polypropylene, the hemp does not improve the tensile strength of socket by much. Thin polypropylene can be used because of the low weight of the patient, making the socket already quite light. I'm using the same hemp-epoxy mix to mould a flat surface to attach a pyramid as shown in figure 7.30, and a polyurethane-sisal extension pylon cut down to 4.5 inches to match the current height of the patient and the selected foot.

A typical SACH (soft ankle cushioned heel) foot will have a low profile and an interior bolt for attaching a pyramid. The Jaipur foot is mostly manufactured without a hole for a bolt, and bolts and screws are simply drilled into the wooden ankle block as needed. This is problematic, because each bolt is attached in some different way, causing bad alignment. To realign, new holes are drilled, leaving the ankle block exposed to moisture at the previous drill site. The Jaipur foot is furthermore not manufactured in a low profile model, and so to have ample space for an extension pylon, I used a SACH foot for testing with the patient. Unfortunately I did not have one in her size, so she was testing with a foot 3 or 4 sizes too large. Low-profile feet could be manufactured at BMVSS in the future.

Figure 7.34: *Patient testing the extension prostheses. The Jaipur foot is only available with a relatively high ankle block (see feet on left), leaving little room for the pylon and its extension. Finally we tested the extension pylon with a low-profile SACH foot (right).*

After fitting the socket with a cotton stockinette, the patient walked on the extension prosthetic for 15 mins. In that time, I observed play in the pylon because the ridges were aligned in the posterior-anterior plane, and the hose clamp was providing a pivot point for them to rotate around during toe-off. I rotated the pylon 90 degrees to align it in the medio-lateral plane, and added a second hose clamp, positioning both hose clamps at the extreme ends of the respective parts of the extension pylon (see figure 7.35). This removed the play effects; however, extending the pylon (while giving the patient a padded shoe to test with) reintroduced problems with play in other parts of the pylon.

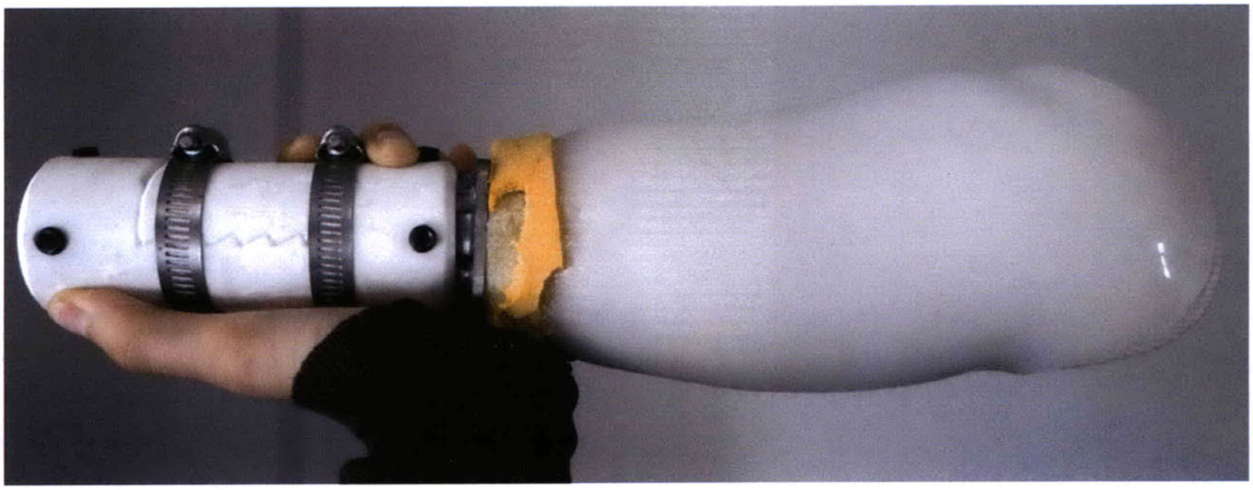


Figure 7.35: *The ridges are now in the medio-lateral plane, with the top hose clamp also providing lateral support to the pylon. The knee here points in the upward direction, marked by the patella tendon indentation.*

Further patient testing resulted in similar feedback. The new alignment system was a big improvement, but the material used for the pylon was suboptimal. Further improvements could be adding a clamping sheet around the extension section of the pylon, using an extension design with different planes of interface, or making an altogether new design, separating the pylon and pyramids again.

Figure 7.36: *The foot used in this test prosthesis is too large for the patient, making her gait poor during testing. She is unsure of her toe-off, and so looks at her feet as she is walking. The pylon makes some noises as some parts with play rub against each other, making her further uncertain of the prototype. As time went on, she became more comfortable, but still had awkward gait due to the wrongly sized foot.*

Finally, facing all of the challenges attempting to manufacture prototypes in India kept me from rapidly continuing design cycles, but many new designs have been discussed with the doctors, technicians and patients that will be of great use continuing my work in developing world prosthetics. Seeing the need for research and development in the field, the directors of BMVSS are now being the fundraising for starting a FabLab for prosthetics and orthotics in Jaipur. This will be of great benefit to both BMVSS's technological development and my (and other engineers) ability to work with the many patients who come to Jaipur daily.

8. SUMMARY AND FUTURE GOALS FOR GREEN(ER) COMPOSITE MATERIALS

Personal and small-scale fabrication is the future for the post mass-market world, where one-size-fits-all is no longer the mantra of cheap consumption. While 3D printing techniques remain in their infancy, other techniques for rapidly manufacturing prototypes and final products for specialised use are improving. Digital fabrication of moulds and jigs for composite lay-up allow faster and cheaper manufacturing of parts that are simultaneously lightweight and strong. Green composites provide non-toxic and low-cost alternative materials for making large-scale structures. When prototyping or manufacturing personal or specialised items, I found green composites are a good choice of material.

This chapter will give a brief summary of the results from this thesis, including green composite materials that are available in small quantities to individual buyers, possibilities for recycling, reusing or disposing of composite parts, and a short review of the case studies included.

8.1. RAPID PROTOTYPING OF COMPOSITE TOOLING WITH DIGITAL FABRICATION

Moulds for making lightweight and strong materials are conventionally made by milling aluminium blanks, a slow and expensive process. For making small runs of specialised components, this is not cost-effective. Instead, I have been using snap-together structures made with 2D CNC processes. The moulds can be made of cheaper materials such as wood, cardboard and foil. Instead of only making specialised snap together moulds, primitive snap together kits can be used to make the mould for a part on the fly.

To replace the need for huge autoclaves for curing large-scale parts, I use a networked mesh of heater nodes and temperature sensors embedded into the composite tooling itself to monitor the heating and curing of a composite part. This reduces the amount of energy needed to heat the part, and allows better monitoring of the cure cycle which enables better time management for the manufacturing process.

8.2. GREEN COMPOSITES

Green fibres, such as kenaf, hemp, or sisal, are starting to replace their toxic and environmentally unfriendly counterparts in certain applications. Their low density, low cost and low wear-and-tear on manufacturing machines makes them particularly interesting as alternatives to glass- and carbon fibres. Cellulose provides most of their tensile strength, but also has drawbacks such as being very hydrophilic and decomposing at a relatively low temperature (140°C). As more natural fibres are used in composite materials, they will become more available with more predictable mechanical properties.

Weaning itself off of petroleum and fossil fuels, the plastics industry has been making progress into the biopolymer field, where plastics are sourced from renewable resources such as corn or soybean crops, and where the polymer products are biodegradable and environmentally sustainable. Because of the high cost of crude oil and the increasingly efficient biopolymer manufacturing plants, these biopolymers are even becoming cost effective. This improvement in biopolymers is also good news for the development of green composites because the biopolymers can be combined with natural fibres to create fully biodegradable composite materials.

Biodegradable thermoplastics such as polylactide and PHA are being successfully combined with kenaf and other natural fibres to create fully green composites. Thermoset resins made from soy protein isolate, cashew nut shell liquid and starches are also being employed alongside natural fibres for fully biodegradable composites in indoor building, automotive and other consumer applications.

For most of the small-scale applications tested in this thesis I used only semi-green composites, because of difficulties with the water resistance of the resins I was using. The resins I used had low-VOC emissions and were non-irritant to work with. However, I found that with the materials available to me, I could expect to start working with full green composites in the near future.

8.3. CRADLE TO CRADLE COMPOSITES

Recycling composite materials is a tricky problem, due to the material's inherent duality. Many methods and processes are especially developed and tested to improve the matrix-fibre adhesion, so separating them for recycling again at the end of the life of the part will be difficult by design.

Parts made from composites can be reused, recycled or disposed of. The reuse may be made easier by designing the parts with deconstruction and reconstruction in mind– for instance like snap-together parts which can become moulds, tables, chairs or even aeroplanes. The recycling process can be done by grinding the composite material down and reusing it in a different process such as injection moulding, or extracting fibres by means of pyrolysis. If the composite material is fully biodegradable, it can be composted at the end of its useful life. If not, disposal might still mean thousands of years in a landfill.

8.4. CASE STUDIES

I attempted to weave natural fibres into useful composite lay-up fabrics, to make biodegradable resins from tree sap, soy bean flour and potato starch, and to combine these materials into projects that would be useful in my surroundings. Not all of these case studies were as successful as others; some resulted in mouldy, sinking model boats, whereas others resulted in customisable paediatric prostheses.

In the MIT class *How to make (almost) anything* and the working weeks at Haystack Mountain School of Crafts, I was able to playfully engage with green composite materials and digital tools for making moulds. This resulted in a number of successful green composite products, including a comfortable hutch, a full-sized canoe and an uncomfortable sisal-rope swing.

At BMVSS in Jaipur, I did work on a adjustable leg that young patients can alter as they age and their bodies grow in size. Using green composites for all the aspects of the prosthesis was difficult, because many of the parts I needed required very high strength which I could not get from the materials and tools I had at hand. However, I was able to incorporate some green fibre reinforcements and improvements while still making a functional prototype that I was able to test on several paediatric patients.

8.5. FUTURE WORK

Of course, continuing research to make natural fibres with more predictable mechanical properties, natural resins with better material properties and better composite manufacturing techniques is key to improving the field of green composites. Especially lacking are good biodegradable resins for composite lay-up. At the moment, there are low-temperature thermoplastics, water-sensitive starches and proteins and irritant semi-green phenolics. This is not mechanically sound enough to begin replacing commonplace composite resin materials or plastics. Much still needs to be done to improve resins for more widespread application of green composites.

However, this thesis touches on more than material science. To improve the field of personal fabrication and rapid prototyping, the world must step away from its fast-track course in separating users and manufacturers. Rapid prototyping should not merely become a geeky pastime for the developed world which is otherwise removed from making the things they actually use in daily life. Nor should rapid prototyping become merely a testing method for mass-manufacturers to see objects designed with CAD in real life.

Digital fabrication has given us the tools to shape the world to come. By making rapid prototyping and digital fabrication accessible to anyone, we blur the distinctions between users, manufacturers and consumers. The passiveness of shopping for a best-fit solution can be replaced by enabling easy design and manufacturing for personal use. Any person is given agency to solve the problems they have with low cost and high speed.

With this thesis, I aimed to contribute some to empowering the world to design and make for themselves. Here I tackled a type of material and a process for making it into what you want. However, in the future, I hope this will be part of a vast library of methods and techniques for personal fabrication. Future work would be to make that happen.

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