Thesis for the Degree of Doctor of Philosophy

Material development of a textile bioreactor

All-polyamide composite for the construction of bioreactors

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Abstract

Bioreactors are manufactured from stainless/carbon steel, concrete, glass, etc., which are costly and time-consuming to install. Recently, several research studies have been initiated to find cost-efficient materials for constructing bioreactors, one of which is coated textiles. Polyvinyl chloride (PVC)-coated polyester textile (PVCT) has been used for this purpose to make bioreactors more cost-effective and easier to install. In this thesis, the thermal insulation property of PVCT was improved, that enhances the energy efficiency of the process carried out within the bioreactor. However, recycling PVCT is challenging, as it is a mixture of PVC, polyester fabric, a plasticizer for the PVC, chemical linkers, and other processing-aid additives.

A possible solution to address these issues is to use a coated textile composed of a single material. The polyester fabric can be replaced with a better performing fabric, such as polyamide, that generally has a longer lifetime as well as higher mechanical stability and is light-weight. A facile method was introduced to make a same-polymer coated textiles composite out of polyamide through the partial dissolution of the fabric’s surface followed by coagulation. The all-polyamide composite coated textiles (APCT) is mechanically stronger and more thermally stable than the PVCT as well as having less weight. Additionally, the APCT is fully recyclable as it contains only a single component. This property can be beneficial for the recyclability of the material. The APCT can be used in the construction of textile bioreactors as well as other applications that require gas-/water-tightness and flexibility at the same time. In addition, a new solvent for polyamide was proposed which can be used for the preparation of the APCT. A computer-assisted theoretical solvent selection method based on the Hansen solubility parameters was also introduced. The findings of this research can increase the economic efficiency of the biofuel production process by decreasing the initial investment. From a technical perspective, the methods introduced in this thesis can encourage researchers in related fields to produce same-polymer composites and find/replace solvent(s) in a more efficient way.

Keywords: textile bioreactor; biofuel, coated fabric; all-polyamide composite, polyvinyl chloride (PVC), solvent replacement, Hansen solubility parameters (HSPs)
Anyone who has never made a mistake has never tried anything new.

*Albert Einstein*

To my family, friends, and teachers,
for their constant support and unconditional love,
and,

*in loving memory of my mother*
List of publications

This thesis is based on the results presented in the following research articles:


Additional publications not included in this thesis:


Statement of contribution

My contributions to the above publications included:

I. Responsible for the concept, performing all of the experimental work, analyzing the data, and writing the manuscript.

II. Responsible for the concept, performing all of the experimental work, analyzing the data, and writing the manuscript.

III. Responsible for a portion of the concept, performing the experimental work (except the fermentation part), analyzing the data, and a major portion of the writing.

IV. Responsible for the concept, analyzing the data, and writing the manuscript.

V. Responsible for the concept, performing all of the theoretical work, writing the codes and developing the software, and writing the manuscript.

VI. Responsible for the concept, performing all of the theoretical work, and writing the manuscript.

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Although the results were favorable for the modification of the existing coated textiles used in making textile bioreactors, there were (and still there are) several challenges involving PVCT including the low mechanical properties, energy-consuming production process (due to the need for curing the coating), complex formulation (due to having various constituents), recycling issues (PVC and polyester), and last but not least, challenges associated with the adhesion between the coating material (PVC) and the textile (polyester).

While I was trying to figure out how to mitigate the aforementioned issues, I started with the question of ‘when will I have a better adhesion between the coating and the fabric?’ My answer to this question was inspired from the old-fashioned chemist’s *rule of thumb* for solubility: ‘like dissolves like’, meaning a solute will be dissolved in a solvent that shares enough similarity to establish a high interaction. I applied the idea in this way: if I choose a coating and a textile from the same kind of polymer, then either the effort to establish the interaction between them (i.e., adhesion) will be less, or in the best scenario, I will need to have only a simple process or use few chemicals. As I had to stick with the company’s material selection, I only had two choices for the textile: polyester and polyamide. The polyester textile did not work with the idea as it was not readily soluble, which is a key factor for making same-polymer composites using partial dissolution. Interestingly, polyamide 66 exhibited a good trade-off among the relative solubility easiness, strength, and durability.

The early tests showed promising results. Then, I decided to develop a new material that eventually led to a novel concept of preparing coated textiles from only a single component (Paper II). I called the new material APCT, which stands for all-polyamide composite coated textile. The simplest way was to make a film (as the coating) out of the polymer and place it onto the textile and press it. It turned out that using this method established somewhat weak interactions and led to a poor adhesion. Then, I decided to dissolve the polymer and then applying it onto the textile. The results were even better than expected. The details of the method will be discussed in the following chapters.

The APCT uses a ‘binder-free’ method to combine the coating and the fabric. Being binder-free makes the material more industrially viable, i.e., there is no need for extra chemicals for adhesion. As the process is carried out at room temperature, the production of this material does not need complex machinery for heating/curing or temperature control. Hence, the machinery can be simple compared to similar of its kinds among conventional counterparts.

I made two textile bioreactors out of PVC-coated textile and APCT as well as performing the biological process (fermentation) in them. Then, I analyzed the performance and characterized the different properties of the two textile bioreactors. The results showed that both textile bioreactors performed similarly in terms of fermentation performance; however, the material characteristics were different. The APCT showed superior properties over the PVC-coated textile in terms of mechanical stability, chemical resistance towards the actual biological media, etc. (paper III).

The progress did not stop there. I tried to make the process of producing the APCT more industrially-friendly. One of the challenges with the APCT was the solvent being used. Formic acid, the sole solvent for the APCT production, is a strong acid, which poses several challenges. It is odorous, corrosive, expensive, etc., which hinders the scale-up procedure for the mass production of the APCT. In the next step, I tried to decrease the usage of formic acid by replacing a significant portion of the solvent with some industrially friendly chemicals, including CaCl₂, urea, and water. Therefore, I introduced a new solvent for polyamides (paper IV). The efforts regarding the solvent search led to the introduction of a computer-aided theoretical solvent selection model based on the Hansen solubility parameters for finding a solvent replacement, which reduces the time and effort of the process significantly (paper V and VI).
Chapter 1

Introduction

1.1 The incentive to perform this research

The world population is increasing, and this explosion has led to a rapid consumption of various resources and a tremendous increase in the volume of wastes generated. Globally, approximately 17 billion tonnes of total solid wastes are generated per year [1], and the amount is estimated to reach 27 billion tonnes in 2050 [2]. Continuous emissions of CO₂, CH₄, and other greenhouse gases from these waste streams and the utilization of fossil fuels have led to a global environmental crisis. Furthermore, intensive agriculture practices for producing food also damages the environment through the use of chemical fertilizers.

Additionally, near 16% of the world population do not have access to electricity, and approximately 38% use solid waste (forest residue, animal manure, crop, and other wastes residues) for residential heating and cooking in poorly ventilated areas [3], which results in environmental and health hazards. Concerns over these environmental pressures and energy insecurity have increased the need for research about energy generation from renewable sources, for example, biofuels. It is worth to mention, fossil fuels are not green but remain inexpensive to replace.
The cost of alternative energy sources must be reduced to compete with fossil fuels. One way is to reduce the initial investment of biofuel production plants. The main cost of a biofuel production plant is the primary investment in the land and infrastructure, including utility, design, etc., among which the investment in the heart of the plant—the bioreactor—is a significant figure [3]. The primary goal of this thesis was to develop a new material of construction for producing a biofuel reactor, which can serve as an alternative to the current stainless-steel-/concrete-based bioreactors. One approach to reach this goal is the replacement of costly conventional bioreactors with cost-effective textile bioreactors, and this is the topic of the thesis.

1.2 Thesis development

1.2.1 The aim of this study

The primary goal of the current thesis was to prepare a textile-based flexible bioreactor. From a materials perspective, this thesis elaborates on the developments that have been made to the textile-based bioreactor for aerobic and anaerobic reactions, using fungi-based bioethanol fermentation within the textile bioreactor as a case study.

1.3 Novelties of this thesis

This thesis’s contribution is incorporating aerogel into an existing PVCT bioreactor to enhance the insulation properties, as well as introducing a method to prepare a single-polymer coated textiles composite through partially dissolving the fabric’s surface using the solvent employed for the polymer solution. Additionally, a new solvent for dissolving polyamide 66 and preparing the composite was reported in this thesis. Furthermore, a computer-aided theoretical solvent selection was also introduced.

1.4 Terminology

In our publications, we used ‘all polyamide-composite coated-fabric’ for the composite developed during my PhD studies. The term was used interchangeably with ‘same-polymer composite’ as well. In this thesis, I used APCT, abbreviated from ‘all-polyamide composite coated textile’.
Bioreactors: materials of construction and requirements

2.1 Bioreactors

A reactor, as a general term, is any container or vessel whereby one/multiple reactant(s) is converted into product(s) in a controlled way. A bioreactor, a type of reactor, is a vessel in which a chemical process is carried out that involves organisms or biochemically active substances derived from such organisms [3]. This process can be either aerobic (in the presence of air/oxygen) or anaerobic (in the absence of air/oxygen).

2.1.1 Types of bioreactors

Various types of bioreactors have been developed and are being utilized. The continuous stirred-tank bioreactor design was introduced to achieve good mass transfer and mixing, with the latter being carried out utilizing mechanical stirrers [3]. Airlift, bubble column and fixed bed bioreactors were introduced for fermentation applications with shear-sensitive microorganisms such as filamentous fungi [4]. For the bubble column bioreactor design, mixing is carried out solely by aeration occurring in one direction, while the airlift design uses aeration with mixing occurring in both the riser and down-comer sections of the bioreactor [3]. Wave or single-use bioreactors were introduced for batch-based fermentation applications, such as plant-based fermentation or shear-sensitive
mammalian cell fermentation, in which the growth rate or productivity is too low to be economic for continuous operation [5]. The wave design uses the rocking motion of the chamber to create a wavelike motion in the fermentation medium inside the bioreactor. Schematic representations of certain bioreactor designs are shown in Figure 2.1.

![Figure 2.1](image)

**Figure 2.1** Common types of bioreactors: a) continuous stirred-tank reactor, b) bubble column bioreactor, c) internal loop airlift bioreactor, e) external loop airlift bioreactor, (adapted from [6, 7]).

### 2.2 Requirements of bioreactors

#### 2.2.1 Chemically inertness

Although bioreactors are a specific type of chemical reactor, they have a key feature that distinguishes them from other chemical reactors; bioreactors work with living microorganisms, cells or enzymes [3]. A bioreactor should be inert to the underlying biological and chemical process conditions [8]. As the fermentation process is a series of chemical reactions, there are abundant chemicals involved in the process. According to Glittenberg [9], seven sets of chemicals are added to or produced during the fermentation process, including ethanol, amino acids, antibiotics, organic acids, polysaccharides, vitamins, and enzymes.

Moreover, microorganisms are added to the medium to achieve the actual fermentation. Some salts (e.g., nitrate salts as a nitrogen source) together with pH-adjusting chemicals (such as sodium hydroxide) are also added to the process [8]. As a result, the fermentation medium becomes a potentially harsh environment for the material of construction of the bioreactor. The bioreactor’s material of construction should not react with any of the constituents making up the cultivation media.

#### 2.2.2 Waterproofness and/or gas-tightness

The presence of oxygen could be lethal for strictly anaerobic microorganisms. Also, for an anaerobic process, possible bad odors leakage is an issue to consider [10]. Therefore, the bioreactor must be made out of gas-proof materials to make the chamber gas-tight so that the air/gas(s) cannot pass through. In some cases, including the production of biogas, the product(s) of the process is in gas form, and the gas-tightness of the bioreactor becomes even more important.
2.2.3 Temperature regulation and thermal stability

The bioreactor should provide adequate temperature control and be stable under sterilization conditions [11]. Comparatively speaking, a system having adequate insulation properties will decrease the heat loss and provide a more constant temperature for the process. Controlling the temperature in a bioreactor, based on its heat transfer requirement, can be achieved by using either an external heat exchange loop, an external heating jacket or an internal vessel surface in the bioreactor. However, the design of such a heat exchange element must be done in a way to avoid exposing the microorganisms to heat shock or oxygen deprivation (for aerobic bioreactors) [12]. On the small scale, such as with laboratory bioreactors, the challenge of sterilization is the limiting factor in the material selection of the bioreactor, as the sterilization occurs at high temperature and pressure. Other methods of bioreactor sterilization, including CIP (clean-in-place), WIP (wash-in-place), SIP (sterilization-in-place), and high-pressure sterilization, are used for large-scale bioreactors.

2.2.4 Heat and mass transfers

Heat transfer describes the flow of thermal energy due to temperature differences, from one entity to another. When bioreactors are in operation, the overall goal in terms of heat transfer is that the temperature should be maintained uniformly throughout the bioreactor within the range needed for growing the microorganisms.

Mass transfer is the movement of mass from one position to another, as evidenced by a concentration change. Good mass transfer in a bioreactor is important to ensure that the transformation of the substrate to the product in the bioreactor proceeds as planned [13]. The mass transfer can be enhanced by using mechanical stirrers, in the case where the microorganisms are not sensitive to shear stresses.

2.2.5 Resistance to external conditions

Bioreactors are usually placed outdoors and exposed to ultraviolet (UV) light from the sun. Furthermore, the wind has the potential to exert a force on the bioreactor, which eventually might rupture as a result. Temperature fluctuation between day and night as well as among different seasons is another risk that threatens the lifetime of the bioreactor. External microorganisms, as well as the roots of surrounding plants, are other sources capable of decreasing the bioreactor’s lifetime. For large-scale bioreactors made out of concrete, the risk of concrete corrosion is a key factor that must be taken into account. In short, a bioreactor has to tolerate external factors, such as sunlight, rain, physical damage, etc., up to a certain extent.

2.2.6 Materials for the construction of bioreactors

Bioreactors are usually constructed with materials such as stainless/carbon steel, carbon steel and borosilicate glass, which are generally suitable for the growth of fermenting microorganisms, inert and corrosion-proof. The materials used for constructing bioreactors must be able to withstand the physiochemical conditions encountered while running the bioreactor, as well as during clean-up and sterilization [14]. Table 2.1 lists some advantages and disadvantages of common materials used for the construction of bioreactors.
Table 2.1 Advantages and disadvantages of common materials of construction for bioreactors [14-17].

<table>
<thead>
<tr>
<th>Material</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel 304</td>
<td>Cheapest of all stainless steels.</td>
<td>Quite expensive.</td>
</tr>
<tr>
<td></td>
<td>Can withstand high temperatures</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and pressures.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Corrosion-resistant.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Long lifespan.</td>
<td></td>
</tr>
<tr>
<td>Carbon steel</td>
<td>Cheaper than 304 stainless steel.</td>
<td>Corrosion and contamination.</td>
</tr>
<tr>
<td></td>
<td>Time-consuming installation process.</td>
<td></td>
</tr>
<tr>
<td>Concrete bioreactors</td>
<td>More cost-efficient than steel-based bioreactors.</td>
<td>Time-consuming installation process.</td>
</tr>
<tr>
<td>Borosilicate glass</td>
<td>Transparent (perfect see-through property).</td>
<td>Fragile.</td>
</tr>
<tr>
<td></td>
<td>Extremely inert to chemicals.</td>
<td>Limited scale.</td>
</tr>
<tr>
<td>Plastic</td>
<td>Cheap.</td>
<td>Leaks and short lifespan</td>
</tr>
<tr>
<td></td>
<td>Light-weight.</td>
<td>Difficult transportation (as small/mid-scale bioreactor)</td>
</tr>
<tr>
<td></td>
<td>Wear-resistant.</td>
<td>Prone to thermal shock.</td>
</tr>
<tr>
<td></td>
<td>Better corrosion resistance.</td>
<td>More susceptible to physical damage (piercing cutting, etc.) compared to stainless steel.</td>
</tr>
<tr>
<td></td>
<td>Relatively low cost. Good sterility.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>More cost-effective than stainless steel.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Can be designed to have transparent regions, for easy process monitoring.</td>
<td></td>
</tr>
</tbody>
</table>

Concrete-based bioreactors (from concrete reinforced with steel rods) are common in most plants (Figure 2.2a). They are generally more cost-effective than steel-based bioreactors; however, the time-consuming installation process hinders concrete-based systems usage in some plants. Stainless-steel bioreactors are fast to install and available in many different sizes (Figure 2.2b). They mainly consist of carbon steel or stainless steel. However, steel-based bioreactors are costly, especially when the annual maintenance costs for material crack inspection are included. The high cost of conventional bioreactors increases the capital investment of fermentation-based facilities. For example, in ethanol production facilities, the bioreactor contributes 25–35% of the fermentation-based capital investment cost [18].

Borosilicate glass is the most common material of construction for glass-based bioreactors. The main perk of these bioreactors is their ‘see-through’ property (Figure 2.2c). Glass-based bioreactors are mostly used for low-/mid-scale fermentations, as the building and reinforcing of large-sized shaped borosilicate glass is challenging. Other materials that can be employed for making bioreactors include carbon steel, borosilicate glass, polytetrafluoroethylene (PTFE) plastic, and ceramics [14].
Chapter 3

Collapsible tanks and textile bioreactors

3.1 Collapsible tanks: portable/flexible containers

Bioreactors are basically tanks (or containers) with some additional features. Over time, the need for storage, transportation and containment have led to the use and development of tanks. Conventionally, tanks are rigid and possess a definite shape once installed. However, certain applications that require easy installation, portability, flexibility and short-term use have led to the introduction of collapsible tanks [19].

Collapsible tanks, also called pillow tanks, inflatable tanks, and bladder tanks, are vessels made with light, easily deformable and flexible materials, thus, giving them a naturally deformable shape defined by the nature of the material contained within them [20]. The benefits of collapsible tanks over rigid tanks include ease of transportation, ease of setup, portability, relatively low cost, ease of utilization, and multiplicity of application [3, 19]. In recent decades, collapsible tanks have always been available as an option for storing liquids. They are economically cheaper than conventional tanks [21]. Unlike rigid tanks, collapsible tanks can be transported while folded, which makes them a logical choice for applications in remote sites (e.g., mining exploration camps) and temporary installations (e.g., military operations).
Figure 3.1 Collapsible tanks containing different fluids: a) 100 m³ pillow-shaped filled with gas (FOV Biogas AB), b) pillow-shaped filled with liquid, c) round-shaped with a self-reinforcement at the top and d) rectangular-shaped with structural support.

3.1.1 Applications and design of collapsible tanks

Collapsible tanks are used for several purposes such as waste storage, fuel storage, water storage, chemical storage, and more recently, as bioreactors [8, 16, 22]. Additionally, an important distinguishing feature of collapsible tanks is that they can be designed for use in nonconventional or customized applications in unusual geometries. Once the collapsible tank is formed, its natural morphology when filled with a fluid becomes similar to that of a pillow. Sometimes, the fluid or material to be contained exerts a high tension on the joints of the collapsible tank [3]. To overcome this challenge, particularly for medium-scale tanks, the joints are usually framed, or extra self-support is added to the collapsible unit (Figure 3.1). Additionally, the natural pillow morphology can be changed by using different methods such as having metallic reinforcement at the joints of the construction material, putting the collapsible tank inside a rigid material to define the shape or using adhesives to join the material of construction to the desired shape.

Considering the properties of the collapsible tanks, they are potential candidates as the material of construction of bioreactors. However, their structure needs to be adjusted to conform to this application. Collapsible tanks comprise coated textiles which consist of a fabric coated with other polymer(s) to make it water-/gas-proof, chemical resistant, decorative, etc.

3.2 Coated textiles

Coated textiles are flexible composite materials comprising two main components: a textile and one or more polymer coatings on the textile, which makes the material impenetrable to liquids, gases, solvents, etc., that protect the textile as well. This configuration provides additional properties and functionalities to the system. The textile substrate contributes to the mechanical strength of the composite, whereas the polymer coating(s) helps to introduce penetration resistance and impermeability (to liquids, gases and dust particles), as well as improve the fabric abrasion strength.

A typical structure of coated textiles is shown in Figure 3.2. It usually consists of a base fabric as the backbone of the composite in the center (when the textile is coated on both sides) or in the bottom/top (when the textile is coated on one side) together with (an) adhesion layer(s) to increase the bonding between the fabric and the next layer. A topcoat with the intended color or special properties, for example, weathering-resistance, is usually included. Synthetic leather is an everyday-use example of a coated textiles. Coated textiles are popular mainly due to their affordable price, high strength, durability,
resistance to wear and tear, good toughness, various colors, and soft texture [23]. The types of fiber commonly used for this purpose are polyester, cotton, and rayon, depending on the end-use requirements [24]. For applications where high strength is required, polyamide and polyester are used, as they possess considerably high strength-to-weight ratios [25].

Figure 3.2 A schematic structure of coated textiles (adapted from mehltexnologies.com).

Coated woven fabrics are exploited in a wide range of structural applications to provide lightweight, architecturally striking solutions [26]. They are often used for wide-span surfaces, membrane-cable structures, hanging roofs (such as roofs of sports structures and stadiums) and pneumatic constructions [27]. Coated textiles are widely employed for permanent works in various applications, such as transportation and commercial constructions [28]. Polymer-coated textiles are extensively used in clothing, agriculture, construction, sports and leisure, inflatable structures, and medical applications. Some examples of these applications are illustrated in Figure 3.3.

Figure 3.3 Examples of different applications of coated textiles: a stadium hanging roof, a military (camping) tent, an airbag, ventilation vanes, and inflatable structures at an amusement center (Cape Cod Inflatable Park).

The combination possibilities between the textile and coating are almost infinite and are dependent upon the final use. The polymer coating can be on one (or both) side(s) of the substrate (with identical or different types of polymers on each side) [24], whereas the substrate can be a woven, knitted or even nonwoven textile material. For structural
applications where a substantial load is exerted onto the composite, a woven fabric is used, while for nonstructural applications, a knitted fabric can be utilized.

Polyvinyl chloride-coated textile (PVCT) is the material of construction for the existing textile bioreactor, produced by FOV Biogas AB, Borås, Sweden. The PVCT, comprising a PVC coating on polyester fabric, has been used and tested starting from the 1950s [29]. Polyester fabric is one of the most common fabrics employed in making coated textiles. A commercially available polyester fiber is polyethylene terephthalate (PET) [24].

3.2.1 Emerging alternatives: textile bioreactors

Because of the aforementioned reasons, alternatives to conventional bioreactors have emerged over time. To address some of these challenges, in recent decades, several biopharmaceutical and protein production facilities have started employing single-use or disposable bioreactors made from polymeric materials [30]. These bioreactors are entirely made of flexible materials, yielding a natural pillow shape when the reactors are filled with liquid [3] while they can also be kept inside rigid vessels to provide the desired geometry and support [31]. As a non-single-use flexible bioreactor, in 2013, a collapsible tank constructed with a textile as its backbone material of construction was introduced for biogas production [22]. Replacing the steel/concrete/glass with textiles imparts the bioreactor with a greater movability, cost-effectiveness and a fast installation. Figure 3.4 presents a picture of one of the textile-based bioreactor vessels. The product was manufactured by a local company, FOV Fabrics AB, Borås, Sweden.

Figure 3.4 Actual and schematic picture of a dome-shaped textile bioreactor (top) [22], and a laboratory-scale prototype of a pillow-shaped textile-based bioreactor (bottom) equipped with a heat exchanger underneath. Both are made of a PVC-coated polyester fabric produced by FOV Biogas AB, Sweden.
Textile bioreactors are foldable (Figure 3.5); hence, they possess a high portability prior to installation at the biofuel production plant.

Figure 3.5 A 100 m³ pillow-shaped textile bioreactor prior to installation (FOV Biogas AB).

Although single-use and textile bioreactors are both made from polymeric materials, textile bioreactors must not be regarded as similar to single-use bioreactors. The single-use bioreactor presents limited applications for several reasons such as the limited scale of its application (below 2 m³ on its own), unsuitability for continuous production and the high potential for incurring damage [30]. In single-use bioreactors, there is no structural reinforcement, while in textile bioreactors the material of construction is reinforced with textiles. As their name implies, such bioreactors are used only once and then discarded, and this restriction makes them unsuitable for facilities with high production rates or for long-term continuous production applications [3]. Due to their structure, single-use reactors have limited scalability [32].

Chapter 4

Improvement in the thermal insulation of textile bioreactors

4.1 Challenges associated with conventional bioreactors

Similar to any other chemical process, the fermentation process within a bioreactor also has an optimum temperature.

4.2 Temperature fluctuations

Microorganisms require an optimum temperature for growth, and their active performance during the biogas process can be divided into psychrophilic (optimum temperature approximately 10 °C), mesophilic (optimum temperature ca. 30–40 °C), thermophilic (optimum temperature approximately 55 °C) and hyperthermophilic (optimum temperature approximately 85 °C).

Temperature fluctuations adversely affect the performance of, for instance, a biogas process. A decrease in temperature may result in the reduced volatile fatty acid production rate, substrate decomposition rate, and metabolic rate of the microorganism [33]. For a given operational temperature type, the fluctuation of a few degrees of temperature can have a severe impact on methane yield, as microorganisms adjust to one
certain temperature and re-adaptation corresponding to a different temperature requires an alternated microbial structure [34]. Noticeably, a variation in mesophilic temperature of ±4 °C and thermophilic temperature of ±1 °C was found to result in a sharp decrease in biogas yield [35, 36]. Therefore, it is necessary to keep the temperature fluctuations within the bioreactor to a minimum for a stable and consistent process. In conventional bioreactors (e.g., stainless-steel bioreactors) this is achieved using external insulation materials (Figure 4.1). In the case of flexible materials (collapsible tanks) using external insulation materials is very difficult, if not undoable. However, this goal can be achieved through an improvement in the insulation properties of the material of construction of the textile bioreactor (coated textile) to decrease the thermal conductivity of the material.

![Figure 4.1](image)

Figure 4.1 A 304 Stainless-steel bioreactor enclosed in an insulation jacket to avoid/decrease temperature fluctuations (adapted from www.pitt.edu).

### 4.3 Insulation and thermal conductivity

The passage of thermal energy through an insulating material occurs through three mechanisms: solid conductivity (conduction), fluid conductivity (convection), and radiative transmission (also known as radiation). The sum of these three components gives the total thermal conductivity of the material [37] (measured in W/m.K, Watt per meter per Kelvin). The less thermal conductivity a material has, the lower its value in W/m.K will be. Table 4.1 summarizes the thermal conductivity values of some common porous insulation materials. To increase the thermal insulative property of the PVCT, aerogel, the most insulative material known, could be incorporated into the material (Paper I).

<table>
<thead>
<tr>
<th>Insulation material</th>
<th>Thermal conductivity (W/m.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral wool</td>
<td>33–40</td>
</tr>
<tr>
<td>Expanded/extruded</td>
<td></td>
</tr>
<tr>
<td>polystyrene</td>
<td>30–40</td>
</tr>
<tr>
<td>Loose-fill cellulose fiber</td>
<td>39–42</td>
</tr>
<tr>
<td>Foam glass</td>
<td>39–45</td>
</tr>
<tr>
<td>Foam glass</td>
<td>5–100</td>
</tr>
<tr>
<td>Aerogel</td>
<td>12</td>
</tr>
<tr>
<td>Enova aerogel IC3120</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 4.1 Thermal conductivity values of some commonly used insulation materials (Paper I)
4.3.1 Aerogel

Aerogel is a synthetic ultralightweight material that has an excellent insulation performance because of its nanoporous structure (several to tens of nanometer) [38-40]. Silica aerogels are a three-dimensional network of silica particles, which are obtained by extracting the liquid phase of silica gels [41] and replacing it with a gas; therefore, they are highly porous solids that hold gas (usually air) within pores or network of solid substances [42]. Silica-based aerogel is an ideal thermal insulator with a composition of up to 99% associated air [43]. It exhibits many intriguing and unique properties, which include an extremely low thermal conductivity (5–100 mW/m-K), very low density (0.003–0.5 g/cm³), high porosity (80–99.8%), high inner surface area (500–1200 m²/g), ultralow dielectric constant (k = 1.0–2.0) and low index of refraction (~ 1.05) [41, 44-48].

Figure 4.2 Demonstration of the superinsulation property and lightness of silica aerogel.

Aerogels have been used in applications, such as windows and glasses, to save energy [49]. Because of the aforementioned fascinating and extraordinary properties, silica aerogels have found an excellent potential for applications in many fields such as adsorption, window insulating systems, drug delivery systems [50-54], and thermal superinsulators [55, 56]. They also are employed in thermal insulation systems for aerospace, systems for environmental cleanup and protection, heat storage devices, transparent insulative windows systems, thickening agents in paints, etc. [41]. Silica aerogel also has many commercial applications, such as acoustic barriers and supercapacitors [57]. As a result of their lightness, low heat conductivity, and large inner surface area, aerogels are useful in many ways such as particle filters, particle trappers, and catalyst supports [42, 58].

4.4 Improving the existing textile bioreactor

To improve the insulation property of the PVC-coated textile and to decrease the weight of the composite, an aerogel was incorporated into the PVC plastisol before the coating process (Paper I). The aerogel was selected as an insulating constituent in the coated textile due to its particular characteristics. This additive had not been incorporated in coated textiles before our experimental work. According to the results of the density measurement and the transient plane source method of thermal conductivity measurement (Figure 4.3), significant improvements in both reducing the thermal conductivity and decreasing the density by 26% (from 205 to 152 mW/m-K) and 17% (from 1.132 to 0.941 g/cm³), respectively, were achieved. As mentioned earlier, improving these properties can enhance the features of the textile reactor made out of PVCT.
Figure 4.3 (a) Density values for 0–4% aerogel-containing PVC-coated textile composites; (b) thermal conductivity values for PVC/aerogel composite-coated textiles (adapted from Paper I).

In composite preparations, a good dispersion of the particles is crucial to maintaining the uniformity of the properties. Scanning electron microscopy (SEM) did not show any agglomeration of the silica aerogel particles on the surface of the PVCT composite (Figure 4.4).

Figure 4.4 Scanning electron microscopy (SEM) micrograph of the aerogel-doped PVC-coated textile composites with different aerogel percentages: (a) 0% (neat composite); (b) 2%, no agglomeration; (c) and (d) 3%, very slight agglomeration; and (e) and (f) 4%, more agglomeration (adapted from Paper I).
Introducing silica aerogel, which is extremely hydrophobic, into the PVC-coated textile, makes the ultimate composite more hydrophobic. The untreated PVC-coated textile exhibits a water contact angle of 76.02°, while with the addition of 3% silica aerogel, the value increases by approximately 17% to 88.67° (Figure 4.5).

Therefore, silica aerogel causes the composite to become more hydrophobic and hence less prone to environmental failure due to humidity (Paper I), which is in addition to the improvement in thermal insulation property and weight decrease. The existing textile bioreactor made out of PVC-coated textile was improved in terms of thermal insulation, weight and surface properties. However, this material continued to present certain challenges that will be addressed as follows.

Figure 4.5 Water contact angle values (above) and pictures of the 0–4% aerogel-containing PVC-coated textile composites (below) (adapted from Paper I).
Chapter 5

All-polyamide composite coated textile bioreactors

5.1 Challenges associated with existing textile bioreactors

The non-single-use flexible bioreactor uses PVC-coated textile as the material of construction; hence, it is mechanically strong and has a good scalability [16, 22]. PVC is dimensionally stable, largely non-flammable, and resistant to weathering, but it possesses a limited thermal stability and it is prone to be attacked by many solvents [59]. The coating (PVC) and the textile (polyester) exhibit a high density (compared to that with other common polymers). The low thermal stability of PVCT makes the thermal sterilization of the bioreactor difficult. The fermentation medium contains various solvents and chemicals that can chemically attack the PVC in the long term. Furthermore, the thermal insulation of the composite can also be improved. The first part of our experimental work involved improvements in the thermal insulation, density, thermal stability, and to some extent, surface hydrophobicity by the incorporation of a highly porous material into the plastisol formulation (paper I).
### 5.2 Other challenges of the existing coated textiles

This section elaborates the challenges of the existing coated textiles, mostly the difficulties associated with adhesion, weight and strength, and recyclability after the lifetime of the material is reached. In the following sections, a solution to address these issues is proposed. One drawback of the materials of construction of collapsible tanks, in comparison with those of rigid tanks, is that they are prone to failure due to the low material strength of the employed polymers (compared to, e.g., stainless steel) or to the separation of the materials of construction where they are welded or joined together. This failure might affect the sealing properties of the joints.

#### 5.2.1 Adhesion

Adhesion is the state in which two surfaces are held together at an interface by forces, an interlocking action or both [60]. Adhesion between different components in a composite is an important parameter to achieve good composite properties. Furthermore, although the components usually have good adhesion between them, they sometimes exhibit a poor matrix–fiber adhesion due to the chemical incompatibility of the components [61, 62]. Poor adhesion results in failure caused by the insufficient stress transfer between the binder and the reinforcing fabric. This is also the case when producing coated textiles. To obtain good adhesion between a coating and fabric, it is also necessary to select the right coating binder that can adhere the coating to the fabric. There are several ways to increase the adhesion (e.g., using linker chemicals, surface treatments, etc.), but they are often associated with drawbacks, including high cost, complicating the formulation, degrading the fabric (to be bonded to the binder), etc [24].

#### 5.2.2 Recyclability and lifetime

Heterogeneous composites pose a recycling challenge [61] as they consist of at least two different components. The growing interest in the recycling of materials is brought about by the desire to preserve the environment, as there is limited landfill space due to the abundance of waste that is being dumped [25]. Global warming is also of concern due to incinerator emissions [63]. These negative impacts can be reduced by recycling the products that would otherwise go into landfills [64, 65]. In addition, a strong need to reduce the energy requirements of the recycling process also exists [61]. This impetus has stimulated interest in the development of environmentally friendly materials [66, 67].

A textile bioreactor has a lifetime that depends on the materials used to produce it. From the resource recovery point of view, when the lifetime is over, the textile bioreactor needs to go through a recycling process. If the textile bioreactor is made of only one component, there is no need for the separation of components (when possible), and it can be used again as a single-component material.

#### 5.2.3 Strength and weight

The weight of the final composite is also another challenge. PVC has a density of approximately 1.4 g/cm³, almost the same as that of the polyester fabric (the other constituent in the PVC-coated textile). A number of polymer candidates for the replacement of PVC and polyester exist. However, I decided to use polyamide 66, as it has a low density (1.14 g/ cm³) and strong mechanical properties (Paper II).

#### 5.2.4 An alternative polymer: why polyamide?

Polyamide is a well-known high-performance engineering plastic with a high strength and good fatigue resistance [68], as well as excellent mechanical and physical properties [69]. Generally, polyamides have a high thermal stability and excellent properties such as a high impact strength, tear resistance, low coefficient of friction and...
excellent tensile strength [70]. Such good properties are due to strong intermolecular hydrogen-bond interactions [70]. Infrared spectroscopy has shown that almost all of the amide groups in polyamide 66 are linked together via H-bonding at room temperature [71]. The high strength, elasticity, and abrasion resistance enable polyamide to be used for a variety of industrial end uses, including filter fabrics, nets, webbings, cordages, parachutes, ropes, and ballistic fabrics [24]. Polyamides have a wide range of applications, from an aroma-proof, transparent packaging film to hydraulic lines, metal coatings, and onto cable pulleys, bearing boxes and fuel oil storage tanks [72]. Due to their mechanical properties and their barrier behavior against gases and aromatics, they are widely used in films for flexible food packaging [73]. In the family of polyamide fibers, polyamide 66 fiber possesses relatively better mechanical properties, and the polymer is applied in the production of tires, airbags, bullet-proof vests [74], and more [68]. Polyamides' properties, more importantly, their tensile and impact strength, relatively low density, good fatigue resistance, and gas barrier characteristics, make the polymer a good candidate to coat textiles for use in bioreactors.

5.3 A solution to the challenges of existing coated textiles

To address some of the challenges of the existing coated textiles, I decided to use polyamides to make a coated textile as the material of construction for the bioreactor. Polyamides possess better mechanical properties and lower densities than do polyester and PVC.

One promising approach to enhance composite recyclability is choosing the composite components out of one sort of polymer, aka single-polymer composite (SPC) [63], which identifies an emerging class of materials that has specific economic and ecological advantages [61]. These materials are often described as one-polymer composites, homocomposites, all-(the same-)polymer composites, self-reinforced, or homogeneous composites [61, 63]. Such composites represent the correct alternative to traditional composites because both the reinforcement and matrix are from the same polymer; therefore, recyclability is enhanced [75]. Apart from recyclability, the interest in the concept of SPCs is based upon the premise that interfacial bonding should improve when matrix and reinforcement are made from the same polymer [67, 76, 77]. The employed method used the noticeable difference in melting temperatures between the high-density polyethylene (HDPE) matrix and the HDPE reinforcement to fabricate an HDPE homocomposite. SPCs were first introduced by Capiati and Porter [78] approximately four decades ago. Among these composites, all-cellulose and all-polypropylene composites are probably the most well-known ones. All-polypropylene composites have a broad processing window, and their exceptionally high fiber volume fraction of approximately 90% makes them extremely competitive with conventional glass-fiber-reinforced composites of substantially lower fiber loadings [79].

One possible method to increase the adhesion (i.e., the holding forces, interlocking action or both between two surfaces together at the interface) involves using the same material in the coating of the polyamide fabric and preparing an SPC-coated textile. By using this method, the surface of the fabric is partially dissolved by the solvent from the coating solution to entangle the polymer chains of the coating with the dissolved polymer chains of the fabric’ surface. As the two components (fabric fibers and the coating) have the same nature and as there is the same solvent between them, the adhesion (which in this case is a nonreactive adhesion) could be strong. In addition, there is no need to use a linker material between the coating and the solvent. By this method, a novel all-polyamide composite coated textiles (APCT) can be obtained.
5.4 Strong adhesion: a possible theory

The theory/mechanism behind the excellent adhesion (Paper II) is proposed in this way: the solvent in the solution penetrates the fabric and swells to the surface of the fabric because it is capable of dissolving the fabric as well (Figure 5.1, b). Once the chains at the surface of the fabric are solvated, the chains in the solution interpenetrate the chains of the solvated surface of the fabric, becoming entangled (Figure 5.1, c). After a certain time (ca. 30 s), the sample is immersed in water (or any other nonsolvent) which extracts the solvent from the solvated polymers, fixing the chains in position. As a result, the coating and the fabric are fused together without using any chemicals or bonding agent.

Figure 5.1 Mechanism proposed in this thesis for adhering the coating to the textile in an all-polyamide composite coated textiles.

Figure 5.2 shows the adhesion between the coating (the non-filamentous part) and the fabric (the yarns). It is clear that the adhesion in APCT (b, c, and d) is stronger the adhesion in the PVC-coated textile (a). In the case of APCT, the adhesion is not only between the fabric and the coating, as some of the yarns closer to the surface appear fused together as well (“merged filaments” in Figure 5.2). This feature can enhance the coating properties, meaning that a less thick coating would be needed to make the composite gas-proof.
Figure 5.2 Cross-sectional SEM pictures of PVCT (a) and APCT (b, c). The fused parts are shown with the ovals (d). In APCT, the first row of the fiber-filaments of the polyamide fabric is merged and adhered to the coating. This arrangement will decrease the chance of delamination over a long span of time (adapted from Paper IV).

All-polyamide composite is a composite in which both the reinforcement and the matrix are made from one kind of polymer. The reports regarding all-polyamide composites in the literature describe the use of two different polyamide grades with different melting points, which have been used to produce laminates [68, 80, 81]. All-polymer composites, with both constituents made from the same polymer, are easily recycled by mechanical methods, as they are composed of the same polymer.

The all-polyamide composite coated textile (APCT) that I have introduced during my PhD is a specific form of single polymer composite intended to replace traditional coated textiles with a good interfacial adhesion and enhanced recyclability. The composite is fully recyclable since it contains no other materials except polyamide 66. The assembly has a wide range of semi-structural applications to provide lightweight, architecturally striking solutions as well as wide-span surfaces, membrane-cable structures, hanging roofs, pneumatic constructions, water-/gas-proof textile reactors, temporary houses and tents, facade coverings, container linings, and tarpaulins.
Figure 5.3 Cross-sectional scanning electron microscopy images of all-polyamide composite coated textile samples. From top to bottom, 17%, 23%, 29%, 35%, 41%, 47%, and 53% polyamide dope concentrations, and from left to right, 15 s, 30 s, and 45 s gelling times.

The micrographs of the specimens were taken after quenching them in liquid nitrogen and breaking by hand. The magnification is 500X for all of the micrographs (adapted from Paper II).

Full recyclability and low recycling cost are additional advantages of the all-polyamide composite coated textiles. Possibility of using waste polyamides to make the coating solution and prepare the APCT is also beneficial (finding an application for a waste: fabric waste). As the entire composite is made of a single polymer, separation is not required for recycling the material, after its life span is met.

5.5 Mechanical properties

Partial surface dissolution of the fabric in the composite might decrease the overall strength of the composite. However, the results (Figure 5.4) show that the decrease in mechanical properties is negligible for the optimum solution concentration and waiting time (Paper II).
Figure 5.4 Max force, elongation at max load and thickness from the tensile test of the APCTs, as well as the fabric, for different solution concentrations at 15 s, 30 s, and 45 s gelling times. The variations can be attributed to several factors, yet mainly involve the dissolution power of the dopes. “Fab” stands for fabric, and it has been added to the graph for comparison purposes (adapted from Paper II).

The thickness of the composite is related to the amount of added coating (the polymer solution), the waiting time before the phase change (immersion in water) and the concentration of the polymer solution. The final thickness varies from approximately 1.2 times to twice the initial thickness of the fabric (Figure 5.4).

5.6 The fermentation process in textile bioreactors

Ultimately, the coated textiles discussed in this thesis were used as the material of construction for textile bioreactors to run a fermentation process (Paper IV). The two textile bioreactors applied showed equally the same performance in the process (Figure 5.5). Therefore, we can conclude that APCT is inert towards the microorganisms in the fermentation process and is capable of maintaining the process.

Figure 5.5 Fermentation performed in the lab-scale prototype of a textile bioreactor at 30 °C showing sucrose (circle) and ethanol (square) as the primary axis and glycerol (triangle) as the secondary axis (adapted from Paper III).

Having the same performance in the fermentation process for both bioreactors might seem to suggest there is no considerable influence of the material type (APCT or
PVCT) as the material of construction for bioreactors. However, apart from the aforementioned prominence of APCT in terms of environmental effects, material-wise, the lifetimes of the two reactors differ significantly. According to Table 5.1 (Paper IV), compared with the PVC-coated textile, the APCT performed better in the presence of chemicals common to the fermentation process during the ageing test.

Table 5.1 Tensile strength comparison of PVC-coated polyester fabric and all-polyamide composite coated textiles (APCT). Un-aged samples represent the material before ageing (adapted from Paper III).

<table>
<thead>
<tr>
<th>Medium</th>
<th>PVCCF</th>
<th>Δ (%)</th>
<th>APCCF</th>
<th>Δ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>un-aged</td>
<td>57.2 ± 2.19</td>
<td>n.d.</td>
<td>68.6 ± 1.77 *</td>
<td>n.d.</td>
</tr>
<tr>
<td>acetone</td>
<td>52.5 ± 2.3</td>
<td>8.2</td>
<td>67.4 ± 1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>acetic acid</td>
<td>49.8 ± 1.71</td>
<td>12.9</td>
<td>63.2 ± 1.21</td>
<td>7.9</td>
</tr>
<tr>
<td>butyric acid</td>
<td>53.1 ± 1.8</td>
<td>7.2</td>
<td>65.7 ± 1.61</td>
<td>4.2</td>
</tr>
<tr>
<td>ethanol</td>
<td>55.3 ± 1.6</td>
<td>3.3</td>
<td>67.4 ± 1.2</td>
<td>1.7</td>
</tr>
<tr>
<td>lactic acid</td>
<td>51.2 ± 1.4</td>
<td>10.5</td>
<td>63.1 ± 2.1</td>
<td>8.0</td>
</tr>
<tr>
<td>glycerol</td>
<td>55.1 ± 1.7</td>
<td>3.7</td>
<td>68.1 ± 1.4</td>
<td>0.7</td>
</tr>
</tbody>
</table>

* The numbers after ‘±’ represent the standard deviations.

This characteristic can be beneficial in terms of a lifetime extension for the textile bioreactor made by using APCT.

Figure 5.6 The comparative density values of PVCT and APCT. PVCT is composed of two main constituents: PVC and polyester. These polymers are both heavier (in mass/volume unit) than polyamide, the sole component of APCT, resulting in a lighter final material when composed of the latter (adapted from Paper III).

Additionally, APCT is approximately 16% lighter than the PVC-coated textile, which is logistically preferable as the material of construction of textile bioreactors (Figure 5.6). Furthermore, less material per cubic meter of the textile bioreactor is required to build, making it more cost-efficient.
Although all-polyamide composite coated textile (APCT) is environmentally friendly in terms of recyclability, it uses formic acid (methanoic acid) in its preparation. I tried to replace this solvent with some less-harsh solvents. For this purpose, one experimental and one theoretical study were carried out.

6.1 Experimental

Solvent selection is a crucial step in all solvent-involved processes. The solution processing of aliphatic polyamides is quite challenging because only a few solvents, such as formic acid and cresol [82] or fluoric solvents [83], can dissolve them, all of which have environmental challenges. A few attempts have been made to replace the existing solvents or to propose new solvents for aliphatic polyamides. Papadopoulou et al. [82] mixed formic acid with trifluoroacetic acid and acetone. Charlet et al., [84], studied the dissolution behavior of polyamide 6-water systems under pressure. Nirmala et al., [85], used formic acid (85 wt%), acetic acid, dichloromethane, 1,1,3,3,3-hexafluoro-2-propanol, trifluoroacetic acid, and chlorophenol in their study.
Basically, dissolving polyamides is difficult due to two reasons: (a) polyamides are highly crystalline, and (b) solvents for polyamides are believed to act by virtue of strong, highly specific polar forces, especially hydrogen bonds [86]. Aside from these limitations, a fast dissolution in the production process of APCT is required, and the only solvent that can provide favorable results is FA. Hence, I tried to replace a substantial portion of formic acid in the ‘solvent’ mixture. Finally, a mixture of FA/CaCl₂/urea (FAUCa) was made to dissolve the polyamide 66. Urea imparts the hydrogen bonding, and calcium ions from the calcium chloride, a Lewis acid, was added to the system to compensate for the pH decrease due to the presence of urea. The results show that the proposed solvent, FAUCa, can readily dissolve polyamides, resulting in a negligible decrease in the mechanical properties during the dissolution (Paper IV). The adhesion between the fabric and the coating is also good (Figure 6.1), as the new solvent is sufficient at dissolving the fabric and penetrating into it.

![SEM micrographs of APCT composite prepared using FAUCa](image)

**Figure 6.1** Selected cross-sectional SEM micrographs of the APCT composite prepared using FAUCa. Strong adhesion is seen between the coating (the top film) and the fibers from the fabric. The fibrils of the fibers closer to the coating are fused to each other (adapted from Paper IV).

The composite prepared using the FAUCa exhibits almost the same properties as the one prepared using the formic acid solution. The solution was applied to a polyamide 66 fabric to make an all-polyamide composite coated textiles, which was then characterized. The FAUCa solution has a higher viscosity than that of the one prepared using the neat formic acid solvent; this property can be an advantage in applications that need a high viscosity. A more viscous solution produces a denser coating, which will increase the water/gas impermeability. In conclusion, experimentally, a mixture of calcium chloride, formic acid, urea and water, which can dissolve polyamide with ease and has the potential to be used in mass production of APCT, was proposed in this thesis.
(Paper IV). Using the FAUCa solvent presents a significant merit: the replacement of 40% formic acid with less harmful and environmentally friendly chemicals.

6.2 Theoretical: Hansen solubility parameters

Solvents, defined as substances able to dissolve or solvate a separate species, are commonly used in many industries and applications [87]. For any solvent-based process, the best-suited solvent or solvent-mixture must be selected [88]. On the other hand, solvent selection and design is a complex process, which requires decision making on several levels to identify the best candidates, and is dependent on different multiobjective criteria, namely, environment, health, safety, process feasibility and economics [89]. Currently, solvent selection relies significantly on previous experience, i.e., trial and error with different solvent candidates. The use of experimental thermophysical properties stored in a reference database for the selection has an advantage in that the results are very reliable; however, the solvent selection is limited to the experimental data pool [88]. Such a heuristic approach, while valuable on its own, is arguably not fit to deal with a complex multicriteria optimization and search problem, which is the case for solvent selection [89].

On the other hand, actual (physical) trials of mixing different solvents and checking the solvation in the laboratory, is a tough and time-consuming job. A number of modern tools are increasingly becoming available to reduce the efforts needed to select the right solvent [90]. The use of prediction models has the advantage that for the selection procedure, any solvent can be considered for which the required group interaction parameters are available, and by using predictive methods, an extended variety of solvents can be taken into account for selection [88].

Several graphing and modelling techniques have been developed to aid in the prediction of polymer solubility [91]. The basic principle has been “like dissolves like”, meaning that polymers will dissolve in solvents whose solubility parameters are not too different from their own [92]. Solubility parameters help attach quantitative values to qualitative textual data [93]. By 1950, Hildebrand had defined the solubility parameter as the sum of all the attractive intermolecular forces, which he found to be empirically related to the extent of the mutual solubility of many chemical species [94]. However, solubility behavior cannot be accurately predicted by only the Hildebrand solubility parameter [91].

In 1967, Charles Hansen improved the concept and introduced his three-dimensional solubility parameters [95]. The Hansen approach provides an empirical yet effective [96] method for determining the dissolution possibility of a solute. The Hansen solubility parameters (HSPs) have been used for many years to select solvents for coating materials [92].

Some authors have proposed methods to find a proper solvent mixture for very specific applications such as electrospinning [97]; however, a more general method that is applicable to a broader range of processes appears necessary to propose. Certain publications used HSPs to predict solvent systems that are likely to dissolve, e.g., Aghanouri et al. [98], but these approaches are empirically based and not computer-aided, meaning they cannot consider a broad range of solvents. Nelson et al. [99] developed a computer-based formulating technique that allows for the selection of minimum-cost solvent blends, but the approach is not capable of suggesting a solvent substitution or solvent mixture for a solute with known HSPs. Moreover, the authors used the Hildebrand solubility parameters, which have been updated and replaced by the more reliable and more accurate values of HSPs. As there has been no report regarding a general computer-aided method of finding a solvent-mixture for a solute with known HSPs, I proposed a computer-aided selection of solvents out of a vast number of solvents’ HSPs values stored in a database (Paper V).
The Hansen model is usually considered as a sphere. The center of the sphere consists of the $\delta d$, $\delta p$, and $\delta h$ values of the polymer (solute) [91]. $\delta$ is square root of the cohesion energy density; $\delta d$, $\delta p$, and $\delta h$ represent the dispersive forces, polar interactions, and hydrogen bonding, respectively. The radius of the sphere, $R_o$, is termed the interaction radius [91]. The values of $R_o$ have been reported for some polymers in the literature. $R_A$ is the distance in HSP space between the solute/polymer and the solvent [95]. The boundary of the spherical characterization is based on the requirement that ‘good’ solvents have a distance from the center of the sphere, $R_A$ (also termed the solubility parameter distance), that is less than $R_o$ [91], where $\delta d_f$, $\delta p_f$, and $\delta h_f$ are the Hansen solubility components for the polymer/solute (our favorite values) and $\delta d_s$, $\delta p_s$, and $\delta h_s$ are the Hansen solubility components for the solvent [91]. Equation 1 was developed from plots of experimental data, where the constant ‘4’ was found convenient and correctly represented the solubility data as a sphere encompassing the good solvent [91].

$$R_A = \sqrt{4 \times (\delta d_s - \delta d_f)^2 + (\delta p_s - \delta p_f)^2 + (\delta h_s - \delta h_f)^2} \quad (1)$$

Although it is possible to find a solvent mixture based on HSPs, the question becomes: how can one screen the vast number of solvents’ combinations to find the correct solvent mixture? Moreover, what is the amount of each solvent (volume fraction) in the mixture?

To address the above questions, a computer-aided method was proposed (Paper V) for selecting solvents and finding the adequate amount of each solvent to form a mixture of solvents to dissolve a solute with known HSPs or to replace a solvent. To achieve this, a sophisticated computer software package was developed to find the optimized mixture using the mathematical Simplex algorithm based on HSPs values from a database of 234 solvents.

Polyamide 11 (or Nylon 11) is a biobased aliphatic polyamide produced by the polymerization of 11-aminoundecanoic acid. It is also produced from castor beans by Arkema under the trade name Rilsan [100]. Polyamide 11 is applied in the fields of oil and gas, aerospace, automotive, textiles, electronics, and sports equipment, frequently in the tubing, wire sheathing, and metal coatings. Bio-based polyamides, like polyamide 11, generally have lower melting temperatures than conventional polyamide 6 and 66 [101]. Polyamide 11 is also more hydrophobic than polyamide 66, which makes it more resistance towards humid conditions. This property makes polyamide 11 a possible candidate to make an all-polyamide composite coated textile in order to be used as the material of construction of textile bioreactors. There has been a number of research articles in the literature related to Polyamide 11 solvents [102-106].

To obtain a list of solvent-mixtures, polyamide 66 (Paper V) and polyamide 11 (Paper VI) were tested using their HSPs as case studies. This technique reduces the laboratory effort required in selecting and screening solvent blends while allowing a multitude of candidate solvents to be considered for inclusion in a blend. The outcome of this model significantly diminishes the time required for solvent development by experimentation via decreasing the possible/necessary trials. Thus, the most suitable solvent/solvent-substitution can be found by the least possible effort; hence, this approach will save time and reduce the cost of all solvent-involved processes in the fields of chemistry, industrial polymers and coatings, chemical engineering, etc.
Chapter 7

Summary of the key findings and future directions

This thesis proposes a new method of making coated textiles intended for the construction of textile bioreactors. In this method, a film-forming solution of polyamide 66 is smeared over the polyamide 66 fabric and then immersed in water to initiate the phase inversion (from solution state to solid-state) process.

In the course of the experiments, firstly, the conventional textile bioreactor material (out of PVC and polyester) was improved by increasing the thermal insulation properties. Then, a novel method of making a same-polymer composite coated textile was developed and introduced to address adhesion and recyclability challenges, as well as enhancing other properties. Furthermore, the new material production method was improved through solvent replacement. Finally, two textile bioreactors, one constructed from the new material and the other from the existing material, were utilized to run a fermentation process, and their performances were evaluated.

Using the textile-based bioreactor is a cost-effective technology that is simple to operate. This environmental and energy solution can be easily accessed by developing countries, where the required expertise may not be available, or in remote villages, where local ‘small-scale’ biofuel production units are going to be installed.
By insulating the existing coated textiles, the thermal conductivity of the whole composite decreases, which eventually reduces temperature fluctuations (favorable for the microorganisms inside the bioreactor). In this thesis, a method to increase the insulation properties of the PVC-coated textile was described. This enhancement was achieved by incorporating silica aerogel into the PVC plastisol. The incorporation of aerogel into the PVC plastisol yielded a final composite that is approximately 1/3 lighter than the unmodified one (Paper I).

As heterogeneous composites suffer from adhesion problems, a new material that exhibits a better adhesion between the textile and coating was developed and introduced (Paper II). The introduced composite, all-polyamide composite coated textile, uses waste polyamide fibers to make a strong composite. The composite is almost ¼ lighter than PVC, which will reduce transportation costs (based on the density). According to Rajendran et al., [22], for a PVC-coated textile-based bioreactor, a 15-year biogas production lifetime was assumed. Making a bioreactor out of APCT is expected to provide a lifetime of more than 15 years (Paper III). For all-polyamide composite coated textile, a replacement solvent was introduced (Paper IV) that is more environmentally and industrially friendly due to the replacing 40 percent of the formic acid. Finally, I introduced a computer-aided method to find replacement solvents for different solutes or polymers and was used to find dolvents for polyamide 66 (Paper V) and polyamide 11 (Paper VI).

All the aforementioned discussions are general assessments and can be taken as the preliminary steps of upscaling of constructing the textile bioreactors for biofuel production. For further industrial development, more elaborative studies and trials are required.

7.1 Future recommendations

Due to the limitation of time, several interesting areas that could affect the safety, economics, application and productivity of the textile-based bioreactors were not covered in this thesis. Consequently, they are recommended for future research or applications of the textile-based bioreactor as follows:

- Supported textile bioreactors with steel beams/frames
- Adding carbon nanotubes to the composite of APCT
- Giving an antifungal property to the outer side of the textile bioreactor
- Loading PCMs (phase change materials) to make the material thermostatic, provides the material with the ability to maintain its desired temperature.
- Determining and improving the flame-retardancy of the APCT
- Replacing the oil-based polymer (polyamide 66) with a bio-based polymer (polyamide11) to make the APCT more environmentally friendly and water-resistant.
- To endow the APCT with a longer lifetime, a post-treatment for stress-releasing can be carried out by annealing.
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Novel lightweight and highly thermally insulative silica aerogel-doped poly(vinyl chloride)-coated fabric composite

Mostafa Jabbari, Dan Åkesson, Mikael Skrifvars and Mohammad J Taherzadeh

Abstract
Novel lightweight and highly thermal insulative aerogel-doped poly(vinyl chloride)-coated fabric composites were prepared on woven fabrics made of polyester fibres using knife coating method, and their performances were compared with neat composite. The composites were prepared by incorporating a commercial aerogel to a ‘green’ poly(vinyl chloride) (PVC) plastisol. The effect of aerogel-content, thermal insulating property, thermal degradation, surface characteristics, tensile and physical properties of the composites were investigated. Results revealed that aerogel could reduce thermal conductivity, density and hydrophilicity of the composites dramatically without significant decrease in other properties. Experimental results showed that thermal insulation properties were enhanced by ~26% (from 205 to 152 mW/m-K), density decreased by ~17% (from 1.132 to 0.941 g/cm³) and hydrophobicity increased by 16.4% (from 76.02 to 88.67) with respect to the unmodified coated fabric. Analyses proved that composite with 3% aerogel is the lightest by weight, while 4% showed the highest thermal insulation. The results showed that 4% is the critical percentage, and preparation of composites with aerogel content higher than 4% has limitations with the given formulation due to high viscosity of plastisol. The prepared composite has potential applications in many fields such as development of textile bioreactors for ethanol/biogas production from waste materials, temporary houses and tents, facade coverings, container linings and tarpaulins. The prepared composite can be considered ‘green’ due to usage of a non-phthalate environment-friendly plasticiser.

Keywords
Poly(vinyl chloride)-coated fabric, silica aerogel composite, thermal insulation, lightweight PVC, thermal conductivity coefficient, Knudsen effect, transient plane source, environment-friendly (green) poly(vinyl chloride)

Introduction
Coated textiles are flexible composites, consisting of a textile substrate and a polymeric coating. The coating could be on one side or on both sides, either with the same or a different polymeric coating per side.1 Coated woven fabrics are used in a wide range of structural applications to provide lightweight, architecturally striking solutions.2 The physical properties of a coated fabric depend on properties of the substrate, coating formulation, coating technique and processing conditions during coating.3 There are two principal types of coated woven fabric: glass fibre fabric with a polytetrafluoroethylene (PTFE) coating and polyester fabric with poly(vinyl chloride) (PVC) coating.2 Both PTFE- and PVC-coated fabrics are employed today in different types of tents and architectural membrane structures all over the world.4 Fabric structures resist environmental loads, as tensile stresses in the plane of the fabric.5 PVC-coated polyester fabrics are the most commonly used material in construction of structural fabrics.3 These fabrics are popular mainly due to their affordable prices, high strength, durability, resistance to corrosion, fire resistance, solar reflectance.
Thermal insulation is the reduction of heat transfer between objects with differing temperatures. The insulating capability of a material is measured by thermal conductivity (often denoted λ), which is the property of a material to conduct heat. Low λ is equivalent to high insulating capability (R-value). The λ values of some common insulation materials are listed in Table 1. The function of insulation materials is to minimise the transport of heat through the construction. Insulation materials are highly porous with small amount of solid structure. Out of all known solid porous materials, aerogels are particularly known for their high specific surface area, high porosity, low density and high thermal insulation value, properties that are required for a high-performance insulator.

Aerogel is a synthetic, ultra-lightweight, highly nano-porous, super-insulation material derived from a gel, made by sol-gel process and supercritical drying technology, which has excellent insulation performance for its nanoporosity structure (several to tens-of-nanometre). Aerogels are the highest efficient thermal insulator with a λ value even lower than for air and with a density as low as only four times that of air, which makes them the lightest solids known so far, up to 1000 times lighter than glass. Aerogels are good conductive insulators because they are composed almost entirely of gas. Since air is a low-λ material, aerogels are super insulating materials, and they have excellent lightweight properties. Aerogels may have a λ which is smaller than the gas they contain. This is caused by the Knudsen effect. Some types of aerogel provide 39 times more insulation than fibre-based insulators, which include extremely low thermal conductivity (5–100 mW/m·K), very low density (0.003–0.5 g/cm³), high porosity (80–99.8%), high inner surface area (300–1200 m²/g), ultra-low dielectric constant (κ = 1.0–2.0) and low index of refraction (n = 1.05–1.07).

PVC is dimensionally stable, largely non-flammable and of low cost, but it has limited thermal stability and high density. Although PVC-based materials (and in general, polymers) are insulators, better insulating properties might be needed for some applications, such as preparing a biogas digester from PVC-coated fabric in which, having a high insulation property in the digester can enhance the process. Although some researchers have been interested in preparing insulated polymers or in enhancing the insulation properties (such as polyurethane and polycysca-nurate), no previous publications have focused on enhancing thermal insulation of PVC-coated fabrics and making this material lightweight.

Thus, the objective of this work was to enhance the thermal insulation property and decrease the density of PVC-coated fabric made from PVC green plastisol, incorporated by aerogel to form a novel composite of PVC/aerogel on technical woven fabrics made of polyester fibres.

Materials and methods

Materials

Enova™ aerogel IC3120 (Cabot Corporation, Boston, MA, USA) was used in this work. It is a fine particle additive suited for insulative coatings with a thermal conductivity half of that still air (12 mW/m·K at 25 °C) and particle density of 0.12–0.15 g/cm³. The plastosols prepared with the given composition are presented in Table 2. Pekovim TM P1412 is a fine particle paste to prepare vinyl chloride homopolymer. Eastman 168™ plastisier is an excellent environment-friendly non-phenylthallium plastisier for PVC, without health concern, whose previous publications have focused on the preparation of thermosets, including aerogel, was applied on both sides of a fabric. The neat and aerogel-loaded composites as well as aerogel powder were analysed using Fourier transform infrared (FT-IR) spectroscopy in attenuated total reflection (ATR) mode within a wave number range of 600–4000 cm⁻¹ on a Nicolet 6700 spectrometer (Thermo Fisher Scientific, Nicolet Instrument, USA, MA). The spectrum data were controlled by Nicolet OMNIC (Nicolet Instrument, USA, MA) software. Contact angle experiments were performed using the Attension Theta optical tensiometer (Biolin Scientific, Finland). OneAttension software was used for data collection and analysis. The sessile drop method was used to apply the droplet on the substrate surface, in which a 4-μL drop was dispensed on the surface, and images were captured. Three individual measurements were obtained for each set of data, and the mean values were calculated. Thermogravimetric analysis (TGA) was performed on the composites using Q500 machine (TA Instruments, MA, USA). About 10 mg of the material was heated from room temperature to 750 °C at a heating rate of 10 °C/min in a nitrogen purge stream. The tensile properties were evaluated in accordance with the standard method ISO 527. The dumbbell-shaped test pieces were cut by a laser cutter. The test bodies were tested on a MTS 20/7 (MTS Systems Corporation, Eden Prairie, MN, USA), fitted with a
According to Einstein’s viscosity law for solid particles due to extra dissipation of the particles and, at higher increases at 4% aerogel loading can be an indication trend, showing a higher density than 3%-aerogel, but percentage, the weight of the composite decreased. eventually makes it lighter. By increasing the aerogel the entrapped air inside the composite increases, which aerogel); thus, by introducing aerogel to PVC plastisol, composite’s matrix and aerogel is the reinforcement of the gas particles, decreasing the thermal conductivity of the gas decreases by decreasing size of the cavity encompassing the air), Berge and activity, in addition to eliminating air convection. For exam-

**Density**

The results of density measurement showed that aerogel had reduced the density of the composites (Figure 1a). It is most likely because aerogel particles carry plenty of air by themselves (inside the nanometric scale pores of silica aerogel); thus, by introducing aerogel to PVC plastisol, the entrapped air inside the composite increases, which eventually makes it lighter. By increasing the aerogel percentage, the weight of the composite decreased. However, the 4%-aerogel composite deviates from this trend, showing a higher density than 3%-aerogel, but still lower than 2%-aerogel. The fact that density increases at 4% aerogel loading can be an indication of aerogel particle damage. The increase in viscosity is due to extra dissipation of the particles and, at higher concentrations, due to particle-particle interactions. According to Einstein’s viscosity law for solid particles in a slurry at low concentrations the relative viscosity is equal to \(1 + \frac{\Phi}{2.5\rho_a}\), where \(\Phi\) is the particle volume fraction in the dispersion. As the aerogel is a very low-density material, its volume is ultimately high (for only 4 wt% of aerogel in the composite, the volume fraction is around 26%, see Table 3); therefore by increasing the loading of aerogel from 3% to 4%, the viscosity of the sol (the plastisol) increases hugely.

For the 3% aerogel loading the following calculation can be made:

\[
\eta_{3\text{-aerogel}} = \frac{1 + (2.5 \times \Phi_{3\text{-aerogel}})}{1 + (2.5 \times 0.259)} = 1.087
\]

It means that by only 1% increasing aerogel content in composite (from 3%-aerogel to 4%-aerogel), the viscosity increases 9%. In other words, if the weight load of aerogel in plastisol increases a bit, then there is a high increase in viscosity. Relative viscosity with respect to the 0%-aerogel sample calculated via Einstein’s viscosity law for solid particles in a slurry versus aerogel loading in composites are shown in Figure 7.

**Results and discussion**

A novel composite of aerogel/PVC on polyester fabric was developed and characterised. During preparation of the plastisol for aerogel-doped PVC-coated fabric composites, it was observed that by increasing the aerogel content in plastisol, the viscosity increases, where 5% aerogel was too viscous and not possible to mix. Therefore, up to 4% aerogel was developed and studied 5% aerogel was too viscous and not possible to mix.

The results of density measurement showed that aerogel has successfully decreased the density of the composite. This is due to the lower density of aerogel particles and the presence of entrapped air inside the composite. The density of aerogel is around 0.12–0.15 g/cm³, which is much lower than the density of PVC (about 1.35 g/cm³). Therefore, by adding aerogel to PVC plastisol, the viscosity of the mixture increases, leading to a decrease in the apparent density of the composite.

The densities of the composite can be calculated through the role of mixtures (ROMs) formula:

\[
D_i = \left(D_{\text{pvc}} \times \Phi_{\text{pvc}} + D_{\text{aerogel}} \times \Phi_{\text{aerogel}}\right)
\]

where \(D_i\), \(D_{\text{pvc}}\), and \(D_{\text{aerogel}}\) are the densities of composite, matrix (PVC together with the fabric) and aerogel, respectively. Here it is assumed that PVC is the composite’s matrix and aerogel is the reinforcement (filler). By inserting the corresponding values from Table 3 into the ROM formula, it is clear that the theoretical densities calculated from the ROM formula for 2% and 3% aerogel loading composite are consistent with the experimental values, with only 0.01 g/cm³ deviation (Δ). But in 4% loading, the difference is 0.10 which is due to aerogel particle damages. The density of aerogel used in ROM formula is the average of 0.12–0.15 g/cm³.

**Tensile strength**

The tensile strength of the composite can be obtained from the tensile strength test. The tensile strength of the composite depends on the properties of the fibers, matrix, and the bonding between them. The bond strength can be improved by using a suitable coupling agent or by increasing the surface area of the fibers. The tensile strength of the composite also depends on the defects present in the composite, such as porosity, voids, and cracks. The tensile strength of the composite can be measured using an ASTM D3039 test method, which involves applying a tensile load to the composite specimen and measuring the load at which the specimen fails.

**Thermal conductivity**

The thermal conductivity of the composite can be measured using a differential scanning calorimetry (DSC) or a Fourier transform infrared (FTIR) spectrometer. The thermal conductivity of the composite depends on the properties of the fibers, matrix, and the bonding between them. The bond strength can be improved by using a suitable coupling agent or by increasing the surface area of the fibers. The thermal conductivity of the composite also depends on the defects present in the composite, such as porosity, voids, and cracks.
the material that contains air, the thermal conductivity increases. Thermal conductivities of the composite can be calculated via ROM:

\[ \lambda = (\lambda_{pc} \times \Phi_{pc}) + (\lambda_{aerogel} \times \Phi_{aerogel}) \]

where the \( \lambda_{pc} \), \( \lambda_{aerogel} \), and \( \Phi_{aerogel} \) are the \( \lambda \) of composite, matrix and aerogel, respectively. The values are calculated and tabulated in Table 3. In this case, the absolute deviation (\( \Delta \)) for 4% aerogel loading is more than 3%. It is probably because of particle damage which was discussed. Interestingly, even with particle damage, the experimental \( \lambda \) values are lower than the theoretical ones, indicating better insulation properties. It might be confusing why damaged or aggregated aerogel particles still can impart their insulation properties to the composite. It can be because of this fact that silica by itself is a poor conductor of heat.\(^{16}\) So even by crushing, although the crushed ones are not perfect insulator (due to not having nanometric pores to show Knudsen effect), they are still good heat insulator because of silica’s nature. Therefore, by incorporating aerogel in a composite, it allows it to become a better thermal insulator. The results showed a regular trend in decreasing thermal conductivity in aerogel-doped PVC-coated fabric composites.

**FT-IR spectroscopic analysis**

The FT-IR spectra was used to verify if there were any changes in surface bonds or if a new bond had been formed between aerogel particles and PVC-coating matrix ingredients, by comparing the aerogel-loaded composites to the spectrum of neat one (0%-aerogel). Here, the aerogel powder was analysed as well. The FT-IR results (Figure 2) indicated that there were no differences in FT-IR spectrum of 0%-aerogel and other aerogel-containing composites’ spectra.

Siloxanes show one or more strong infrared bands in the region 1130–1000 cm\(^{-1}\). Disiloxanes and small-ring cyclodisiloxanes show a single Si—O—Si band. As the siloxane chains become larger and more complex (like silica aerogel, which has a three-dimensional siloxane network), the Si—O—Si absorption becomes broader.\(^{25}\) These peaks are characteristic, showing a typical silica aerogel network structure. Therefore, the broad and strong peaks in the aerogel powder’s FT-IR spectra belong to Si—O—Si bond in the aerogel.\(^{26,27}\) The strong absorption peaks near 1100 and 1220 cm\(^{-1}\) (vibration band\(^{20}\)) and the weak peak around 800 cm\(^{-1}\) were assigned to the asymmetric and symmetric bending modes of Si—O—Si, respectively. The peaks for Si—CH\(_3\) occur at near 2950 and 850 cm\(^{-1}\), as shown in the spectra. Aerogels by themselves are hydrophilic, but chemical treatment can make them hydrophobic. Hydrophobic aerogels have higher stability.\(^{20}\) If aerogels absorb moisture, they usually suffer a structural change, such as contraction and deterioration, but degradation can be prevented by making them hydrophobic. Aerogels with hydrophobic interiors are less susceptible to degradation than aerogels with only an outer hydrophobic layer, because maybe a crack penetrates into the surface. The peaks at 1250, 1150 and near 830 cm\(^{-1}\) indicate the presence of Si—C bond \(^{31–33}\) (and also the peak around 750 cm\(^{-1}\) corresponds to Si—C bond\(^{29}\)). The presence of Si—C bond peaks in the aerogel powder’s spectrum originates from the fact that the aerogel powder had been hydrophobic to some extent by replacing some end–OH groups (in Si—OH) with methyl (—CH\(_3\)) groups (Si—CH\(_3\)). The peaks show that the aerogels are modified into a hydrophobic form.\(^{31}\)

The FT-IR spectra of the four composites do not show much significant difference, indicating that there are no changes in the bonds existing in the surface, because in the ATR mode, the infrared ray cannot penetrate into the composite too much. The penetration depth into the material under analysis is typically between 0.5 and 2 micrometres, with the exact value being determined by the wavelength of light, the angle of incidence, the indices of refraction for the ATR crystal and the medium being probed.\(^{25}\) Therefore, the spectrum shows the bonds existing in the surface of the composite. None of the aerogel characteristic peaks is shown in the aerogel-doped composites’ FT-IR spectrum. Even if we consider that they may be overlaid by the other peaks of PVC-coated fabric, there is no difference between 0%-aerogel composite’s spectra and the other aerogel-containing composites. From this result, we can conclude that the aerogel particles are mostly in the inner part of the surface (near the middle fabric) rather than near the surface. In other words, until the depth of two micrometres, no aerogel particles exist. The aerogel particles are not in or near the surface, so the surface properties have not changed. Silica aerogels are fragile and sensitive at relatively low stresses, which limits their application;\(^{9}\) therefore, not existing the fragile and less-impact material (in comparison to high impact properties of plasticised PVC) in near the surface is beneficial, because the surface remains in a high-impact state.

**Contact angle measurement**

The water contact angle measurement results (Figure 3) show that by increasing the aerogel-content (a hydrophobic particle), the surface of the PVC-coated fabric becomes more hydrophobic, which is expected. The trend is true up to 3%-aerogel, but the hydrophobicity of 4%-aerogel is between 2%-aerogel and 3%-aerogel. This trend is similar to the trend in density, and it is due to aggregation of aerogel particles and also maybe because the brittle aerogel particles are crushed at 4% loading and the particles interior is hydrophilic.
because aerogel particles have been surface-treated to have hydrophobic surface, as mentioned before). The decrease in contact angle at 4% loading could be due to exposing some crushed particles’ hydrophobic interior. Therefore, aerogels may not impart and show its hydrophobicity completely.

Although based on FT-IR results there is no aerogel near the surface, aerogel particles can affect the orientation and reorganisation of the PVC chains near the surface in a way that the more hydrophobic part becomes exposed to the outside of the surface.

**Morphology**

The microscopic photographs from cross section of the aerogel-doped PVC-coated fabrics are shown in Figure 4. Figure 4(b) represents the 2%-aerogel composite, indicating the good dispersion of aerogel particles inside the composite. This is also valid for 3%-aerogel containing composite (Figure 4c and d), but some ‘very slight’ agglomerations are seen as well, indicating a very good dispersion of aerogel particles on the surface. It can be related to the results from TGA, because more parts of the composite can be affected from aerogel particles to increase the onset decomposition temperature (ODT). The agglomeration is much higher in 4%-aerogel composite (Figure 4e and f). By increasing the size of the agglomerates of aerogel particles, they might play the role of plasticizer in a more stronger way; this interpretation is consistent with the results from tensile testing, that is, as the size of agglomerates increases, the plasticising effect becomes more noticeable (composite 4%-aerogel has a higher elongation than for composites 2%-aerogel and 3%-aerogel). It is also consistent with results from the density measurements. It can be interpreted that by increasing the aerogel percentage in the aerogel-doped PVC-coated fabric, agglomeration increases and the effect of aerogel particles on the composite (like decreasing density and increasing thermal decomposition temperature) decreases because of agglomeration. In other words, by agglomeration, the surface area of the aerogel particles decreases (a larger collection of particles are closely together); therefore, they cannot impart their properties to PVC.

**Thermal properties**

From TGA results (Figure 5), it was observed that the effect of aerogel percentage on thermal stability of PVC-coated fabrics has no obvious effect on thermal stability. The ODT values of the three composites are just a little lower than that of the neat composite, which perhaps originates from hindrance in partially cross-linking and catalysing the decomposition reaction by means of oxygen atoms in the aerogel structure.

TGA curves (Figure 5a) revealed that the thermal degradation of the analysed materials comprises two stages. During the thermolysis of PVC, both HCl and benzene evolutions reach a maximum at 380°C, suggesting that the dehydrochlorination process and the cyclisation of triene segments from polyene segments to form benzene are simultaneous, which is obvious in the neat and aerogel-doped PVC-coated fabric TGA curves, with only a slight deviation from the mentioned temperature. The experimental phenomena of the composite pyrolysis would verify the above-mentioned procedure. Table 4 lists the key temperature points of the TGA curves of every composite, containing initial pyrolysis temperature (ODT) for with-/without-fabric composites, residue at 750°C (%), and their corresponding differences (between with-/without-fabric). The values extracted from the TGA curves are shown in the charts in Figure 5(b). Fundamental information regarding the thermal stability of the composites materials can be obtained from TGA analysis. The mechanism of PVC thermal degradation has been a controversial and extensively studied topic. The weight loss proceeds by two different steps. In general, it is established in literature that the thermal decomposition for PVC takes place in two processes. The first step, arising from the dechlorination from the side group, forms HCl, leaving a conjugated polyene structure and increasing the weak point on the main chains. Secondary processes in PVC thermal degradation includes crosslinking and gel formation, cyclisation, chain scission and benzene formation, Diels-Alder reaction with additives as well as oxidation of polyenes. During the second stage, usually only one reaction is expected by the majority of people, that is, with the occurrence of crosslinking and depolymerisation of polyene chain, the evolution of toluene together with a small quantity of other alkyl aromatics takes place, yielding a residual char.

The characteristic difference of the composites may lead to the fluctuation of the kinetic parameters; in particular, the additives could hinder or improve the
temperature than 3%-aerogel (without fabric), proba-
bly due to agglomeration of aerogels, which makes it hard for oxygen atoms in the aerogel particles to play their catalytic decomposition role. With regard to the difference between ODT of with- and without-fabric composites, it may be that the coating has closely adhered to the fabric, more so than the others, which is why the ODT of with-fabric composite has more of a difference than without-fabric of 3%-aerogel compos-
ite, with respect to the others. It is concluded that the thermogravimetric behaviour for aerogel-doped com-
posites are similar to that of PVC, which reveals that the pyrolysis mechanism of the aerogel-doped compos-
ites is mainly dominated by PVC, its main ingredient. Therefore, results obtained through thermal analyses can be regarded as good, as the addition of the additive (aerogel) did not prejudice the thermal properties of the composites. It is worth mentioning that at normal uses, the material will never experience temperatures above 200°C, for example the application of this material in preparing biogas textile reactor.  

Tensile strength measurement test  

The results of tensile strength test are tabulated in Table 5 and also shown as drawn charts (Figure 6). A typical stress-strain curve for 0%-aerogel composite is shown in Figure 6. Tensile strength tests showed that the tensile modulus and stress upon breakage of the aerogel-doped composites are slightly lower than that of neat composite. The decrease in tensile strength is probably due to the increase of interfacial properties and has to be low in weight.

Figure 6. (a) Tensile at max and elongation at max versus aerogel percentage; (b) A typical example of stress-strain curve for aerogel-doped PVC-coated fabric composite (0%-aerogel).

Figure 7. Relative viscosity with respect to the 0%-aerogel sample, calculated via Einstein’s viscosity law for solid particles in a slurry, versus aerogel loading in aerogel-doped PVC-coated fabric composites.

Conclusions  

In this work, a novel PVC/aerogel composite was obtained by mixing commercial aerogel powder with green PVC plastisol. It was found that silica aerogel could enhance thermal insulation, density and surface properties of PVC-coated fabrics without significantly changing the other properties. Analyses proved that composite with 3% aerogel is the lightest by weight, while 4% showed the highest thermal insulation. The novel lightweight and highly thermal insulating PVC fabric-reinforced composite has potential applications in some fields such as development of biogas textile reactor (which needs to be water/gas-tight, thermal insulant and light-weight), temporary houses and tents, facade coverings, container linings and other advanced tarpaulins, which need high thermal insulation properties and has to be low in weight.

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Nomenclature  

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<th>Symbol</th>
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Introducing all-polyamide composite coated fabrics: A method to produce fully recyclable single-polymer composite coated fabrics

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ABSTRACT: Novel all-polyamide composite (APC) has been developed to replace traditional coated fabrics with good interfacial adhesion and enhanced recyclability. The composite is fully recyclable since it contains no other materials except polyamide. APC was prepared by partially dissolving a polyamide fabric by treatment with a film-forming polyamide solution. The effect of the polyamide solution concentration and gelling time on tensile and viscoelastic properties of APCs was investigated to explore the optimum processing parameters for balancing the good interfacial adhesion. The composite properties were studied by dynamic mechanical thermal analysis (DMTA), tensile testing and scanning electron microscopy (SEM). The results showed a good adhesion between the coating and the fabric. A new method was introduced to convert a low value added textile waste to a high value-added product. The composite is tunable, in terms of having a dense or a porous top-layer depending on the end-use requirements. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2015, 132, 42829.

KEYWORDS: coatings; films; polyamides; recycling; textiles; coated fabrics; single-polymer composites

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INTRODUCTION

Heterogeneous composites pose a recycling challenge1 because of their composition. Furthermore, they often suffer from poor matrix-fiber adhesion due to the chemical incompatibility of the components.2–4 The growing interest in the recycling of materials is brought about by the desire to preserve the environment, as there is limited landfill space due to the large amount of wastes that is being dumped.5 Global warming is also of concern due to emissions from waste incineration.6 These challenges have stimulated an interest in the development of environmentally friendly materials.7 One promising approach to deal with the composites recycling challenge is the introduction of single-polymer composite (SPC).8 In SPCs both the reinforcing and the continuous phase are polymers with the same chemical composition; therefore, recyclability is enhanced8,9 as no material separation is necessary. These materials are often described as one-polymer composites, homocomposites, all-(the same)polymer composites, self-reinforced, or homogeneous composites.2–5 Besides recyclability, the interest in the concept of SPCs is based upon the premise that interfacial bonding should improve if matrix and reinforcement are made from the same polymer.2–5

Polymer-coated textiles are flexible composite materials comprising a coating (the polymer) and a substrate (textile/fabric layer(s)) adhered together through a specific coating process.10 The coating may be on one side or both sides either with the same or a different polymeric coating per side.11 Coated woven fabrics are used in a broad range of semi-structural applications to provide lightweight, architecturally striking solutions.12 They are often used for wide-span surfaces, membrane-cable structures, hanging roofs (e.g., roofs of sports structures like stadiums), pneumatic constructions,3 transportation, and commercial constructions.14 The combination of the different properties of each layer determines the overall properties of the system.10 Coated fabrics can be tailored to be used as a textile reactor, temporary houses and tents, facade coverings, container linings, and tarpaulins.10 Fabric structures resist environmental loads, as the tensile stresses are dispersed in the plane of the fabric.12 This means that the textile substrate contributes to the mechanical strength (tear, tensile), elongational, and dimensional properties of the system in general; whereas, the polymer coating helps to introduce penetration resistance and impermeability (to liquids, gases, and dust particles), as well as improve fabric abrasion strength.16 They can also help to modify the appearance for decorative purposes.10 Coated fabrics are popular mainly due to their affordable prices, high strength, durability, resistance to wear and tear, good toughness, various colors, and soft texture.8 A wide range of textile materials are used as substrates for coated fabrics such as cotton, rayon, polyamide (PA), and...
The aim of this paper was to introduce a novel, facile, low cost, and environmentally-friendly method to produce an APC coated fabric from a PA by solvent-casting of only one component, specifically, PA66 onto the PA66 fabric in order to have strong adhesion between the coating and the fabric as well as enhanced recyclability.

**MATERIAL AND METHODS**

**Materials**

The formic acid used in this work was supplied by Sigma-Aldrich (ACS reagent grade, 99.8%). The Polyamide 66 fabric was provided by FOV Fabrics AB (Borås, Sweden). As a polymer source to produce a solution, PA fiber production waste from the weaving process at FOV Fabrics was used.

**Composite Preparation**

All polyamide composites were prepared in the form of a flat laminate on the substrate fabric by an isothermal immobilization-precipitation method. Seven solutions of PA production waste were made by dissolving 17, 23, 29, 35, 41, 47, and 53 g of PA in 100 g (82 ml) formic acid at room temperature. In low concentrations (less than ∼30% w/w), PA66 readily dissolves in the formic acid at room temperature, but for higher concentrations, the solution should be agitated for a longer time. In order to assure the completion of dissolution and have the same agitation condition for all the solutions, the sealed solution flasks were put in a shaker at the speed of 100 rpm for 20 h at 55°C to obtain a homogeneous solution (thermal and concentration equilibrium). The dopes were cooled to room temperature, and after centrifugation at 10 minutes at the speed of 16,000 g, to remove the bubbles, the dopes were casted on a PA fabric with the size of 18 mm × 24 mm fixed with a glass plate. The fabric and a layer of the PA solution on top of it was immersed and induce polymer precipitation (phase separation). From then on, the waiting time, which is the time between applying the solution to the fabric and immersion in the coagulant, is called gelling time (phase separation). After the gelling time in the water bath, the composites were obtained after washed three times with distilled water and then they were held under light press between two sheets of filter papers and dried at 55°C in a vacuum oven for 2 h. The composites were named according to their corresponding solution concentrations and gelling time (Table 1).

**Characterization Methods**

The tensile properties were evaluated in accordance with the standard method ISO 527-1.25 Dumbbell shaped test bodies, 75 mm long (with the width of 4 mm), were tested on a MTS/C25 tensile tester (MTS Systems Corporation, Eden Prairie, MN), fitted with a 5 kN load cell and a special grip for films, using a crosshead speed of 5 mm/min. The gauge length, pre-load force, and first approach speed were 0.5 N, 2 mm/min and 33 mm, respectively. The thickness of the composites was measured by Elastocron thickness meter (Elastocron AB, Sweden). A minimum of five test bodies was tested for each material. The specimens were all cut in the warp direction of the fabric. To investigate the viscoelastic properties of the composites, dynamic mechanical thermal analysis (DMA Q800, TA Instruments, Waters LLC) was performed on the prepared composites. The specimens were run with a film tension clamp using the temperature ramp procedure with a sample dimension of 15 × 9 mm. The temperature ranged from room temperature to 180°C with a heating rate of 3°C/min, and the frequency and the amplitude were 2 Hz and 15% strain, respectively.

Scanning electron microscopy (SEM) was used to monitor the fracture surface morphology of the cross-sections of the composites. The specimens were obtained by quenching in liquid nitrogen and breaking by hand. The surface was sputtered with a layer of gold before the measurements. SEM analysis, performed using ASX200 (Seeron Technology, Korea) operated at an acceleration voltage of 18 kV.

**RESULTS AND DISCUSSION**

To overcome the recyclability problem of the PA-coated fabric and to increase the adhesion between the coating and the fabric, a PA-coated PA fabric single-polymer composite out of PA66 was prepared. It was done by applying the PA66 solution to the PA fabric by means of a universal film applicator and consecutively, coagulation in a water bath as a non-solvent to induce phase separation (phase inversion). As a result, a composite composed of a thin continuous PA layer (the coating) and a PA textile fabric out of the most common type of aliphatic PA (PA66) was obtained. The hypothesis in this work was that since the coating and the fabric were the same, and there was a common solvent in between them, the adhesion would be very strong; however, the results were analyzed, and the process parameters were optimized.

**Mechanical Properties**

The maximum force needed to break the composite in the tensile mode, as well as elongation at max, and the thickness of the APCs are shown in Figure 1. As the thickness of the composites was not the same, the maximum force was chosen as the criterion to compare the mechanical properties of the composites. This was decided since the mechanical characteristics of the fabric (a spun fiber, high crystallinity), and the formed film (an amorphous film, low crystallinity) differs greatly with each other. Moreover, in different composites, different amounts of PA film exists; thus, in this case, the stress, that is, force divided by cross-sectional area, is not a good criterion to compare the strength of the APCs.

The results from the tensile testing giving the maximum force (Figure 1) showed a slightly good trend. The results indicated the increase of mechanical strength with the concentration of the dope for each gelling time group individually. If only the 15 s gelling time composites were considered, the maximum force needed to break the composites increased as the corresponding dopes contained more PA (higher concentrations). This trend was valid for 30 s and 45 s gelling times. However, if the thermal stability of the composites was taken into consideration, the tendency was not the same for all the 7 groups. There is no clear trend in increasing the gelling time. Some dope concentration (for example 17%) possibly showed a decreasing trend in the mechanical strength when the gelling time is increased. However, the trend is not so significant considering the standard deviations.

Comparing the fabric maximum force (Figure 1) with the other APCs, showed that by applying PA dope on PA fabric, the fabric became weak in terms of mechanical strength that can be attributed to the dissolution of the surface of the fabric by the solvent existing in the dope. However, the 53% APCs had very close maximum force values to those of the fabric. This decreasing in mechanical properties is acceptable in the context of providing a new property to the fabric (making the fabric gas-water-proof) and resulting a coated fabric. For elongation at max, more or less the same trend was valid with the exception that the APCs made out of concentrated PA dopes (especially 47% and 53%) had higher elongation at max values. This was due to the difference between elastic properties of amorphous and crystalline polymers. The fabric is made from a spun polymer fiber that has a higher crystallinity than the formed-film that is an amorphous polymer. Therefore, by increasing the amorphous (more elastic) polymer in the composition, the max value increases. It is in accordance with the rule of mixtures mechanical model, which says the resulting mechanical properties of a composite, is the individual property of the components based on their volume fraction.
increases. The more the fabric surface dissolves, the more the strength of the fabric diminishes. On the other hand, in order to obtain a good adhesion of the PA layer to the fabric substrate, it is necessary to have a certain amount of surface dissolution. It is obvious that for higher concentrations of the dope, the composite has a higher maximum force and is thus mechanically stronger. It is due to the higher concentration of the film formed (higher loading of PA) on the fabric and better opportunities to form entanglements between the formed film’s polymer chains and the polymer chains of the fibers in the fabric. The mentioned trend is slightly valid when increasing the gelling time for each dope concentration. By increasing the penetration time for the solvent into the fabric surface (and dissolving the surface of it), logically the amount of penetrated solvent (and hence the number of polymer chains that can entangle with the chains of the polymers in the film) increases; while the concentration of the solvent is the same for the three different gelling times.

The thickness of the composites (Figure 1) varied with different concentrations of the dopes and even with varying gelling times. It can be explained as follows: by increasing either the dissolution power (lowering concentration) of the solvent or the dissolution time of the solvent in the dope to dissolve the fabric (gelling time), a greater amount of the fabric is dissolved; hence, the thickness decreases. The trend is more or less valid for all the composites except for APC2945, which can be related to a critical concentration or experimental errors. Although the same universal film applicator (with the thickness of 175 μm) was used for all of the composites, the thickness varied. The thickness decreasing with the gelling time indicated that the time dedicated to the solvent to dissolve and go through to the fabric, had an inverse proportion with the thickness due to the dissolution power, as mentioned before. The increasing of the thickness by increasing the dope concentration may very well be attributed to increased polymer content in the formed-film. A film with more polymer content would more than likely have an increased thickness. However, the decreasing the thickness in each group by increasing the gelling time, supported the “dissolution power” proposal for the thickness variation.

We propose that entanglement effects may explain the trend in the maximum force and elongation data shown in Figure 1. At low polymer solution concentrations, there are fewer entanglements formed polymer can more easily order its chains.26 These ordered regions can serve as nucleation sites, promoting more crystallization in the precipitated sample.26 If the polymer entanglement proposal is correct, the increasing elongation at max by increasing the dope concentration is due to having a higher amount of amorphous regions at the higher concentrations of the dope. Therefore, they are more elastic than those at the lower concentrations. At higher dope concentrations, however, polymer entanglements can interfere with the ordering (making the ordering difficult) and thus reduce the number of ordered formed regions.26

If the polymer entanglement proposal is correct, then there is a critical concentration, \( C^* \), at which entanglements begin to form, and the solution becomes semi-diluted.29,30 This critical concentration can be approximated as follows:

\[
C^* = \frac{1}{\eta}
\]

where \( \eta \) is the intrinsic viscosity. Intrinsic viscosity \( \eta \) is related to the molecular weight \( M \) by the Mark-Houwink equation, defined as:

\[
\eta = K M^a
\]

where \( K \) and \( a \) are constants, that depend on the polymer, solvent, and temperature.28 \( K \) depends on the width of the molecular weight distribution, and \( a \) is a measure of the polymer-solvent interactions.14 Thus, by increasing the molecular weight of PA, \( C^* \) will decrease, and entanglements will occur at lower concentrations. This means that every time that PA scraps (as PA source in this work) with a different molecular weight is going to be used, the parameters need to be optimized again.

Another reason for improved mechanical properties by increasing the dope concentrations is probably due to increased mass (surface weight). Higher dope concentrations contain a higher amount of polymer and form a denser layer on the fabric. At very low dope concentrations (less than 35%), the concentration of the solvent is so high that the dissolution of the fabric is too much and more or less destroys the fabric according to maximum force results. But at higher concentrations, especially at 41%, 47%, and 53%, the amount of the solvent seems to be optimized so it does not dissolve the fabric more than what is needed; i.e., dissolves the fabric’s surface only to an extent that is required to establish the adhesion. Therefore, the higher concentrations (41%, 47%, and 53%) are more optimized concentrations to prepare the APC in terms of the mechanical properties. With the same argument, the longer gelling times in each of the aforementioned three optimized concentrations give better mechanical properties to the corresponding composites.

**Viscoelastic Properties**

The three composites APC1715, APC1730, and APC 1745 were yielded during the analysis in the DMA machine at 56°C, 43°C, and 32°C, respectively; therefore, no results were reported for them. An exemplary DMA graph for the APC4745 composite with appointed maximums, onset-, mid- and end-points, as well as step transition, are shown in Figure 2. Although there is no regular trend for the peak of the loss modulus (\( \tan \delta \)) of the composites, as for the peak of the loss modulus versus temperature curve (Figure 3), it is clear that APC4130 has the highest value. For the two more concentrated dopes, i.e., 47 and 53%, loss modulus (and hence the number of polymer chains that can entangle with the chains of the polymers in the film) increases; while the concentration of the solvent is the same for the three different gelling times.
for 30 s gelling time is greater than for 15 s and 45 s. However, for the rest dopes, it is smaller than the other two gelling time. The physical and mechanical properties of the coating, along with its glass transition temperature and its thickness are key parameters affecting properties, such as the interfacial strength and the fracture toughness.\cite{32} Loss modulus describes the viscous properties, meaning that composites with longer gelling time have better elastic properties than those with shorter gelling time. The variations in the viscoelastic results (Figure 3) are probably related to a larger part of the PA fabric being dissolved and changing it from a higher crystalline form (spun fiber) to a more amorphous polymer, from lower to higher dope concentrations as well as from shorter to longer gelling times. Since amorphous polymers are disorganized, they can align in the direction of the force imposed on them, and by this, they can dampen the energy, at least more than the amount of dampening energy in more crystalline regions. By increasing the temperature, the stiffness of the polymer decreases. The temperatures at which the drop in stiffness occurs are shown in Figure 3. Comparing the stiffness step transition onset point and gelling time of the APCs at various dope concentration, it is difficult to infer the effect of the gelling time/dope concentration on the stiffness. Again there is no clear and regular trend, but longer gelling time composites have higher storage moduli (see Figure 4). When the gelling time is longer, the solvent has more time to penetrate into the fabric, resulting in better adhesion. This indicates that the polymer chains in the formed film and the polymer chains in the dissolved parts of the fabric can form more entanglements with each other. Therefore, the longer gelling time gives not only better adhesion, but also improved damping properties that can dissipate more energy, which, as a result, gives higher tan delta (loss tangent) (Figure 4). In this system, there might be a critical entanglement degree in which the polymer chains can entangle in each other enough to make the resulting composite stiff, but not to the extent that make it rigid. The variations, especially in 35% and 41% dope concentrations, can be due to the critical degree of entanglements. As Varelidis et al.\cite{33} discuss, the glass transition temperature and the thickness of the flexible interlayer have been identified as the major parameters affecting the end properties of the composite. Therefore, in this regard, APC4130 is the optimum APC.

Morphological Properties

According to the scanning electron microscopic images of the cross-section (Figure 5), in almost all the APC specimens there is a good adhesion between the formed film and the fabric. In other words, the boundaries between the fiber of the fabric and the formed film are not clear because they have faded due to the adhesion of the two components.

Figure 4. Tan delta, storage modulus, and loss modulus for some selected All-Polyamide Composite (APC) coated fabrics. Although there is no clear and regular trend, longer gelling time composites have higher storage moduli. Longer gelling time gives more opportunity for the solvent to penetrate into the fabric, resulting in better adhesion and more entanglements, which eventually improved damping properties that can dissipate more energy, which as a consequence gives higher tan delta. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
the solvent leaves the channel and creates a void. Because of the entanglement, the chains next to the migrating solvent molecules are not able to rearrange themselves to fill the channel formed by the solvent while leaving. In other words, the solvent creates a route for itself to be able to come out and by this, leaves behind a channel. This property can be useful for some applications, in which the porosity of the composite is required, like supported membranes.

CONCLUSIONS
The preparation of a novel all-polyamide composite (APC) coated fabric, a specific form of single-polymer composites, made through a phase inversion method is described in this report. The prepared composite has a strong adhesion between the two constituents due to the use of the same polymer (PA66) in the constituents and a common solvent. The composite is fully recyclable since it contains no other materials except PA, which can be melted or dissolved and reused like a virgin PA source. The optimum concentration is 47% if a dense film is needed, but if it is necessary to present a porous film on the fabric, then 53% solution should be used to prepare the APC membrane, that can be regarded as a fiber-supported membrane. The composite can be tailored in various ways with different properties depending on the end-use requirements. The prepared composite has a wide range of semi-structural applications to provide lightweight, architecturally striking solutions as well as wide-span surfaces, on the end-use requirements. The prepared composite has a strong adhesion between the two constituents due to the use of the same polymer (PA66) in the constituents and a common solvent. The composite is fully recyclable since it contains no other materials except PA, which can be melted or dissolved and reused like a virgin PA source. The optimum concentration is 47% if a dense film is needed, but if it is necessary to present a porous film on the fabric, then 53% solution should be used to prepare the APC membrane, that can be regarded as a fiber-supported membrane. The composite can be tailored in various ways with different properties depending on the end-use requirements. The prepared composite has a wide range of semi-structural applications to provide lightweight, architecturally striking solutions as well as wide-span surfaces,

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Paper III
All-Polyamide Composite Coated-Fabric as an Alternative Material of Construction for Textile-Bioreactors (TBRs)

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Abstract: All-polyamide composite coated-fabric (APCCF) was used as an alternative material for the construction of textile-bioreactors (TBRs), which are prepared as a replacement of the traditional stainless steel bioreactors (SSBRs) or concrete-based bioreactors. The material characteristics, as well as the fermentation process performance of the APCCF-TBR, was compared with a TBR made using the polyvinyl chloride (PVC)-coated polyester fabric (PVCCF). The TBRs were used for the anaerobic fermentation process using baker’s yeast; and, for aerobic fermentation process using filamentous fungi, primarily by using waste streams from ethanol industries as the substrates. The results from the fermentation experiments were similar with those that were obtained from the cultivations that were carried out in conventional bioreactors. The techno-economic analysis conducted using a 5000 m³ APCCF-TBR for a typical fermentation facility would lead to a reduction of the annual production cost of the plant by $128,000,000 when compared to similar processes in SSBR. The comparative analyses (including mechanical and morphological studies, density measurements, thermal stability, ageing, and techno-economic analyses) revealed that the APCCF is a better candidate for the material of construction of the TBR. As the APCCF is a 100% recyclable single-polymer composite, which was prepared from Nylon 66 textile production-line waste, it could be considered as an environmentally sustainable product.

Keywords: single-polymer composite; textile bioreactor; all-polyamide coated-fabric; polyvinyl chloride (PVC) coated-textile; waste management; Nylon 66; yeast fermentation; edible filamentous fungi cultivation; techno-economic analysis

1. Introduction

‘Energy’—its production and its use in contemporary society—is a formidable topic [1]. Renewable energies are being increasingly adopted across Europe, partly due to the European Union’s (EU’s) energy policy based on its 20-2020 commitments, i.e., 20% renewables by 2020 [2]. As biofuels must compete with fossil fuels, any attempt to reduce their investment and operational costs will contribute to stimulate their consumption [3]. During the last few years, several research projects have been conducted to minimise biofuel production costs [4], regarding the process technologies, as well as the equipment or infrastructure facilities, such as the bioreactors or distillation columns. A bioreactor is a vessel that provides an environment suitable for fermentation reactions where the controlled growth of microorganisms result in the production of biofuels [5]. Bioreactors are made out of stainless steel or concrete, which are expensive and time-consuming to install [5]. To be used as a bioreactor, the construction material has to meet several prerequisites, such as the ability to provide a suitable environment for the microbial proliferation, withstand high pressure [6], be inert to the underlying biological and chemical process conditions [3], corrosion proof, and water-proof and/or gas-proof, depending on the fermentation process. Recently, research studies have come-up with...
alternative material for making microbial bioreactors [3]. One such example is using polyvinyl chloride (PVC)-coated polyester fabric (hereafter referred to as PVCCF). Polyester being one of the most conventional but less advanced fabric in the textile industry, could be replaced with a better performing textile, such as polyamide (PA) that possess a longer lifetime, has a higher mechanical and dimensional stability, and is light weighted [7]. However, for economic reasons polyester fabric has to be used as the base material in many cases. Nevertheless, the coating of the PVC onto the polyester fabric involves chemical formulations that might be harmful to the microorganisms. Additionally, the recycling of the materials used will also pose severe challenges, as it consists of the mixture of PVC, polyester fabric, a plasticizer for the PVC, chemical linkers, and some other processing aid additives [8].

A possible solution to effectively address these issues is to use a coated-fabric composite made of a single material—single-polymer composite—called all-polyamide composite-coated-fabric (APCCF), which is mechanically stronger and thermally stable and weighs less than PVCCF [9]. Additionally, APCCF is fully recyclable as it contains only a single material [PA] that is prepared by adhesion of the PA fabric and the PA solution made out of waste, making them a cost-effective and eco-friendly material [9]. In the perspective of environmental sustainability, the recycling of fabric and textiles decreases the use of natural resources, such as water or petroleum, that are being used for generating new fabric or textiles [10]. It also lowers the extent of chemical usage and the associated pollution that is encountered during the textile manufacturing process [11]. Currently, the most common method of recycling textiles is to use them as composite filler [12]. This method is however not effective as they do not maintain the quality or properties of the composites [13]. Hence, the development of a fabric-based bioreactor using recycled textile opens up the possibility of resource recovery and energy balance for an economically sustainable biofuel process.

This study hence introduces a novel and first-of-its-kind ‘single-polymer composite-based bioreactor, which is made from recycled textile or fabric waste. The potential application of APCCF bioreactor in a conventional ethanol industry was achieved by using it as a bioreactor for biofuel production using yeast and fungi to convert sugar and organic waste streams (thin stillage or vinasse) into valuable products (ethanol and protein-rich fungal biomass). A series of material performance analysis together with an economic analysis were also carried out to compare the performance and cost-effectiveness of APCCF-based bioreactor with the conventional bioreactors.

2. Materials and Methods

2.1. Material

Formic acid that was used in this study was supplied by Sigma-Aldrich (Saint Louis, MO, USA, ACS reagent grade, >98%). Acetic acid, ethanol, DL-lactic acid, glycerol, butyric acid, and acetone were purchased from Sigma-Aldrich and were used without further modifications. The PA66 plain woven fabric was provided by a local supplier. The PA66 fibre production waste from the weaving process at a local Swedish textile company (FOV Fabrics AB, Borås, Sweden) was used as a polymer source. Sugar-to-ethanol industry waste stream, vinasse, was provided by Sepahan Bio-product Company (Isfahan, Iran). Thin stillage, a residual product from the wheat-based first-generation ethanol facility, was provided by Lantmännen Agroetanol (Norrköping, Sweden). Both of the substrates were used directly without any further laboratory treatment and were stored at 4°C cold room prior to its use. Detailed chemical characteristics of vinasse and thin stillage are described in previous studies [14].

2.2. Composite Material and Reactor Design

All-polyamide composites were prepared in the form of a flat laminate on the substrate fabric following an isothermal immersion-precipitation non-solvent induced phase separation (NIPS) method, according to our previous report [9]. The glass plate (carrying the fabric and a layer of the PA solution) was immersed in a distilled water bath at room temperature to induce polymer precipitation (phase separation) at the end of the casting process. The coagulation process (in the water bath to obtain the composites) was prolonged for 1 h, following which the composites were washed with distilled water (consecutively for at least 3–4 times) and were subsequently held under the filter-paper press to remove the moisture. The composites (hereafter referred to as APC sheet) were further dried at 55°C in a vacuum oven (≈0.1 bar) for 2 h. For the lab scale APCCF bioreactor design, the APC sheets were attached at their sides and were glued using a commercial adhesive—Universal Power Epoxy (Loclur, Düsseldorf, Germany) to attain the shape of the bioreactor. To assure the adhesion, the adhesive-containing edges were placed under a hot press (60°C and 220 kN) for 15 min. The detailed design of the fabric reactor is depicted in Figure 1. As the APCCF is made of PA, which is known as a thermally-resistant polymer, sterilization using heat (autoclave condition) will not have any detrimental effect on the properties of the composite. The thermal stability properties of the APCCF are tabulated in Figure 2. The reactor did not have any frame; hence, made as a stand-alone bioreactor. The cap (inlet/outlet) was a polyethylene bottle cap glued to the bioreactor using epoxy adhesive.

Figure 1. (a) Schematic of the laboratory scale prototype of the all-polyamide composite-coated-fabric (APCCF) bioreactor; (b) General schematic representation of APCCF bioreactor.
with a 5kN load cell and a special grip for films, using a crosshead speed of 5 mm/min. The gauge with the diameter of 35 mm was placed in the cell, filled with 25 mL ultrapure water, with subsequent APCCF and PVCCF, the PVCCF was prepared according to the method previously reported [8]. The thickness of the composites was measured by Elastocon thickness meter (Elastocon AB, Brämhult, Sweden). A minimum of five test bodies was tested for each material. The specimens were all cut in the warp direction of the fabric. To conduct the tensile strength comparison between the composites, the most possible accurate weight, and the volume was measured by a graduated cylinder containing distilled water. Five specimens were tested for each composite.

Characterization of the Reactor Material

The water impermeability of the APCCFs was analysed using a dead-end diffusion cell. AP sheet with the diameter of 35 mm was placed in the cell, filled with 25 mL ultrapure water, with subsequent pressure (in the range 0.5, 1, 1.5, 2, and 2.5 bar) being applied to the cell using nitrogen gas. The APCCF volume. Measurements of the composites' weights were performed by using a balance to determine the most possible accurate weight, and the volume was measured by a graduated cylinder containing distilled water. Five specimens were tested for each composite.

The aging test was performed in the following way: a piece of sample from either PVCCF and APCCF (70 mm x 20 mm) were cut with normal scissor and were placed in six different media, including acetic acid, ethanol, DL-lactic acid, glycerol, butyric acid, and acetone, all used in 100% purity. The beakers containing the samples and the media were kept at the room temperature for 14 days. Then, the samples were taken out, washed three times with distilled water subsequenty three times with acetone. Then, the samples were dried in a ventilated oven at 50 °C for 24 h. The samples were analysed using the tensile strength testing machine and thermogravimetric analysis (TGA) Q500 machine (TA Instruments, MA, USA). About 10 mg of the material was heated from room temperature to 600 °C at a heating rate of 10 °C/min in a nitrogen purge stream.

2.3. Yeast Fermentation

Dry yeast red yeast (Saccharomyces cerevisiae) from Fermentis (Strasbourg, France) was used to carry out the yeast fermentation experiments. A starting concentration of 10 g/L of the dry yeast was used for the process. Fermentation was performed in a 2 L laboratory scale prototype of the bioreactor with a working volume of 1 L at 30 °C. The dimensions of the bioreactor were 25 cm length, 20 cm breadth, and 4 cm width. A schematic of the lab scale prototype is shown in Figure 1a. Sucrose (280 g/L) was used as energy and carbon source, while 7.5 g/L (NH4)2SO4, 3.5 g/L KH2PO4, 0.75 g/L MgSO4 7H2O, and 1.0 g/L yeast extract were also added to supply additionally needed nutrients. Sucrose concentration dropped to 293.3 ± 1.5 g/L after the feed was autoclaved. Temperature control was carried out using a GD 120 grant thermostatic circulator (GD Grant Instrument Ltd., Cambridge, UK). The thermostatic circulator was connected to a 4 m PVC tubing, which was wound eight times and was placed at the bottom of the bioreactor to maintain the desired temperature.

2.4. Fungi Cultivation

A filamentous fungus Neurospora intermedia CBS 131.92 (Centraalbureau voor Schimmelcultures, Utrecht, The Netherlands) was maintained on potato dextrose agar (PDA) slants containing (g/L): potato extract 4, D-glucose 20, agar 15, and the plates were renewed every six months. For the regular experimental purpose, the fungus was transferred to fresh PDA plates. The lab scale prototype of the incubated aerobically for three to five days at 30 °C. For preparing spore suspension, fungal plates were flooded with 20 mL sterile distilled water and the spores were released by gently agitation the mycelium with a disposable cell spreader. An inoculum of 50 mL spore suspension per L medium with a spore concentration of 6.3 ± 0.8 x 10^6 spores/mL was used for the cultivations. The fungal cultivations were carried out aerobically in thin stillage, and vinassee using 3 L capacity APCCF bioreactor, with a total working volume of 2 L. Aeration at the rate of 1.0vvm (volumeair/volumefermentation/mL/min) was maintained throughout the cultivation, using a perforated sparger with a pore size of 100 µm. Filtration of the inlet air was achieved by using a membrane filter (0.1 µm pore size, Whatman, Florham Park, NJ, USA). Samples were collected every 24 h and were stored at 4 °C until analyses (unless otherwise specified). Temperature control was carried out using a GD 120 grant thermostatic circulator (GD Grant Instrument Ltd., Cambridge, UK). The pH was adjusted with either 2 M HCl or 2 M NaOH. All of the experiments and analyses were carried out in duplicate and the results were reported with error bars and intervals representing two standard deviations.

2.5. Fermentation Analyses

High-Performance Liquid Chromatography-HPLC system (Waters 2695, Waters Corporation, USA) was used to analyze all liquid fractions from the fermentation experiment. A hydrogen-based ion-exchange column (Aminex HPX-87H, Bio-Rad Hercules, CA, USA) at 60 °C with a Micro-Guard guard column (Bio-Rad) and 0.6 mL/min 5 mM H2SO4 (eluent), was used with a refractive index detector (WatersS2414, Waters Corporation, Millford, MA, USA) and a UV detector (Waters 19487). The samples that were used for the HPLC analysis were centrifuged for 10 min at 10,000 × g and the liquid portion stored for analysis. The samples were stored at −20°C prior to HPLC analysis. All of the experiments and analyses were carried out in duplicate and the results are reported with error bars.

Figure 2. Comparative onset decomposition temperatures for polyvinyl chloride (PVC) coated-fabric (PVCCF) and APCCF samples in different conditions (un-aged: before the ageing test, the rest are corresponding to ageing the samples in various mediums). The dark-black corresponds to ‘before ageing’ and the grey columns correspond to the ‘aged samples’.
and intervals representing two standard deviations. The yield from the fermentation experiment was calculated using concentration values after autoclaving, as reported by the HPLC.

2.6. Economic Analysis

The investment cost that was needed for procurement of stainless steel, the predominating material of construction for the conventional bioreactors used by the industries [3], was estimated using Equation (1):

\[
C = F_m \exp[11.662 - 0.6104 \ln(V) + 0.04536 (\ln(V))^2]
\]

(1)

where \(C\) is cost ($), \(F_m\) is 2.4 for 304 stainless steel and \(V\) is volume (gallons) [15]. The procuring cost of the stainless steel reactors was updated to 2017 using the projected Chemical Engineering Plant Cost Index (CEPCI) for 2017, which was 574.1, based on the current low oil price [16]:

\[
C_{updated} = C \left( \frac{I_{updated}}{I} \right)
\]

(2)

The purchasing cost of the fabric material for reactor construction was obtained from the estimates at a local textile company in Borås, Sweden. The investment cost in the bioreactor is a key part of the capital expenditure on the fermentation or waste-to-product transformation process. It influences the cost of handling waste or production of the desired products, as shown in Equation (3) [17], where \(FC\) is the cost of feedstock ($/tonnes), \(Y\) is product yield ($/tonne), \(ACE\) is the annual capital expenditure ($/m²), \(OC\) is the operation cost ($/m³), \(Ye\) is the electricity yield (kWh/m³), and \(EC\) is electricity credit ($/kWh):

\[
\text{Annual production cost (APC) = FC/Y + (ACE + OC)} - Ye \cdot EC
\]

(3)

3. Results and Discussion

To overcome the challenges that are associated with the conventional microbial bioreactors, a robust polymer composite (APCCF) was used to prepare the textile bioreactor in this study. A PA-coated PA fabric single-polymer composite (based out of PA66) was prepared in the study to address the issues surrounding the current coated-fabrics (material of construction of textile-bioreactors (TBs)), such as the recyclability, the adhesion between the coating, and the fabrics. This was achieved by applying the PA66 solution to the PA fabric using a universal film applicator with subsequent coagulation in a water bath, to induce phase separation (phase inversion). Hence, a composite composed of a thin continuous PA layer (the coating) and a PA textile fabric encompassing the most common type of aliphatic polyamide (PA66) was obtained, which forms the base material for the APCCF bioreactor.

3.1. Material Development

Mechanical stability of materials that are used for constructing bioreactors is generally of high importance [3]. Both stainless steel and concrete, which are conventionally being used for bioreactor construction, have got higher level of tensile strength than any available commercial polymer. The fabric-based bioreactor possesses several merits, such as being cost-effective, less time consuming to install, easiness with transportation, and foldability. However, the bioreactors made from PVCCF will have several challenges, such as being susceptible to shear stresses, and in some cases, the delamination (detaching of the coating from the fabric). The results from this study suggest that in the all-polyamide composite-coated-fabric (APCCF), the mechanical properties have been improved (Table 1). Hence, it was clear that the APFCF has superior mechanical properties (increase by around 20%) than the PVCCF. This could be attributed to the nature of the polymers. PA generally contains amide groups that have several challenges, such as being susceptible to fast-breaking. Hence, the APCCF could be more robust, resulting in an extended lifetime for the APCCF bioreactor material.

Table 1. Comparison between the tensile strength properties of PVC-coated polyester fabric (PVCCF) and all-polyamide composite-coated-fabric (APCCF). Un-aged samples are the ones before ageing.

<table>
<thead>
<tr>
<th>Medium</th>
<th>PVCCF</th>
<th>APCCF</th>
</tr>
</thead>
<tbody>
<tr>
<td>un-aged</td>
<td>57.2 ± 2.19</td>
<td>68.6 ± 1.77*</td>
</tr>
<tr>
<td>acetic acid</td>
<td>49.8 ± 1.71</td>
<td>63.2 ± 1.21</td>
</tr>
<tr>
<td>acetic acid</td>
<td>52.5 ± 2.3</td>
<td>67.3 ± 1.9</td>
</tr>
<tr>
<td>butyric acid</td>
<td>53.1 ± 1.8</td>
<td>65.7 ± 1.61</td>
</tr>
<tr>
<td>ethanol</td>
<td>55.3 ± 1.6</td>
<td>67.4 ± 1.2</td>
</tr>
<tr>
<td>lactic acid</td>
<td>51.2 ± 1.4</td>
<td>63.1 ± 2.1</td>
</tr>
<tr>
<td>glycerol</td>
<td>55.1 ± 1.7</td>
<td>68.1 ± 1.4</td>
</tr>
</tbody>
</table>

* The numbers after ‘*’ represent the standard deviations.

In the ageing test, the APCCF as well as the PVCCF, were kept in six different organic solvents, which are the most commonly produced metabolites in the microbial processes [20]. According to the results (Table 1), in all of the test solvents, both APCCF and PVCCF were affected with a decline in its mechanical properties; however, in all of the cases, the decrease in tensile strength value for the APCCF were lower than the one for the PVCCF. For acetic acid, which is the second strongest unmodified organic acid (after formic acid), the PA chain was found interacting with acetic acid molecules. According to Chen et al. [21], there is an interaction between acids and the PA polymer at the surface. The aforementioned interaction can weaken the intramolecular interactions, as each of the amide groups can only have two hydrogen bonding interactions with other amide groups. While there is better hydrogen bonding between donor/acceptor exists in the vicinity of the surface PA chain, the amide groups prefer them and loosen the previous interaction with the inner PA chains. In this case, acetic acid is a better hydrogen bonding acceptor (due to having a partially negative charge on the oxygen in its carbonyl) and a better hydrogen bonding donor from the acidic hydrogen. Apart from this interaction, as PA can behave like a base, there could be another interaction in the form of acid/base interaction. Both of these two interactions decrease the internal chains (from the surface towards the bulk of the polymer), which leads to the decrease in crystallinity of the polymer, which in turn decreases the tensile strength value. This is the case with other acids (lactic/butyric acid) with the difference in the intensity of the effect.

Butyric acid has the same structure similar to acetic acid, with a longer hydrophobic chain, which in this case, decreases the hydrogen bonding ability. The lower hydrogen bonding ability is due to having a longer electron-donor alkyl group that decreases the density of partially positive charge on the carbon atom in the carbonyl group, which in turn decreases the difference in charge density between carbon and oxygen in the carbonyl group. Furthermore, the longer aliphatic chain decreases the mobility of the molecule and creates a bigger repellence between the butyric acid molecule and the PA chain, which leads to less interaction between them [22]. Less interaction between the PA and butyric acid means that more intramolecular interactions will remain. Hence, the crystallinity will be changed less. It can be confirmed with the tensile strength values in Table 1.

For the case of lactic acid, although it has a longer aliphatic chain than acetic acid, it has one more hydrogen bonding site—hydroxyl group—which will increase the interactions between lactic acid and PA. That might be the reason of a lower measured value for lactic acid than acetic acid in tensile strength testing. The values for ethanol and glycerol are reasonable with the above proposal; however, for acetic acid, which has less hydrogen bonding ability when compared to all of the other five solvents, the decrease in the tensile strength value should not be more than the one for glycerol, if the above proposal is correct. We assume that there might be other interactions involved between acetone and PA, which needs to be elaborated in a separate study. Although the action of the chemical substances towards the materials of construction of the bioreactor might be weak
(as cultivation media mainly consists of water), we used the pure chemicals to accelerate the ageing process. Since the ageing study was a comparative-based study between APCCF and PVCCF, the effect of the chemicals’ concentration would be the same for both composites. Hence, the results could be assumed as meaningful findings.

PVC is also affected by protic and polar solvents [23]. The reason for more decrease in tensile strength value for PVCCF when compared to APCCF in different mediums could be related to the reason that PVC contains a soft chlorine ion in its structure, which increases the tendency of establishing hydrogen binding between the surface PVC chains and the medium surrounding it. Also, PVC in nature is a more amorphous polymer when compared to PA [24,25], which makes it more susceptible towards surrounding chemicals/medium.

Figure 2 shows the TGA results for the un-aged samples and the samples that are aged in six different solvents. Similar to the above proposal for the tensile strength testing, in all of the cases, there is a decrease in the onset decomposition temperature (ODT) value after ageing, which could be related to the hydrogen bonding (discussed above). Although the differences are not significant, the decrease in ODT values for APCCF samples are less than the ones for APCCF, meaning that APCCF has superior thermal stability. Though the textile bioreactor will never experience those high temperatures (e.g., 300–400 °C), having a higher ODT value (both in un-aged and aged samples) will give a better long-term stability to the APCCF [26]. From the tensile strength testing and TGA results, both in the un-aged sample and in the aged samples in different mediums, we can conclude that APCCF is a better candidate for making textile bioreactor than PVCCF. As the APCCF has the ODT (371 °C) above the autoclave temperature (121 °C), one can assume that the APCCF as an ‘autoclave-proof’ material.

PA is a polymer containing monomers of amides joined by peptide bonds. They can either occur naturally (for instance, proteins such as wool and silk) or can be made artificially, for example, nylons, aramids, and sodium poly (aspartate). According to McCrum and Buckley [27], in general, polyamides presents a proper conciliation between toughness and strength with a low coefficient of friction and high thermal resistance (melting temperatures above 200 °C and thermal deflection—under low load superior to 160 °C). Using this polymer can hence impart superior properties to the fabric bioreactor rather than using other commercially available polymers. Polyamide 66, with its high abrasion properties together with the high strength, can be considered as the most suitable candidate polymer for the development of fabric bioreactor. Polyamide 66, hence imparts high strength (withstanding the high pressure of fermentation media inside the reactor), as well as enough chemical resistance towards the chemical or biological process occurring within the reactor.

Figure 3 demonstrates the cross-sectional morphology of the two coated-fabrics. One can observe that only a few of the fibre-filaments in the PVCCF are attached to the coating, while in the APCCF, almost all of the fibre-filaments in the first row of the side of the fabric facing to the coating are adhered to the coating as well as adhering to each other. Adhesion on coating industries plays a crucial role [28]. If the adhesion is not good enough, then the coating will be detached from the fabric after a certain time, called delamination [29]. In our case, the adhesion is much enough for the first-row fibre-filaments to be fused to each other. The fibre-filaments not only are adhered to the coating but are also fused to each other making the coating stronger.

Figure 4 shows the comparative density of the PVCCF and APCCF. PVCCF is composed of two main ingredients, PVC and polyester, which are heavy in comparison with other conventional polymers [30]. PVC and polyester are both heavier (in volume/mass unit) than PA—the sole ingredient of the APCCF, making APCCF a lighter material. The decrease in density (by around 16%) shows that the transportation cost of the bioreactor would be lower and also it would be easier. On the other hand, the total weight of the reactor in case of using APCCF as the material of construction of the bioreactor would be less than the cost of the PVCCF one.
PA chains contain amide groups (a weak organic base), so they are not susceptible to mild acidic conditions (up to pH > 3), that represents the pH conditions of most fermentation media (pH 5–7). In this regard, polyolefins (polyethylene and polypropylene) are also comparable with polyamides; however, they are not readily soluble, unlike polyamides, hence posing potential challenges during the production process. Another excellent property of PA that makes it the sole material for the single-polymer composite is its thermal stability. Due to the presence of nitrogen along with the hydrogen atoms on each polymer chain, they pose strong hydrogen bonding that hinders the disentanglements of the chains, which in-turn limits the thermal decomposition of the polymer. However, the argument that the fabric-based bioreactor will never experience high temperatures (more than 40–50 °C), which also eliminates the need to consider the onset thermal decomposition temperature for this material, could remain valid. Nevertheless, the long-term exposure of the industrial scale APCCF bioreactor to the atmospheric temperature (around 35 °C) could be considered since the polymers will thermally decompose both at high temperatures (for the relatively short time) and also at moderate/low temperatures for a longer exposure time. In this regard, the use of material such as PA66, with a higher thermal resistance will guarantee a longer shelf-life for the bioreactor. Additionally, in an environmental perspective, the use of single-polymer composite material (i.e., PA66) that is recycled from the textile industry presents the opportunity for making the fabric based reactor an environmentally sustainable product.

3.2. APCCF Bioreactor for Valorization of Waste-Stream from Conventional Ethanol Industries

Introduction of the APCCF bioreactor to the conventional ethanol industries that follows either starch or sugar-based processes was achieved by using edible filamentous fungi. The use of filamentous fungi for generating value-added products from ethanol industry waste streams, such as thin stillage (from the starch-based process) or vinasse has been previously studied in conventional bioreactors [14]. Comparable results were obtained from the present study using the fungus Neurospora intermedia, proving the potential application of fabric bioreactor (APCCF bioreactor) for filamentous fungi cultivation. The results from the fermentation of thin stillage and vinasse in the fabric are depicted in Figure 5. Fermentation of thin stillage resulted in the formation of 3.5 ± 0.3 g/L of dry weight fungal biomass corresponding to a biomass yield 24.6% from the total fermentable sugar, which is comparable to 4 g/L of dry weight biomass obtained from bubble column bioreactor that used thin stillage for a continuous cultivation process [14]. An ethanol maximum of 4.9 ± 0.6 g/L was observed at the cultivation time of 36 h with a high rate of fermentable sugar assimilation within the first 24 h of fungal growth (93.3% reduction). Similarly, the fermentation of vinasse at a dilution rate of 10% resulted in the formation of 8.5 ± 0.7 g/L of dry weight fungal biomass. The higher fungal biomass production in vinasse could be attributed to the presence of essential mineral components that are present in it, which support prolific fungal growth. As opposed to the thin stillage cultivation, a much slower sugar assimilation rate was observed with vinasse, with only 22.2% reduction within the first 24 h. However, the complete utilization of the fermentable sugar was observed within the next 12 h, with no sugar being left after 36 h of the cultivation time (Figure 5). Cultivations at the pilot scale APCCF bioreactor resulted in the growth of fungal biomass that attributes for a total crude protein content of 51%.

3.3. APCCF Bioreactor for Conventional Ethanol Production

Fermentation was carried out in the lab scale prototype of the APCCF bioreactor at 30 °C and pH of 6.0 ± 0.2 using the ethanol-producing yeast as explained in Section 2.3. The result of the fermentation is shown in Figure 6. Ethanol yield 96.3% of the theoretical maximum was attained using average ethanol concentration during the stationary phase. Ethanol specific productivity and substrate-specific consumption rate of 4.0 g/L/h and 0.7 g/g/h were attained in the bioreactor, which are comparable to the reported values from sugarcane-based ethanol production facilities [31,32].
3.4. Economic Evaluation and Cost Comparisons

A cost-competitive bioreactor installation is one of the many opportunities that are currently evaluated to create an economically sustainable biofuel process. The procuring cost of conventional stainless steel bioreactor vessels at different volumes was estimated using Equations (1) and (2), as depicted in Table 2. Similarly, the procuring cost of varying textile bioreactor volumes is also shown in Table 2. It can be observed that the textile bioreactor capital investment cost is at least thrice less expensive than the cheapest of the stainless steel reactor that meets the requirements of a bioreactor, which is 304-stainless steel.

Table 2. Comparative procurement cost for APCCF bioreactor and 304-SSBR vessels.

<table>
<thead>
<tr>
<th>Reactor Size (m³)</th>
<th>Purchase Cost of Developed TBR ($)</th>
<th>Purchase Cost of 304 SSBR ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>25,000</td>
<td>108,000</td>
</tr>
<tr>
<td>200</td>
<td>35,000</td>
<td>137,000</td>
</tr>
<tr>
<td>300</td>
<td>45,000</td>
<td>160,000</td>
</tr>
<tr>
<td>400</td>
<td>58,000</td>
<td>181,000</td>
</tr>
<tr>
<td>500</td>
<td>66,000</td>
<td>200,000</td>
</tr>
</tbody>
</table>

The estimated operation and investment cost of a stainless steel reactor is 1.7 times of its procurement cost after it has been installed [15], while that for a fabric bioreactor is 1.5 times of its procurement cost for a 15 year period [13]. This contributes to the annual production cost, as shown in Equation (3). Assuming that the production facility requires a 500-m³ bioreactor for producing the desired product, and the capital expenditure is depreciated using straight-line depreciation for 15 years. The developed bioreactor would contribute $7700/m³/year to the annual production cost, while the procurement cost after it has been installed [15], while that for a fabric bioreactor is 1.5 times of polyamide fabric, the PVC-coated polyester fabric and the polyamide 66 scraps. This project was financially supported by University of Borås, Borås, Sweden and FOV Fabrics AB.

4. Conclusions

A textile-bioreactor, prepared using the industrial waste polymer (all-polyamide composite coated-fabric (APCCF)), was introduced in this study. The tensile strength testing, density measurements, ageing test, and thermal stability analyses showed that the APCCF poses superior characteristics than the PVCCF—the material that is currently being used to prepare the conventional textile-bioreactors. Hence, APCCF could be considered as a better candidate for the material of construction of the textile-bioreactors. Introduction of the APCCF bioreactor to the ethanol industry was achieved using a reduction of the annual production cost by $128,000,000. In an environmental perspective, the use of single-polymer composite material (i.e., polyamide 66) that is recycled from the textile industry, presents the opportunity for making the fabric-based bioreactor an environmentally sustainable product.

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Author Contributions: M.J. developed and designed the bioreactor; M.J., R.B.N., and O.A.O. conceived, designed, and performed the experiments; M.J., O.A.O., and R.B.N. contributed to analyzing the data and writing the paper; M.J.T. supervised the study and revised the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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Research Article

New Solvent for Polyamide 66 and Its Use for Preparing a Single-Polymer Composite-Coated Fabric

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Polyamides (PAs) are one of the most important engineering polymers; however, the difficulty in dissolving them hinders their applications. Formic acid (FA) is the most common solvent for PAs, but it has industrial limitations. In this contribution, we proposed a new solvent system for PAs by replacing a portion of the FA with urea and calcium chloride (FAUCa). Urea imparts the hydrogen bonding and calcium ion from the calcium chloride, as a Lewis acid was added to the system to compensate for the pH decrease due to the addition of urea. The results showed that the proposed solvent (FAUCa) could readily dissolve PAs, resulting in a less decrease in the mechanical properties during the dissolution. The composite prepared using the FAUCa has almost the same properties as the one prepared using the FA solution. The solution was applied on a polyamide 66 fabric to make an all-polyamide composite-coated fabric, which then was characterized. The FAUCa solution had a higher viscosity than the one prepared using the neat FA solvent, which can be an advantage in the applications which need higher viscosity like preparing the all-polyamide composite-coated fabric. A more viscous solution makes a denser coating which will increase the water/gas tightness. In conclusion, using the FAUCa solvent has two merits: (1) replacement of 40% of the FA with less harmful and environmentally friendly chemicals and (2) enabling for the preparation of more viscous solutions, which makes a denser coating.

1. Introduction

Aliphatic polyamides (PAs), also called nylons, are a class of semicrystalline polymers that contain amide groups which are intercalated along linear alkane chains [1]. Solution processing of aliphatic PAs is quite challenging due to the fact that only a few solvents, such as formic acid (FA) and cresol [2] or fluoric solvents [3], can dissolve them. All of the solvents being used for the dissolution of PAs have severe environmental challenges. A few attempts have been made [2] to replace the existing solvents or propose new solvents. Papadopoulos et al. [2] mixed FA with trifluoroacetic acid and acetone. Charet et al. [4] studied the crystallization and dissolution behavior of polyamide 6-water systems under pressure. Nirmala et al. [5] used FA (85 wt%), acetic acid, dichloromethane, 1,1,1,3,3,3-hexafluoro-2-propanol, trifluoroacetic acid, and chlorophenol in their study. Basically, dissolving PAs is difficult due to two reasons: (a) polyamides are highly crystalline, whereas the above treatment holds for amorphous polymers, and (b) solvents for polyamides are believed to act by virtue of strong, highly specific polar forces [6].

Polyamide (PA) is a well-known high-performance engineering plastic (technical thermoplastic [7]) with high strength and good fatigue resistance [8] and excellent mechanical and physical properties, which is why it is increasingly used in industrial machinery [7]. Nylon is the common name of linear aliphatic PAs. Nylons are important commercial polymers, with uses ranging from fibers to cooking bags to coatings [9], carpets, upholstery, and apparel [10].

Coated fabrics are flexible composites, consisting of a fabric substrate and a polymeric coating [10]. The coating could be on one side or on both sides, with either the same or different polymeric coating per side [10]. Coated woven fabrics are used in a wide range of structural applications to provide lightweight, architecturally striking solutions [11]. The physical properties of a coated fabric depend on the specific properties of the substrate, coating
formulation, coating technique, and processing conditions during coating [10]. There are two primary types of coated woven fabric: a glass fiber fabric with a PTFE (polytetrafluoroethylene) coating and a polyester fabric with PVC (polyvinyl chloride) coating [12]. Both PTFE- and PVC-coated fabrics are employed today in different types of tents and architectural membrane structures all over the world [13]. As the fabric is prepared from a high-crystalline polymer (spun fiber), it can resist environmental loads, as tensile stresses in the plane of the fabric [12]. These fabrics are popular mainly due to their affordable prices, low durability resistance to wear and tear, various colors, and soft texture [11]. They are often used for wide-span surfaces, membrane-cable structures, and pneumatic constructions [11]. One recent application of coated fabrics is for a textile bioreactor, which is a vessel to conduct the biological processes (fermentations) [14]. The PVC-coated fabric was the first material proposed for this purpose. The recent promising candidate was the all-polyamide composite-coated fabric (APCCF), which showed superior properties over the former one [14]. However, using a high amount of formic acid as the solvent is still one industrial challenge for scaling-up the production.

The aim of this paper was to introduce a new solvent based on the replacement of FA with urea, calcium chloride (industrially abundant chemicals), and water to produce an all-polyamide composite-coated fabric from a PA by solvent casting of only one component to have strong adhesion between the coating and the fabric as well as enhanced recyclability.

2. Material and Methods

2.1. Materials. The formic acid, urea, and calcium chloride used in this work were supplied by Sigma-Aldrich (ACS reagent grade) and polyamide 66 (PA-66) (70 grams per square meter (gsm)) was provided by FOV Fabrics AB (Boras, Sweden). As a polymer source to produce a solution, PA fiber fabrication production waste from the weaving process at FOV Fabrics was used.

2.2. Solvent Preparation. The solutions were prepared by adding 35 g of PA waste scraps into 100 g solvent mixtures, which, in turn, were obtained by mixing different amounts of formic acid (FA), urea (U), calcium chloride (Ca), and distilled water (W) at room temperature, according to the values tabulated in Table 1. For the cases that had more urea and calcium chloride, it took a while (1–3 minutes) to get a clear solution.

2.3. Composite Preparation. All-polyamide composites were prepared in the form of a flat laminate on the substrate fabric using an isothermal immersion–precipitation method. The solutions were filtered using a Millipore (Bedford, MA, USA) 0.45 μm PTFE filter. The filtration was done by trying to keep the percentage of the FA as low as possible. The PA, it can disrupt the intermolecular interactions (H-bonding) with the amide groups in PA, and 15% elongation at max, respectively. Scanning electron microscopy (SEM) was used to monitor the fracture surface morphology of the cross sections of the composites and to check the adhesion between the coating (the FA film) and the fabric. The specimens were obtained by quenching in liquid nitrogen and breaking by hand. As the samples contained fabric, using only quenching will not do. As the samples contained fabric, using only quenching will not do. Therefore, after quenching, the unbroken parts were cut by a sharp blade. The studied surface was patterned with a layer of gold before the measurements. SEM analysis was performed using a Philips XL30 (Philips, Eindhoven, Netherlands) operated at an acceleration voltage of 15 kV. The viscosity measurements were carried out with a Brookfield viscometer (MA, USA) at 40 °C. The tests were done according to the protocols in the literature. Thetemperature measurements were carried out using a JENWAY 3505 thermometer (Stadhouders, UK) at room temperature. The pH sensor was placed in the samples for 30 seconds while being stirred at 200 rpm to reach an equilibrium.

3. Results and Discussion

The most common solvent for polyamides is formic acid (FA), which is neither easy to handle. To replace a portion of the FA to make it more appropriate, more economical, and safer to handle solvent mixtures, different amounts of urea, calcium chloride, and water were mixed and the PA was perfomed. As the polymer chains decomposes the PA chains during the dissolution process. As a result, a composite composed of a thin continuous PA layer (the coating) and a PA fabric out of the most common type of aliphatic PA (PA66) was obtained. The precipitation was done using a bath of FA, which contains four hydrogen and can establish strong intermolecular interactions (H-bonding) with the amide groups in the PA, it can disrupt the intermolecular interactions (H-bonding) among the polymer chains, therefore resulting in an easier dissolution. In general, the dissolution of semicrystalline polymers such as polyamide composites involves several stages including (i) dissolution (decrystallization of crystalline domains, amorphous polymer swelling, and chain untangling) [17]. Formic acid (as the main solvent) has enough penetration power to penetrate the PA chain and to form a composite, which is a promising candidate was the all-polyamide composite-coated fabric from a PA by solvent casting of only one component to have strong adhesion between the coating and the fabric as well as enhanced recyclability.
the tensile strength values are not higher than those of the composite 100-0-0-0 (with pure FA). Although it might seem contradictory with the above proposal for increasing the tensile strength value, it could be the effect of the urea/calcium chloride content (and even water content) on the crystallization of the PA chains in the phase inversion process. Regarding the elongation at max, all the composites prepared from the new proposed solvent mixtures in this work have lower values compared to the 100-0-0-0 composite. This might be related to the effect of the localization of the paired electron on the amide groups of PA chains, which plays a role like a spacer [24] during the phase inversion process. We can conclude that the main reason for dissolving PA with the least possible decomposition/degradation is 60% (the sample 60-7-20-13).

3.2. Viscosity. The loss modulus is a measure of energy dissipation. In the region of the glass transition, molecular segmental motions are activated; however, motions occur with difficulty, described as the molecular friction that dissipates the energy. Although the hydrogen bond deactivates the movement through the material is less stiff, more force is dissipated as heat, increasing the loss modulus. However, after that region, as the chains are free to move (at the temperature higher than the glass transition temperature), much less energy is stored since the molecules can move with the force, resulting in a rapid decline in the storage modulus. As evident in Figure 2, in the sample prepared from pure PA, the maximum in the curve of the loss modulus decreases with the reduction in the amount of FA in the solution. The solvent 60-7-20-13 contains water, and there might be some water molecules left. As the water molecules can act as a plasticizer for polyamide [25], it could plasticize the polymer. More so, it might be related to the effect of higher density of hydrogen bonding on a urea-containing solvent (in 60-7-20-13) as well as the localization of the paired electrons of the amide groups from the PA chains. One of the main characteristics of PAs is the strong interchain interaction that arises from the hydrogen bonding between the amide groups on adjacent chains [26]. In other words, in the solution process, the amide groups from the PA chains meet a higher density of hydrogen bonding (offering by urea), leading to weaker intramolecular interactions among the PA chains, which, in return, decreases the interaction among them. Therefore, they have much more freedom to move in the solvent. This freedom increases the Brownian motion of the chains, which increases their distances from each other [27]. Finally, when they are about to change their phase from solution to solid (coagulation process in the latest hot), they come together in a relatively less-packed structure. Moreover, when they are less-packed in the solid form (having lower crystallinity), their Tg is slightly lower (Figure 2 for tan delta), and the peak of the loss modulus is seen at a lower temperature for a solution with a higher amount of urea. This proposed reason is intensified with the presence of calcium ion as a Lewis acid in a different way. Calcium ion has free orbital to localize the paired electrons of the nitrogen from the amide group of the PA chains; hence, the hydrogen bonding ability of the amide groups of the PA chains also decreases, and finally the same effect happens. The same trend is seen in the storage modulus as well as in the tan delta.

3.3. Viscosity. The viscosity values are different for various solutions (Figure 3). However, in all solutions, the viscosity value is higher than the one for the solution using only formic acid as a solvent (100-0-0-0). Regarding the merit of the increase in viscosity, during the process of making the APCCF, it was observed several times that when the viscosity of the solution is low, the formed film (coating) does not have enough coherency. It makes sense as it might be due to the less aggregation of polymer chains on top of the fabric and also letting the solution go through more into the fabric which is not favorable. Because, for the application of making the APCCF, only the surface of the fabric must be dissolved partially, not the whole fabric which will decrease the whole tensile strength of the composite, a solvation which has higher viscosity is more favorable for making APCCF as it makes a well-formed coating on top of the PA fabric. When the viscosity of the solution is low, the formed film does not have enough coherency. Comparatively, when the same percentage of PA solutions in different solvents gives a different viscosity and, on the other hand, the viscosity of around 4000 cP (for the solution 100-0-0-0) is enough to make a proper coating, the solution 75-8-17-0 (which has the highest viscosity value, around 10,500 cP) will use less polymer. Additionally, as the APCCF must be waterproof and be as tight as possible, the coating being formed from a higher viscosity solution will be denser and will increase the APCCF’s gas tightness. The reason for the difference in the viscosity values in different solutions could be related to the difference in the intermolecular interactions between the solvent’s molecules and the PA’s molecules. The ones that have a higher amount of urea have higher values in viscosity. This is due to the fact that urea can establish hydrogen bonding (up to four units) from two sides, which can make a bridge between two PA chains (two bonds from the solution side and two bonds from the other side). By establishing these four bidirectional hydrogen bonds, the fluidity of the PA solution decreases, which, in turn, increases the viscosity.

3.4. Morphological Properties. According to the scanning electron microscopic images of the cross section (Figure 4), in almost all the APCCF specimens, there is an excellent adhesion between the coating (formed film) and the fabric. In other words, the boundaries between the fiber of the fabric and the coating are not clear because they have faded due to the adhesion of the two components. It is obvious that a large part of the cross-sectional area of the fabric is dissolved, and the polymer chains are interdiffused with each other, enabling the APCCF to have a good adhesion between the coating and the fabric, both of which are made out of PA. Although higher surface dissolution helps to create a better adhesion between the fabric and the coating, it also disintegrates the fabric structure and changes the fabric, from being a fibrous form to an amorphous film. Fibers are spun and pose a high crystallinity and thus a good strength while the films are amorphous as they do not have enough time to rearrange their chains in a nice ordered way (fast coagulation in water). Therefore, converting PA from a highly crystalline form to a less crystalline (highly amorphous) form is not favorable from a mechanical point of view. The amount of the surface dissolution should be as low as possible to impart a good adhesion between the fabric

![Figure 1](image1.png)  
**Figure 1:** An exemplary stress-elongation max curve for the sample 60-7-20-13 (a), and the tensile strength and the elongation at max values for the composites (b).

![Figure 2](image2.png)  
**Figure 2:** Loss modulus, storage modulus, and tan delta for the composites prepared from the new solvents.

![Figure 3](image3.png)  
**Figure 3:** The viscosity values for the composites. The solution made from the solvent mixture 75-8-17-0 is the most viscous solution due to the intermolecular interactions between the ingredients of the solvent mixture and the polymer.
The preparation of all-polyamide composite-coated fabric (APCCF), a specific form of single-polymer composites, made through a phase inversion method using a new solvent is described. The solvent was obtained by replacing 40% of the FA with less harmful, cost-effective, more environmentally friendly, safer-to-handle, and industrially available chemicals: urea, calcium chloride, and water. The APCCF prepared in this work using the new solvent mixture does not have inferior properties over the one prepared through FA, such as mechanical and thermal properties. The prepared composite has a strong adhesion between the two constituents due to the use of the same polymer (PA66) in the constituents. The composite is fully recyclable since it contains no other materials except PA, which can be melted or dissolved and reused as a PA source. This might be related to the lower pH they have compared to the others, which have higher pH. However, the pH by itself is not a good criterion to judge the dissolution power of these solutions. For example, in the solution 35-6-48-12, which has a pH value very close to the pH of FA (~1.66 vs. ~1.74), the observation showed that the solution does not have a high power of dissolution. This might be related to the calcium chloride content (100 Ca/(FA + urea + W)), which is 92.59%, while the value is less than 25% in those showing “excellent” dissolution. The reason for this might be due to the effect of the counterion, chloride. Chloride is a relatively big ion. In lower numbers, they can help the dissolution; however, when they are increased, they most probably promote some interferences with the interactions of other ingredients (FA, urea, and water) with polyamide chains. Therefore, it could be concluded that the calcium chloride content should be less than 25%.

4. Conclusions

and the coating, but a higher dissolution is not favorable [11]. Using this new solvent helps the fabric’s surface to be partially dissolved more quickly, due to the higher hydrogen bond intensity (due to the presence of urea); hence, the adhesion between the fabric and the coating—the coating (formed film) on top of the fabric—would be stronger.

3.5. Thermogravimetric Analysis (TGA). The TGA curves showed almost the same values and shape (Figure 5). The only composite that deviates more from the rest is the 75-8-18-0, which tends to decompose slightly earlier than the others, though the difference is not significant. However, it has higher residue percentage compared to the rest of the composites (except the 64-7-14-14). Although PA66 is partially crystalline, all good solvents penetrate the crystallites, disrupting them completely [6]. Calcium ion (which is the acidic ion) is smaller than the urea molecule, resulting in an easier entrance to the crystallites. The final swollen gel is thus amorphous, even though the initial polymer is crystalline [6]. In the composite 75-8-17-0, the ratio of urea to calcium chloride (the source of calcium ion) is 0.5 (Table 2) and the ratio of U/FA is 0.11. These ratios are the same as those of the composites 69-8-15-8 and 64-7-14-4; however, their Ca/(FA + U + W) and U/(FA + Ca + W) are different. From the last two ratios and the TGA curves, it could be concluded that out of the four ingredients of the new solvent mixture (U, FA, Ca, and W), the ratio of U and Ca to the other ingredients should be kept as low as possible to have the least disruption of PA crystallites in order not to sacrifice the thermal stability. It is noteworthy that the composite 82-9-9-0, which has the same Ca/(FA + U + W) and U/(FA + Ca + W) ratios (equal to 10), has the lowest residue in the TGA curve, meaning that the closer the two ratios, the less the thermal stability of the composite.

3.6. pH Values and Observations. From the pH measurements, it is obvious and reasonable that the solutions that have a higher amount of FA have lower pH. The amine group -(NH2) in urea can accept a hydrogen ion, making it a basic substance. However, the carbonyl group -(C=O) offers a significant opportunity for resonance, which will stabilise the amine group, meaning that the paired electrons on N is in resonance. This means that urea is very slightly basic (and very close to neutral). However, in the presence of an acid, the basicity of urea increases (as there is plenty of H+ in the solution and the -(NH2) is converted to -(NH3+)). Hence, in the solution, urea is a base, so the reason for adding calcium chloride (which acts as a Lewis base) was to decrease the pH to make the solution as similar as possible to the pure FA solution. The highest pH is attributed to the solution 75-0-0-25 in which 25% of the water has increased the pH from ~1.74 to ~0.30. Basically, polyamides are polymers with a relatively high density of hydrogen bonds [1]. As PA is a weak acid, a solvent with acidic properties can protonate the amide group; consequently, the amide group will have less possibility to establish hydrogen bonding with other chains. Therefore, it will be easier for the solvent to swell into the polymer and dissolve it. In the first six solutions of the solutions tabulated in Table 2, it was observed that the solution 90-0-0-10 was excellent in terms of homogeneity and dissolution power. This might be related to the lower pH they have compared to the others, which have higher pH. However, the pH by itself is not a good criterion to judge the dissolution power of these solutions. For example, in the solution 35-6-48-12, which has a pH value very close to the pH of FA (~1.66 vs. ~1.74), the observation showed that the solution does not have a high power of dissolution. This might be related to the calcium chloride content (100 Ca/(FA + urea + W)), which is 92.59%, while the value is less than 25% in those showing “excellent” dissolution. The reason for this might be due to the effect of the counterion, chloride. Chloride is a relatively big ion. In lower numbers, they can help the dissolution; however, when they are increased, they most probably promote some interferences with the interactions of other ingredients (FA, urea, and water) with polyamide chains. Therefore, it could be concluded that the calcium chloride content should be less than 25%.

Figure 5: TGA curves of the composites prepared via the new solvent.
Table 2: Values for the pH and the relative components and also the observations.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>pH</th>
<th>U/Ca</th>
<th>U/Fa</th>
<th>100°U/(U + Ca + W)</th>
<th>100°Ca/(U + W)</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-0-0-0</td>
<td>–1.74</td>
<td>—</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>Excellent</td>
</tr>
<tr>
<td>60-7-20-13</td>
<td>–0.74</td>
<td>0.33</td>
<td>0.11</td>
<td>7.14</td>
<td>25.00</td>
<td>Excellent</td>
</tr>
<tr>
<td>64-7-14-14</td>
<td>–0.54</td>
<td>0.11</td>
<td>0.11</td>
<td>7.69</td>
<td>16.67</td>
<td>Excellent</td>
</tr>
<tr>
<td>90-0-0-10</td>
<td>–1.10</td>
<td>—</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>Excellent</td>
</tr>
<tr>
<td>90-10-0-0</td>
<td>–0.18</td>
<td>—</td>
<td>0.11</td>
<td>11.11</td>
<td>0.00</td>
<td>Excellent</td>
</tr>
<tr>
<td>82-9-9-0</td>
<td>–0.75</td>
<td>1.00</td>
<td>0.11</td>
<td>10.00</td>
<td>10.00</td>
<td>Excellent</td>
</tr>
<tr>
<td>69-8-15-8</td>
<td>–0.74</td>
<td>0.50</td>
<td>0.11</td>
<td>8.33</td>
<td>18.18</td>
<td>Good</td>
</tr>
<tr>
<td>67-4-30-0</td>
<td>–1.64</td>
<td>0.13</td>
<td>0.06</td>
<td>3.85</td>
<td>42.11</td>
<td>Good</td>
</tr>
<tr>
<td>82-0-0-18</td>
<td>–0.56</td>
<td>—</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>Good</td>
</tr>
<tr>
<td>75-8-17-0</td>
<td>–0.95</td>
<td>0.50</td>
<td>0.11</td>
<td>9.09</td>
<td>20.00</td>
<td>Good</td>
</tr>
<tr>
<td>75-0-0-25</td>
<td>–0.30</td>
<td>—</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>Fairly good</td>
</tr>
<tr>
<td>55-6-39-0</td>
<td>–1.69</td>
<td>0.15</td>
<td>0.11</td>
<td>6.43</td>
<td>65.00</td>
<td>Fairly poor</td>
</tr>
<tr>
<td>58-6-42-0</td>
<td>–1.61</td>
<td>0.20</td>
<td>0.17</td>
<td>9.09</td>
<td>71.43</td>
<td>Fairly poor</td>
</tr>
<tr>
<td>47-8-39-5</td>
<td>–1.50</td>
<td>0.20</td>
<td>0.17</td>
<td>8.57</td>
<td>65.22</td>
<td>Fairly poor</td>
</tr>
<tr>
<td>56-6-25-13</td>
<td>–0.91</td>
<td>0.25</td>
<td>0.11</td>
<td>6.67</td>
<td>33.33</td>
<td>Poor</td>
</tr>
<tr>
<td>50-6-28-17</td>
<td>–0.90</td>
<td>0.20</td>
<td>0.11</td>
<td>5.88</td>
<td>38.46</td>
<td>Poor</td>
</tr>
<tr>
<td>43-7-36-14</td>
<td>–1.08</td>
<td>0.20</td>
<td>0.17</td>
<td>7.69</td>
<td>55.56</td>
<td>Poor</td>
</tr>
<tr>
<td>38-6-43-3</td>
<td>–1.42</td>
<td>0.15</td>
<td>0.17</td>
<td>6.82</td>
<td>74.07</td>
<td>Poor</td>
</tr>
<tr>
<td>35-6-48-12</td>
<td>–1.66</td>
<td>0.12</td>
<td>0.17</td>
<td>6.12</td>
<td>92.59</td>
<td>Poor</td>
</tr>
</tbody>
</table>

*The markings were assigned based on the homogeneity of the solutions and the uniformity of the cast film on the glass.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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References

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Paper V
Computer-Aided Theoretical Solvent Selection using the Simplex Method Based on Hansen Solubility Parameters (HSPs)

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Abstract

Solvent selection is a crucial step in all solvent-involved processes. Using the Hansen solubility parameters (HSPs) could provide a solvent/solvent-mixture, but there are two main challenges: 1) What solvents should be selected? 2) From each solvent, how much should be added to the mixture? There is no straightforward way to answer the two challenging questions. This contribution proposes a computer-aided method for selecting solvents (answer to the question 1) and finding the adequate amount of each solvent (answer to the question 2) to form a mixture of 2, 3 or 4 solvents to dissolve a substance with known HSPs or to replace a solvent. To achieve this, a sophisticated computer software package was developed to find the optimized mixture using the mathematical Simplex algorithm based on HSPs values from a database of 234 solvents. To get a list of solvent-mixtures, polymide 66 was tested using its HSPs. This technique reduces the laboratory effort required in selecting and screening solvent blends while allowing a large number of candidate solvents to be considered for inclusion in a blend. The outcome of this paper significantly diminished the time of solvent development experimentation by decreasing the possible/necessary trials. Thus, the most suitable solvent/solvent-substitution can be found by the least possible effort; hence, it will save time and cost of all solvent-involved processes in the fields of chemistry, polymer and coating industries, chemical engineering, etc.

Keywords: Hansen solubility parameters; Solvent mixture; Solvent substitution; Simplex method; Linear programming; Quadratic minimization; Solvent screening

Abbreviations: H1CE:1,1-Dichloroethane; H2CE: 1,2-Dichloroethane; HCIP: Butyl-chloropropylene; HCE: Isobutylchloroethane; BC: Bromo-chloro-methane; 1,2: Dichloroethane; 1,1-Dichloro-ethylene; DCM: Dichloromethane; DCE: 1,2-Dichloroethane; THF: Tetrahydrofuran; DME: 1,2-Dimethylene glycol mono-Methyl ether; DGEOM: Diethylene glycol monoethyl ether; EG2M: Ethylene glycol monoMethyl ether acetate; MIAK: Methyl isoAmyl ketone; MMA: Methyl methacrylate; oxCB: 1,2-DichloroBenzen; oxDEP: o-MethylPhenol; PG: Propylene glycol; pC: Propylene chloride; TCF: Tetrahydrofuran; DMFD: 2,2,4-triMethyl-1,3-pentanediol

Introduction

Solvents, defined as substances able to dissolve or solvate other substances, are commonly used in many industries and applications [1]. For any solvent-based process, the best-suited solvent or solvent-mixture must be selected [2]. On the other hand, solvent selection and design is a complex problem, which requires decision making in several levels for identifying the best candidates depending on different multi-objective criteria namely environment, health, safety, process feasibility and economics [3]. Currently, solvent selection relies very much on previous experiences, trial and error with different solvent candidates. Use of experimental thermo-physical properties stored in a factual database for the selection has the advantage that the results are very reliable; however, solvent selection is limited to the experimental data pool [2]. Such heuristic approach while valuable on their own, however arguably are not fit to deal with a complex multi-criteria optimization and search problem, which is the case for solvent selection [3].

On the other hand, actual (physical) trials in the laboratory of mixing different solvents and checking the solvation, is a tough and time-consuming job. A number of modern tools are increasingly becoming available to reduce the efforts needed to select the right solvent [4]. The use of prediction models has the advantage that for the selection procedure, any solvent can be considered for which the required group interaction parameters are available and by using predictive methods, an extended variety of solvents can be taken into account for selection [2]. Solubility parameters have found their greatest use in the selection of solvents [5].

Although it is possible to find a solvent mixture based on Hansen solubility parameters (HSPs), the question is how one can screen the vast number of solvents to find the desired ones? Moreover, which solvents should be selected? Also, how much is the amount of each solvent (volume fraction) in the mixture? Selection of the appropriate solvents and finding the best volume fractions could be made by computer programming through minimization of $R_A$ formula (discussed in ‘background’ section), however, finding the minimum of $R_A$ takes much time for each set of solvents by normal linear programming. Because it has to sweep all the decimal values of the volume fraction from 0 to 1 for all the solvents, while by using the Simplex algorithm (discussed in ‘background’ section), it can be done within a few milliseconds, hence, more combinations of solvents would be taken into account for solvent selection.

Some authors proposed methods to find a proper solvent mixture for very specific applications like electro-spinning [6], however, a more general method applicable to a broader range of processes seems to be necessary to propose. Some publications use HSPs to predict solvent systems that are likely to dissolve, like Aghanouri and Sun [7], but they are empirically based and not computer-assisted, meaning that they...
Solubility parameters help put numbers into this simple qualitative idea [5]. Liquids with similar solubility parameters will be miscible, and polymers will dissolve in solvents whose solubility parameters are similar to that of the polymer. The Hansen model is usually considered as a sphere. The center of the sphere, R, is termed the solubility parameter distance. Its value less than R limits the dissolution possibility of solutes [9].

The basic principle has been "like dissolves like" [5]. By taking the solubility parameters of a solvent mixture is a linear function of composition. In this case, the composition value is to be calculated using solubility parameters for solvent mixtures is the volume fraction (φ) for each component (13). For a binary (two-solvent) mixture, the equation for all three solubility parameters is

\[
\delta_{blend} = c_1 \delta_{comp1} + (1-c_1) \delta_{comp2}
\]

(2)

where c1 and c2 are the weight fractions of the two solvents, and \(\delta_{comp1}\) and \(\delta_{comp2}\) are the solubility parameters of the components.

The Hansen space, as mentioned in the "code" section, the HS parameter values are known [13]. Traditionally, without specific data, it is usually assumed that there is no volume change upon mixing of solvents. That is

\[
R = \sqrt{\delta_{disp}^2 + \delta_{pol}^2 + \delta_{h}^2}
\]

(1)

where \(\delta_{disp}\), \(\delta_{pol}\), and \(\delta_{h}\) are the Hansen solubility components for the polymer/solvent (our favourite values), and \(\delta_{disp}^2 + \delta_{pol}^2 + \delta_{h}^2\) is the Hansen solubility for the solute [9].

The computer-assisted selection of solvents out of a vast number of solvents' HS parameter values stored in a database.

The core part of the program

```java
Dim solver = SolveContext.GetSolverContext()
Dim model = solver.CreateModel()

x1+Dx(1)+x2+Dx(2)+x3+Dx(3)+x4+Dx(4)+x5+Dx(5)+x6+Dx(6)

model.AddConstraint(sg1n1, x1+x2+x3+x4=1)

model.AddConstraint(sg1n2, x1+x2+x3+x4=1)

model.AddConstraint(sg1n3, x1+x2+x3+x4=1)

model.AddConstraint(sg1n4, x1+x2+x3+x4=1)

model.AddConstraint(sg1n5, x1+x2+x3+x4=1)

model.AddConstraint(sg1n6, x1+x2+x3+x4=1)

```

The sweeping loops

The aforementioned calculation is only for one single combination while we need to check all the possible combinations. To do this, we have to take the values of all the solvents in the database:

```java
For i=0 To NumberOfSolventsInDB - 3
For j=i+1 To NumberOfSolventsInDB - 2
For k=j+1 To NumberOfSolventsInDB - 1
For l=k+1 To NumberOfSolventsInDB
```

The sweeping loops

When we need to check all the possible combinations. To do this, we have to take the values of all the solvents in the database:

```java
For i=0 To NumberOfSolventsInDB - 3
For j=i+1 To NumberOfSolventsInDB - 2
For k=j+1 To NumberOfSolventsInDB - 1
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```

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For j=i+1 To NumberOfSolventsInDB - 2
For k=j+1 To NumberOfSolventsInDB - 1
For l=k+1 To NumberOfSolventsInDB
```

The sweeping loops

When we need to check all the possible combinations. To do this, we have to take the values of all the solvents in the database:

```java
For i=0 To NumberOfSolventsInDB - 3
For j=i+1 To NumberOfSolventsInDB - 2
For k=j+1 To NumberOfSolventsInDB - 1
For l=k+1 To NumberOfSolventsInDB
```
Next
For j=Me.i+1 To NumberOfSolventsInDB - 1
For i=0 To NumberOfSolventsInDB - 2


Results for PA66


Page 5 of 6

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therefore, more research is needed in this field to increase the quality of the proposed set of solvent-mixtures. As Jia studied [21], there is a relationship between HSPs and acidity of the polymers/solutes. Therefore, in the future studies in this regard, pKa/pKb values could be taken into account in order to get better results.

References
20.맡주 D, Boys D, Gargallo L (1977) Viscosity studies of some polyamides dissolved in mixed solvents (cosolvents). Polymer. 18: 121-123.
Finding Solvent for Polyamide 11 Using a Computer Software

Abstract: The solvent finding step has always been a time-consuming job in chemical-involved processes. The source of difficulty mainly comes from the trial-and-errors, as a repetitive process of choosing solvents and mixing them in different proportions. Computers are good at doing repetitive processes; however, they can only deal with numerical values, rather than qualitative scales. Numerification of qualitative parameters (like solubility) has already been introduced. The most recent one is the Hansen solubility parameters (HSPs). Using the HSPs could provide a solvent or solvent-mixture. In our previous study, we introduced a computer-aided model and a software to find a solvent mixture. In this study, we have used the computer-aided solvent selection model to find some solvent mixtures for polyamide 11, a biobased polymer which has attracted enormous attention recently. Using this numerical model significantly diminished the time of solvent development experimentation by decreasing the possible/necessary trials.

Keywords: Hansen solubility parameters; polyamide 11; nylon; solvent mixture; solvent screening; solvent substitution; the Simplex method.

1 Introduction

Solvents are inseparable elements in chemical-involved processes, from solar cells [1] to the production of biofilms [2]. Solvent selection and design is a complex problem, which requires decision making in several levels for identifying the best candidates depending on different multi-objective criteria namely environment, health, safety, process feasibility and economics [3, 4]. The conventional method of solvent selection is based on previous experiences, trial, and error with...
different solvent candidates. This limits the candidates to the already existing experimental data pool [4, 5]. A number of modern tools are increasingly becoming available to reduce the efforts needed to select the right solvent [6]. In our previous study [4] we introduced a computer-aided model and software to find a solvent mixture which uses the Simplex numerical model for minimizing the ‘unsimilarity’ of the solvent and the polymer.

Solubility is essentially a thermodynamic property related to the cohesive energy between the polymer in question and the solvent, which could be in the form of another solid, liquid, or gas. Solubility theory is based on the notion that “like” dissolves “like”, where a molecule can be considered “like” another one, if it has similar cohesive energy [7].

The means for predicting the extent of solubility between a polymer and solvent is to determine the difference in solubility parameters for each component. The total (or Hildebrand) solubility parameter (δ) is a measure of the cohesive energy for a given substance [8]. Materials having similar values of δ are likely to interact with each other and exhibit high mutual solubility (or swelling) [7]. In Hansen solubility parameters (HSPs), the total solubility parameter is separated into the following three subparameters [2, 6]:

1. δD, the dispersive energy
2. δP, the polarity intermolecular force, and
3. δH, the hydrogen bonding.

These three parameters serve as coordinates for a site in three dimensions also known as the Hansen space. The distance between two molecules in this space determines how likely they are to dissolve into each other; the closer they are, the more likely they are to mutually dissolve each other (become miscible). For solid materials (solutes), their HSPs define the coordinates (location) of the center of a sphere, the radius of which is known as the interaction radius. The interaction radius represents a region of high solubility, and solvents having HSP values that are inside this sphere are considered highly soluble with the polymer solid, while those outside the sphere are not [8].

The use of prediction models has the advantage that for the selection procedure, any solvent can be considered for which the required group interaction parameters are available and by using predictive methods, an extended variety of solvents can be taken into account for selection [5]. Solubility parameters have found their greatest use in the selection of solvents [9]. Selection of the appropriate solvents and finding the best volume fractions could be done by computer programming through minimization of RA formula (discussed in ‘Section 3’); however, finding the minimum of RA takes much time for each set of solvents by normal linear programming. Because it has to sweep all the decimal values of the volume fraction from 0 to 1 for all the solvents; while by using the Simplex algorithm (discussed in ‘Section 3’), it can be done within a few milliseconds; hence, more combinations of solvents would be taken into account for solvent selection [4].

2 Polyamide 11

Polyamide 11 (or Nylon 11) is a biobased polyamide, a member of the nylon family of polymers produced by the polymerization of 11-aminoundecanoic acid. Bio-based polyamides, like polyamide 11 (PA 11), generally have lower melting temperatures than conventional PA 6 and PA 66 [10]. This enables the melt processing of wood fiber reinforced composites before the start of thermal degradation of the wood fibers, which has been reported to be at around 220 °C [11]. Nylon 11 is applied in the fields of oil and gas, aerospace, automotive, textiles, electronics, and sports equipment, frequently in the tubing, wire sheathing, and metal coatings. It is produced from castor beans by Arkema under the trade name Rilsan [12]. Researchers Joseph Zeltner, Michel Genas, and Marcel Kastner, perfected the monomer process of polyamide 11 (Figure 1) in 1944 [13]. There has been a number of research articles in the literature related to polyamide 11 solvents [14–18].

In this contribution, we used computer software for finding a solvent-mixture for polyamide 11. To set the scene for this paper, we bring a brief description of the Hansen approach to solving the problem of finding a solvent-mixture. The following overview is to facilitate reading for those who are not familiar with these concepts; therefore, experts can skip it.

3 Background

Solubility parameters help put numbers into this simple qualitative idea [9]. Liquids with similar solubility parameters will be miscible, and polymers will dissolve in solvents whose solubility parameters are not too different from their own [9]. Several graphing and modeling techniques have been developed to aid

Fig. 1: The structure of polyamide 11.
in the prediction of polymer solubility [8]. The basic principle has been “like dissolves like” [9]. By 1950, Hildebrand had defined the solubility parameter as the sum of all the attractive intermolecular forces, which he found to be empirically related to the extent of mutual solubility of many chemical species [19]. Solubility behavior cannot be accurately predicted by only the Hildebrand solubility parameter [8]. In 1967, Charles Hansen improved the concept and introduced his three-dimensional solubility parameters. The Hansen approach provides an empirical, yet effective [20] method for determining the dissolution possibility of solutes. The solubility parameter has been used for many years to select solvents for coatings materials [9].

The Hansen model is usually considered as a sphere. The center of the sphere has the $\delta d$, $\delta p$, and $\delta h$ values of the polymer in question (solute) [8]. $\delta$ is the square root of cohesion energy density $\delta d$, $\delta p$, and $\delta h$ represent the dispersive forces, polar interactions, and hydrogen bonding, respectively. The radius of the sphere, $R_0$, is termed the interaction radius [8]. The values of $R_0$ have been reported for some polymers in the literature. $R_A$ is the distance in HSPs space between the solute/polymer and the solvent [21]. The boundary of the spherical characterization is based on the requirement that ‘good’ solvents have a distance from the center of the sphere, $R_A$ (also termed the solubility parameter distance) less than $R_0$ [8]. $R_A$ is given by the following relation:

$$R_A = \sqrt{4 \times (\delta d - \delta d_f)^2 + (\delta p - \delta p_f)^2 + (\delta h - \delta h_f)^2} \quad (1)$$

where $\delta d_f$, $\delta p_f$, and $\delta h_f$ are the Hansen solubility components for the polymer/solute (our favorite values), and $\delta d_s$, $\delta p_s$, and $\delta h_s$ are the Hansen solubility components for the solvent [8]. Equation 1 was developed from plots of experimental data where the constant ‘4’ was found convenient and correctly represented the solubility data as a sphere encompassing the good solvent [8].

Solubility parameters of mixtures are linear [22]. That is, each of the three HSPs of a solvent mixture is a linear function of composition. In this case, the composition value to be used in calculating solubility parameters for solvent mixtures is the volume fraction ($\varphi$) for each component [22]. For a binary (two-solvent) mixture, the equation for all three solubility parameters is Equation 2 [22].

$$\delta_{\text{blend}} = [\varphi_{\text{comp1}} \times \sigma_{\text{comp1}}] + [\varphi_{\text{comp2}} \times \sigma_{\text{comp2}}] \quad (2)$$

This equation is correct for more than two components where the HSPs values are known [22]. Traditionally, without specific data, it is usually assumed that there is no volume change upon mixing of solvents. That is:

$$\text{(vol. Fraction)}_1 = \frac{\text{(Wt. Fraction Density)}_1}{\text{(Wt. Fraction Density)}_1 + \text{(Wt. Fraction Density)}_2} \quad (3)$$

In Eq. 2, $\varphi$ is the volume fraction of component 1, and $\delta$ is any solubility parameter. It is understood that $\varphi_{\text{comp1}} + \varphi_{\text{comp2}} = 1$. The volume fraction is easy to compute because solvents are stored in pails or drums and used by volume, although they are sold by weight.

Linear programming (LP) is a technique for the optimization of a linear objective function, subject to linear equality and linear inequality constraints. Although the R formula is not linear (it is quadratic), its constraint is linear. Its feasible region is a convex polytope, which is a set defined as the intersection of finitely many half spaces, each of which is defined by a linear inequality [23]. Its objective function is a real-valued affine (linear) function defined on this polyhedron. A linear programming algorithm finds a point in the polyhedron where this function has the smallest (or largest) value if such a point exists. There are a few LP methods such as ellipsoid and interior-point, but for more than 35 years now, George B. Dantzig’s Simplex-Method has been the most efficient mathematical tool for solving linear programming problems [24]. It is probably that mathematical algorithm for which the most computation time on computers is spent. This fact explains the great interest of experts and of the public to understand the method and its efficiency [24].

A convenient single parameter to describe solvent quality is the relative energy difference, RED, number: RED = $R_A/R_0$ [8]. According to the basic principle in dissolutions, “like dissolves like” [9], the more similarity, the less $R_A$ and hence, the higher the probability of dissolution. In other words, the distance in HSPs space between the solute/polymer, the Hansen space, should be as small as possible ($R_A = 0$) [21]. By taking square root from both sides of Eq. 1, we have:

$$R_A^2 = 4 \times (\delta d - \delta d_f)^2 + (\delta p - \delta p_f)^2 + (\delta h - \delta h_f)^2 \quad (4)$$

Therefore, we need to minimize $R_A^2$ as much as possible. In this paper, we minimize the $R_A^2$ with the Simplex method by development of a computer program.

### 4 Methodology

The Microsoft Visual Studio software package was used to develop the program. The Microsoft.SolverFoundation.Services.dll library that contains the Simplex
Tab. 1: Solvent values used in the software for polyamide 11.

<table>
<thead>
<tr>
<th>#</th>
<th>Solvent name</th>
<th>CAS registry number</th>
<th>( \delta T ) (( \sqrt{\text{MJ/m}^3} ))</th>
<th>( \delta D ) (( \sqrt{\text{MJ/m}^3} ))</th>
<th>( \delta P ) (( \sqrt{\text{MJ/m}^3} ))</th>
<th>( \delta H ) (( \sqrt{\text{MJ/m}^3} ))</th>
<th>MV (mL/mol)</th>
<th>MW (g/mol)</th>
<th>Health index (NFPA)</th>
</tr>
</thead>
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<td>20.3</td>
<td>3.1</td>
<td>4.1</td>
<td>139.066</td>
<td>207.07</td>
<td>2</td>
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<td>1-Butanol</td>
<td>71-36-3</td>
<td>23.2</td>
<td>16</td>
<td>5.7</td>
<td>15.8</td>
<td>91.5</td>
<td>74.12</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1-Octanol</td>
<td>111-87-5</td>
<td>21</td>
<td>17</td>
<td>3.3</td>
<td>11.9</td>
<td>157.7</td>
<td>8787</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1-Pentanol</td>
<td>71-41-0</td>
<td>21.6</td>
<td>15.9</td>
<td>4.5</td>
<td>13.9</td>
<td>108.6</td>
<td>8787</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>2-Butanol</td>
<td>78-92-2</td>
<td>22.2</td>
<td>15.8</td>
<td>5.7</td>
<td>14.5</td>
<td>92</td>
<td>74.12</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>4-Methyl-2-pentanol</td>
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<td>2</td>
</tr>
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<td>157.01</td>
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<td>17.3</td>
<td>5.7</td>
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<td>64.982</td>
<td>129.38</td>
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<td>2</td>
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<td>3.9</td>
<td>55.4</td>
<td>8787</td>
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<tr>
<td>13</td>
<td>Cyclohexanol</td>
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<td>22.4</td>
<td>17.4</td>
<td>4.1</td>
<td>13.5</td>
<td>106</td>
<td>100.158</td>
<td>1</td>
</tr>
<tr>
<td>14</td>
<td>Cyclohexyl chloride</td>
<td>542-18-7</td>
<td>18.3</td>
<td>17.3</td>
<td>5.5</td>
<td>2</td>
<td>118.6</td>
<td>8787</td>
<td>2</td>
</tr>
<tr>
<td>15</td>
<td>Dibenzyl ether</td>
<td>103-50-4</td>
<td>19.1</td>
<td>17.3</td>
<td>3.7</td>
<td>7.3</td>
<td>192.7</td>
<td>33.333</td>
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</tr>
<tr>
<td>16</td>
<td>diEthyl carbonate</td>
<td>105-58-8</td>
<td>18</td>
<td>16.6</td>
<td>3.1</td>
<td>6.1</td>
<td>121</td>
<td>8787</td>
<td>1</td>
</tr>
<tr>
<td>17</td>
<td>Diisobutyl carbinol</td>
<td>108-82-7</td>
<td>18.7</td>
<td>14.9</td>
<td>3.1</td>
<td>10.8</td>
<td>177.8</td>
<td>8787</td>
<td>1</td>
</tr>
<tr>
<td>18</td>
<td>DPGME (diPropylene glycol methyl ether)</td>
<td>34,590-94-8</td>
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<td>15.5</td>
<td>5.7</td>
<td>11.2</td>
<td>157.4</td>
<td>8787</td>
<td>2</td>
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<tr>
<td>19</td>
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<td>15.3</td>
<td>3.1</td>
<td>7</td>
<td>148.8</td>
<td>33.333</td>
<td>1</td>
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<tr>
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<td>isobutanol</td>
<td>78-83-1</td>
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<td>15.1</td>
<td>5.7</td>
<td>16</td>
<td>92.421</td>
<td>74.122</td>
<td>1</td>
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<tr>
<td>21</td>
<td>Methyl butyl ketone</td>
<td>591-78-6</td>
<td>17</td>
<td>15.3</td>
<td>6.1</td>
<td>4.1</td>
<td>123.6</td>
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Tab. 1 (continued)

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<thead>
<tr>
<th>#</th>
<th>Solvent name</th>
<th>CAS registry number</th>
<th>( \delta T ) (( \sqrt{\text{MJ/m}^3} ))</th>
<th>( \delta D ) (( \sqrt{\text{MJ/m}^3} ))</th>
<th>( \delta P ) (( \sqrt{\text{MJ/m}^3} ))</th>
<th>( \delta H ) (( \sqrt{\text{MJ/m}^3} ))</th>
<th>MV (mL/mol)</th>
<th>MW (g/mol)</th>
<th>Health index (NFPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>Methyl oleate</td>
<td>112-62-9</td>
<td>15.5</td>
<td>14.5</td>
<td>3.9</td>
<td>3.7</td>
<td>340</td>
<td>296.8794</td>
<td>1</td>
</tr>
<tr>
<td>23</td>
<td>Methyl Amyl acetate</td>
<td>108-84-9</td>
<td>16.9</td>
<td>15.2</td>
<td>3.1</td>
<td>6.8</td>
<td>167.4</td>
<td>8787</td>
<td>1</td>
</tr>
<tr>
<td>24</td>
<td>n-Butyamine</td>
<td>109-73-9</td>
<td>18.6</td>
<td>16.2</td>
<td>4.5</td>
<td>8</td>
<td>98.838</td>
<td>73.14</td>
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<tr>
<td>25</td>
<td>o-diChloroBenzene</td>
<td>95-50-1</td>
<td>20.5</td>
<td>19.2</td>
<td>6.3</td>
<td>3.3</td>
<td>112.8</td>
<td>8787</td>
<td>2</td>
</tr>
<tr>
<td>26</td>
<td>Propylene glycol methyl ether</td>
<td>107-98-2</td>
<td>20.4</td>
<td>15.6</td>
<td>6.3</td>
<td>11.6</td>
<td>93.8</td>
<td>8787</td>
<td>1</td>
</tr>
<tr>
<td>27</td>
<td>sec-Butyl acetate</td>
<td>105-46-4</td>
<td>17.2</td>
<td>15</td>
<td>3.7</td>
<td>7.6</td>
<td>133.517</td>
<td>116.16</td>
<td>1</td>
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<td>28</td>
<td>TetraChloroEthylene</td>
<td>127-18-4</td>
<td>20.3</td>
<td>19</td>
<td>6.5</td>
<td>2.9</td>
<td>101.1</td>
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<td>2</td>
</tr>
<tr>
<td>29</td>
<td>triEthylene glycol monoOleyl ether</td>
<td>9004-98-2</td>
<td>16</td>
<td>13.3</td>
<td>3.1</td>
<td>8.4</td>
<td>418.5</td>
<td>8787</td>
<td>1</td>
</tr>
</tbody>
</table>
The algorithm was imported at the beginning of the program's codes. The codes were written in Visual Basic programming language that operates within the Microsoft.Net framework. All the HSPs values of 234 solvents together with their names and CAS number, health NFPA index were imported into a database (Table 1). The database was connected to the program in a way that each time the program initiates, it loads the solvents' $\delta_d$, $\delta_p$, and $\delta_h$ values to predefined arrays – D(), P(), and H(), respectively. Out of 234 solvents, 81,085 different combinations were examined for polyamide 66 (PA 66) as the case study. It was counted by a counter variable in the program's code. The HSPs values of the solvents obtained from ASTM STP1133, Hansen [9], Mark [25], and Barton [26]. The values for NFPA health index were obtained from Sigma-Aldrich material safety data sheets, sciencelab.com, cameochemicals.noaa.gov, synquestlabs.com, and mathesongas.com. A detailed description of the software code is available in our previous study [4].

### Results and discussion

The subset of solvent-mixtures results was obtained from running the software with the HSPs of the selected polymer (PA 11) out of 234 organic solvents. Using the five main descriptors, namely, the dispersive ($\delta_d$), polar ($\delta_p$), and hydrogen ($\delta_h$) Hansen solubility parameters, CAS registry number, and the health indexes according to the NFPR classifications. The Rlimite was assigned equal to "0.2".

#### 5.1 Miscibility challenge

Solvents used in this study are of different sorts – polar, non-polar, protic, aprotic, etc. The closeness of HSPs values of solvent-mixture and the solute only guarantees the likeness of the interactions between the solvent-mixture and the solute; however, there is no guarantee for miscibility of all the components of a solvent-mixture. As the "polar" interactions of molecules are numerated in $\delta_p$ values (in Hansen theory, see the 'Section 3'), we assumed that the closeness in $\delta_p$ values of the components could increase the possibility of miscibility, i.e. the difference in $\delta_p$ values (called $\Delta P$, hereinafter) will decrease the chance of immiscibility of each solvent in the other one.

#### 5.2 Results for polyamide 11

The solubility of polyamide 11 was reported as 17.0, 4.4, and 10.6 for $\delta_d$, $\delta_p$, and $\delta_h$, respectively [7, 27]. The results were sorted first by $\Delta P$, and then by R and then $\phi$ values.

### Table 2: Proposed solvents using the developed software for polyamide 11.

<table>
<thead>
<tr>
<th>#</th>
<th>R</th>
<th>$\phi_1^a$</th>
<th>$\phi_2$</th>
<th>$\phi_3$</th>
<th>Health</th>
<th>$\delta_d$, $\delta_p$, $\delta_h$ ((\sqrt{\text{MJ}/\text{m}^3}))</th>
<th>$\Delta P^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.001</td>
<td>Butyric acid: 15.142%</td>
<td>Cyclohexan: 63.459%</td>
<td>Cyclohexyl chloride: 21.399%</td>
<td>Methyl oleate: 18.033%</td>
<td>1.063</td>
<td>17, 4.4, 10.6</td>
</tr>
<tr>
<td>2</td>
<td>0.002</td>
<td>Cyclohexan: 66.661%</td>
<td>Dichloromethane: 15.306%</td>
<td>2-Butanol: 49.967%</td>
<td>Dibutylcarbin: 19.461%</td>
<td>1.306</td>
<td>17, 4.399, 10.6</td>
</tr>
<tr>
<td>3</td>
<td>0.003</td>
<td>1-bromonaphthalene: 30.572%</td>
<td>2-Methylpentanol: 24.314%</td>
<td>Chloroform: 35.41%</td>
<td>Triethylene glycol monooxyle ether: 9.14%</td>
<td>1.243</td>
<td>17, 4.398, 10.6</td>
</tr>
<tr>
<td>4</td>
<td>0.003</td>
<td>1-Tridecanol: 5.01%</td>
<td>2-Methylpentanol: 24.626%</td>
<td>Chloroform: 35.41%</td>
<td>Triethylene glycol monooxyle ether: 9.14%</td>
<td>1.355</td>
<td>17, 4.398, 10.6</td>
</tr>
<tr>
<td>5</td>
<td>0.004</td>
<td>1-Octanol: 63.3%</td>
<td>1-Octanol: 63.3%</td>
<td>1-Octanol: 63.3%</td>
<td>1-Octanol: 63.3%</td>
<td>1.053</td>
<td>17, 4.403, 10.6</td>
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<tr>
<td>6</td>
<td>0.004</td>
<td>1-Tridecanol: 5.279%</td>
<td>1-Octanol: 63.3%</td>
<td>1-Octanol: 63.3%</td>
<td>1-Octanol: 63.3%</td>
<td>1.507</td>
<td>17, 4.402, 10.6</td>
</tr>
<tr>
<td>7</td>
<td>0.004</td>
<td>1-Tridecanol: 5.279%</td>
<td>1-Octanol: 63.3%</td>
<td>1-Octanol: 63.3%</td>
<td>1-Octanol: 63.3%</td>
<td>1.143</td>
<td>17, 4.402, 10.6</td>
</tr>
<tr>
<td>8</td>
<td>0.005</td>
<td>1-Octanol: 63.3%</td>
<td>o-Dichlorobenzene: 14.326%</td>
<td>o-Dichlorobenzene: 5.822%</td>
<td>o-Dichlorobenzene: 5.822%</td>
<td>1.478</td>
<td>17, 4.396, 10.6</td>
</tr>
<tr>
<td>9</td>
<td>0.005</td>
<td>1-Octanol: 63.3%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>1.27</td>
<td>17, 4.396, 10.6</td>
</tr>
<tr>
<td>10</td>
<td>0.005</td>
<td>1-Octanol: 63.3%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>1.384</td>
<td>17, 4.396, 10.6</td>
</tr>
<tr>
<td>11</td>
<td>0.005</td>
<td>1-Octanol: 63.3%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>1.384</td>
<td>17, 4.396, 10.6</td>
</tr>
<tr>
<td>12</td>
<td>0.006</td>
<td>1-Octanol: 63.3%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>1.384</td>
<td>17, 4.396, 10.6</td>
</tr>
<tr>
<td>13</td>
<td>0.007</td>
<td>1-Octanol: 63.3%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>1.384</td>
<td>17, 4.396, 10.6</td>
</tr>
<tr>
<td>14</td>
<td>0.008</td>
<td>1-Octanol: 63.3%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>n-Butylamine: 41.941%</td>
<td>1.384</td>
<td>17, 4.396, 10.6</td>
</tr>
</tbody>
</table>

---

$^a$ Calculated as a weight percent.

$^b$ Calculated as a mole percent.
Table 2 (continued)

<table>
<thead>
<tr>
<th>#</th>
<th>R</th>
<th>ϕ1a</th>
<th>ϕ2</th>
<th>ϕ3</th>
<th>Health</th>
<th>Δδ, δp, δh (√(MJ/m³))</th>
<th>ΔPb</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.009</td>
<td>Butyl chloride: 22.53%</td>
<td>Cyclohexanol: 72.214%</td>
<td>sec-Butyl acetate: 5.255%</td>
<td>1</td>
<td>17.003, 4.394, 10.599</td>
<td>1.8</td>
</tr>
<tr>
<td>17</td>
<td>0.009</td>
<td>Cyclohexanol: 52.738%</td>
<td>n-Butylamine: 41.389%</td>
<td>TetraChloroEthylene: 5.873%</td>
<td>1.473</td>
<td>16.997, 4.407, 10.601</td>
<td>2.4</td>
</tr>
<tr>
<td>18</td>
<td>0.009</td>
<td>1-Butanol: 19.369%</td>
<td>4-Methyl-2-pentanol: 51.614%</td>
<td>Bromobenzene: 29.018%</td>
<td>1.806</td>
<td>16.996, 4.403, 10.599</td>
<td>2.4</td>
</tr>
<tr>
<td>19</td>
<td>0.009</td>
<td>1-bromonaphthalene: 22.636%</td>
<td>3-Chloro-1-propanol: 50.331%</td>
<td>triEthylene glycol monoOleyl ether: 27.033%</td>
<td>1.226</td>
<td>16.998, 4.409, 10.598</td>
<td>2.6</td>
</tr>
<tr>
<td>20</td>
<td>0.01</td>
<td>Butyl chloride: 23.955%</td>
<td>Cyclohexanol: 73.221%</td>
<td>triEthylene glycol monoOleyl ether: 2.824%</td>
<td>1</td>
<td>16.997, 4.407, 10.601</td>
<td>2.4</td>
</tr>
<tr>
<td>21</td>
<td>0.01</td>
<td>1-bromonaphthalene: 30.984%</td>
<td>1-Butanol: 38.682%</td>
<td>Butyric acid: 30.333%</td>
<td>1.006</td>
<td>16.998, 4.409, 10.597</td>
<td>2.6</td>
</tr>
<tr>
<td>22</td>
<td>0.01</td>
<td>Chloroform: 11.784%</td>
<td>Cyclohexanol: 67.141%</td>
<td>Methyl butyl ketone: 21.075%</td>
<td>1.329</td>
<td>17.005, 4.404, 10.6</td>
<td>3</td>
</tr>
<tr>
<td>23</td>
<td>0.011</td>
<td>1-bromonaphthalene: 27.359%</td>
<td>1-Butanol: 50.398%</td>
<td>MethylAmyle acetate: 22.433%</td>
<td>1.274</td>
<td>16.994, 4.41, 10.597</td>
<td>2.6</td>
</tr>
<tr>
<td>24</td>
<td>0.012</td>
<td>Butyl chloride: 17.451%</td>
<td>Cyclohexanol: 66.338%</td>
<td>n-Butylamine: 16.211%</td>
<td>1.162</td>
<td>16.996, 4.409, 10.602</td>
<td>1.4</td>
</tr>
<tr>
<td>25</td>
<td>0.012</td>
<td>Chloromethane: 18.44%</td>
<td>Cyclohexanol: 63.344%</td>
<td>Dibenzyl ether: 18.216%</td>
<td>1.184</td>
<td>16.995, 4.396, 10.6</td>
<td>2.4</td>
</tr>
</tbody>
</table>

ϕ represents volume fraction; therefore: \( \phi_1 + \phi_2 + \phi_3 = 1 \). ΔP refers to the difference in the \( \delta_p \) values of the solvents in each mixture, greatest \( \delta_p \) - smallest \( \delta_p \) in the set of three solvents.

### 6 Conclusion

A sophisticated software package for the selection of the most suitable solvent-mixture for a solute/polymer with known HSPs or solvent-substitution for any solvent-involved process, e.g. liquid-liquid extraction was used to find a solvent for polyamide 11. The technique introduced in this paper decreases the time of solvent selection for polyamide 11. The technique reduces the laborious number of solvents and hence, it reduces the time of solvent selection process, e.g. liquid-liquid extraction. The time-saving method proposed in this paper is depicted in Figure 2. While using the method proposed in this paper, the chances of being applicable to all polymers/polymer are higher than the practical method. Therefore, a greater number of applicants can be taken into account to be the candidates.
References
