Degradation of flax PLA biocomposites
during and after manufacture

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Abstract

With rapidly increasing interest in green composites, natural fibre reinforced plastic (NFRP) biocomposites are becoming a very real alternative composite to the synthetic/man-made composites in indoor applications. Sustainability concerns of the public and recently approved regulations made by governments, in order to reduce the landfill materials, are among the factors that have intensified interest in natural fibre composites. Natural fibres can be used as renewable, sustainable reinforcement due to their small (perceived) environmental footprint. Apart from the environmental concerns, natural fibres possess some desirable engineering related characteristics such as low cost, low density, high stiffness- and strength-to-weight ratio. Among various natural fibres, flax is one of the oldest cultivated and used fibres. It has been utilized with success in a variety of applications, and can be used as a replacement for synthetic fibres in some applications.

Thermal stability and degradation, which are common drawbacks of natural fibres, are constraints for further extending the range of applications for flax fibre reinforced biocomposites. This problem can be significantly more critical for manufacturers and users when the matrix is also intended to be a sustainable material such as poly lactic acid (PLA). Since exposing flax/PLA biocomposites to high temperatures or outdoor environments leads to degradation, more research studies are necessary in order to increase our understanding about the mechanisms for degradation. In particular, a key point of interest is thermal stability when flax/PLA biocomposites are subjected to high temperatures during the manufacturing process.

Degradation is a key issue and occurs in both flax fibre and PLA matrix of a biocomposite. At high temperatures, flax components such as cellulose, hemicellulose and lignin degrade. The thermo-chemical degradation of these components subsequently limits the mechanical properties of flax fibre as reinforcement. In the case of PLA, in addition to low stability at manufacture temperatures, its biodeterioration can become a significant drawback in terms of durability when exposed to moisture related environments. The degradation process during and after manufacturing of flax/PLA biocomposites can also cause separation in the bonding of flax and PLA, and further
reduction in mechanical properties. Important gaps in the existing studies in this field are a lack of: (i) a methodology to construct a map or window of degradation during compression moulding for setting practical upper and lower limits to the consolidation temperature and process time, (ii) an analytical model to calculate the deterioration of PLA due to the chain-scission degradation process, (iii) a demonstrated procedure to calculate the effect of transient temperature on the degradation of flax/PLA biocomposites, (iv) study on the degradation rate of flax/PLA biocomposites at high temperatures in association with molar mass changes or degree of polymerisation, (v) a complete study on the performance of flax/PLA biocomposites in moisture related environments such as wet, freezing and humid conditions. Thus, the key objectives of this study were designed to fulfil these gaps/requirements in the existing body of knowledge. The research was divided into four stages which were carried out and the findings were published in four journal papers and one book chapter.

In order to set practical upper and lower limits to the consolidation temperature and processing time (in the form of a processing window), an in-depth investigation of the degradation processes of natural fibre biocomposites during thermal processing was done. The properties and processes considered in defining the processing window were the melting temperature, thermal penetration, impregnation of matrix into fibres, pyrolysis of matrix and fibre, and thermochemical degradation of matrix and fibre. To set lower limits to the processing time, critical studies and calculations were performed on the thermal penetration as a result of heating the platens of the compression moulding machine to higher than the melting point of the PLA, and on the impregnation of matrix into flax fibres. Upper limits to the processing temperature were achieved by comparing reaction process in terms of pyrolysis and thermochemical degradation. Evaluations on the pyrolysis degradation of PLA, flax fibres and their main compositions (including cellulose, hemicellulose and lignin) were conducted based on TGA data from the literature. Moreover, assessments on the thermo-chemical (chain-scission) degradation of PLA, flax fibres and natural fibres’ main compositions were conducted; and by bringing them all together, an optimum processing window for a biocomposite was constructed. The proposed processing window was tested experimentally. Several tests measuring changes in the tensile properties of a flax/PLA biocomposite were performed to examine the validity of the concept within and outside the borders for the optimized window. Thus, the key considerations were highlighted
and a quantitative guide was proposed for moulding time limits based on the available literature, along with a practical study of a representative flax/PLA biocomposite.

Since calculation of the extent of the chain-scission degradation of biopolymers is the key consideration for monitoring degradation of mechanical properties during compression moulding, it is of value to develop accurate calculation procedures that can be readily implemented. Models in the current literature for biopolymer degradation require a simultaneous solution of at least three chemical rate equations making the analysis somewhat complex and cumbersome. To facilitate the calculation, a simplified and revised model was proposed which no longer requires the solution of simultaneous differential equations and, for isothermal conditions; an analytical solution is readily available. The model was examined and validated against the more complex model and experimental results for PLA degradation reported in the literature.

The effect of the temperature history on the degradation progress and effects on the tensile strength was studied. A thermal degradation model which accounts for the effect of time-dependent process temperature variation during manufacture of green composites was proposed. Kinetic data was used to calculate the degradation progress parameters, defining experiment process maps for identifying the effect of the temperature history on the degradation progress and effects on the tensile strength. Thus it was demonstrated that the present model is a useful tool for predicting the degradation effect of any temperature history to which the composite is subjected during manufacture.

Molar mass degradation or reduction in degree of polymerisation was taken into account as a critical indicator of the extent of thermo-chemical degradation, making it possible to determine the rate of deterioration of mechanical properties for both matrix and fibre. A link between the chemical degradation of NFRP biocomposite during thermal processing and their mechanical properties was introduced. For the first time, this study has brought the thermochemical degradation concepts together with the models which have been used for composites, to predict the tensile strength of NFRP biocomposites after thermal processing. The following processes were taken into
account: (i) mechanical properties of the biocomposite can be calculated by estimating their relationship with the changes of degree of polymerization over temperature and time. This relationship has separately been proposed for both matrix and fibre, (ii) the modulus of elasticity for both the flax fibre and for PLA may be assumed to be independent of the thermal processing, (iii) a linear relationship between strength and (degree of polymerization)$^{-1}$, as proposed in the literature, was used to calculate the tensile strength of matrix and fibre, and for the first time used to predict the mechanical properties of NFRP biocomposites, (iv) to predict the tensile strength of NFRP biocomposite, the linear model was found to be unreliable for extended periods of time and subsequently a new exponential model was proposed which is realistic within 10% uncertainty.

The sensitivity of properties of flax/PLA biocomposites to different moisture-related environments was studied. Composites were exposed to the following conditions: water immersion, warm humid, and ‘freeze-and-thaw’ cycling environments. The mechanical performance (tensile and flexural properties), moisture content and physical changes (dimensional stability) of the composites during the exposure to the different environments were analysed. The findings were also compared with those of previous works which had been produced for various applications, and are as follows for each condition: (i) when the flax/PLA composites were immersed in water, water absorption followed Fick’s law. Tensile and flexural modulus and strength decreased significantly due to the quantity of water absorbed by the composites, which led to the development of different degradation mechanisms, such as the weakening of the flax/PLA interface and plasticisation. However, the tensile strain value found for the saturated specimens almost doubled that of “as manufactured” specimens due to the plasticising effect of water in the flax/PLA biocomposites. Physical changes were relatively large, as the thickness of the samples increased considerably during the test, (ii) after the saturation moisture content was reached in the immersion tests, some samples were completely dried to analyse the residual properties of the composites. The drying process proved to be effective in partially restoring the mechanical properties. However, the “as manufactured” properties were not reached, inferring that some permanent damage was caused after the immersion tests, which was attributed to the degradation of the fibre-matrix interface. Nevertheless, the results suggest that it is advantageous to completely dry biocomposite prior to use in structural applications if the fibres have high water
content, (iii) when exposed to a warm humid environment, both water absorption and physical changes were much lower than for water immersion, leading to less significant reductions in mechanical properties. In addition, the hydrolysis process can be involved in the PLA degradation, decreasing the properties of the matrix and degrading the interfacial bonding between flax and PLA by molar mass degradation, (iv) Freeze and thaw cycling has small negative impacts on tensile and flexural properties owing to small water absorption and physical changes, causing internal stresses, (v) Freeze and thaw cycling of water-saturated specimens shows further deterioration of properties in comparison with the water saturated only specimens. Water saturated and freeze/thaw cycling damages the material because of the negative synergy caused by water trapped in the microstructure and freeze/thaw cycles, which leads to the development of internal stresses, Altogether, based on the measurements and analysis, direct contact with liquid water is the most deteriorating environment for biocomposites, and therefore underwater applications of these materials are strongly discouraged. In such cases, a drying process can restore partially the mechanical performance of these materials. On the other hand, biocomposites can endure reliably in warm humid environments and in those that could create freeze-and-thaw cycles for short-term outdoor applications. Finally, a discussion was provided for practitioners who are considering using natural fibre reinforced biomatrix products.

Over all, the degradation of flax/PLA biocomposites during and after manufacturing process was studied and the findings were published in four journal papers and one book chapter. A summary of the research contributions, suggestions and recommendations for the future research in the field of NFRP biocomposites are also provided in this thesis.
Declaration of Originality

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

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List of Acronyms

AF  aramid fibre
AM  as-manufactured
ASTM International (formerly American Society for Testing and Materials)
BF  bast fibre
BFRP bast fibre reinforced polymer matrix composites
CF  carbon fibre
CFRP carbon fibre reinforced polymer matrix composites
CSA cross-sectional area
DP  degree of polymerization
FACF fibre area correction factor
FRP fibre reinforced polymer matrix composites
FF  flax fibre
F/T  freeze/thaw
GF  glass fibre
HDPE high density poly(ethylene)
HDT heat distortion temperature
HF  hemp fibre
HS  humid saturated
JF  jute fibre
KF  kenaf fibre
LCA life cycle analysis
MC  moisture content
MW  molecular weight
NF  nettle fibre
NFRP natural fibre reinforced polymer matrix composites
NW  non-woven
PBS poly (butylene succinate)
PC polycarbonate
PET poly (ethylene terephthalate)
PLA poly (lactic acid)/poly (lactide)/

xviii
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tr>
<td>PLLA</td>
<td>poly (L-lactic acid)</td>
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<tr>
<td>PP</td>
<td>poly (propylene)</td>
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<tr>
<td>PU</td>
<td>polyurethane</td>
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<tr>
<td>PVA</td>
<td>poly (vinyl alcohol)</td>
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<tr>
<td>PW</td>
<td>plain weave</td>
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<td>RH</td>
<td>relative humidity</td>
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<td>RF</td>
<td>ramie fibre</td>
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<tr>
<td>RoM</td>
<td>rules-of-mixture</td>
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<tr>
<td>UD</td>
<td>unidirectional</td>
</tr>
<tr>
<td>UP</td>
<td>unsaturated polyester resin</td>
</tr>
<tr>
<td>v/o</td>
<td>(fibre) volume percentage</td>
</tr>
<tr>
<td>WA</td>
<td>water absorption</td>
</tr>
<tr>
<td>WS</td>
<td>water saturated</td>
</tr>
<tr>
<td>WSF/T</td>
<td>water saturated and freeze/thaw</td>
</tr>
<tr>
<td>WSD</td>
<td>water saturated and completely dried</td>
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<tr>
<td>w/o</td>
<td>(fibre) weight percentage</td>
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Acknowledgement of Published and Unpublished Papers Included in this Thesis

Section 9.1 of the Griffith University Code for the Responsible Conduct of Research ("Criteria for Authorship"), in accordance with Section 5 of the Australian Code for the Responsible Conduct of Research, states:

To be named as an author, a researcher must have made a substantial scholarly contribution to the creative or scholarly work that constitutes the research output, and be able to take public responsibility for at least that part of the work they contributed. Attribution of authorship depends to some extent on the discipline and publisher policies, but in all cases, authorship must be based on substantial contributions in a combination of one or more of:

- conception and design of the research project.
- analysis and interpretation of research data.
- drafting or making significant parts of the creative or scholarly work or critically revising it so as to contribute significantly to the final output.

Section 9.3 of the Griffith University Code ("Responsibilities of Researchers"), in accordance with Section 5 of the Australian Code, states:

Researchers are expected to:

- Offer authorship to all people, including research trainees, who meet the criteria for authorship listed above, but only those people.
- Accept or decline offers of authorship promptly in writing.
Acknowledgement of published and unpublished papers

- Include in the list of authors only those who have accepted authorship.
- Appoint one author to be the executive author to record authorship and manage correspondence about the work with the publisher and other interested parties.
- Acknowledge all those who have contributed to the research, facilities or materials but who do not qualify as authors, such as research assistants, technical staff, and advisors on cultural or community knowledge. Obtain written consent to name individuals.

In accordance with contemporary thesis writing practice, this document includes reformatted versions of already published outputs from the PhD study process. This thesis includes 4 peer-reviewed journal papers (chapter 3 to 6), one published peer-reviewed book chapter (section 2 of chapters 4) and one peer-reviewed journal paper. All these manuscripts have been co-authored with the one principal supervisor and two co-supervisors of this PhD study. At the front of each chapter, I have highlighted my contribution to that paper.

The detailed information of these papers are:

**Chapter 3**

**Chapter 4**

And
Acknowledgement of published and unpublished papers


Chapter 5

Chapter 6

______________________________  (Date)___15/Mar/2018___________

Hossein Mohammad Khanlou
Acknowledgement of published and unpublished papers

_______  _______ (Date)____08/Mar/2018__________

Supervisor: Wayne Hall (supervisor and co-author)

_______________ _______ (Date)____12/Dec/2017__________

Co-supervisor: Peter Woodfield (co-supervisor and co-author)

_______Appendix G______       (Date)_______12/Jan/2014_______

Co-supervisor: John Summerscales (co-supervisor and co-author)
Chapter 1: Introduction

This thesis explores the degradation process of flax fibre reinforced PLA biocomposites during and after the manufacturing process. Measures to achieve this goal were:

i) models of thermal penetration (the interplay of thermal conductivity and specific heat), melt infusion, thermal degradation and chemical degradation of natural polymers were brought together to construct an optimum processing window for a natural fibre reinforced biocomposite;

ii) a well-established model for simulation of the thermo-chemical degradation of bio-polymers was simplified, and a new model was proposed which was employed to determine the effect of time-dependent process temperature variation during manufacture of a green composite;

iii) a correlation between the processing temperature history and the tensile strength of flax/PLA biocomposite was identified, with a further proposal of a more reliable or practical model for application over longer periods of time; and

iv) the sensitivity of flax/PLA biocomposite to moisture-related environments (including water immersion, humidity and freeze-thaw cycles) was examined.

This chapter provides a brief description of the research background, the objectives of the study, and an overview of the research method. The chapter concludes by providing details on the layout and structure of the thesis. The introductory background information pertinent to the research is described in the following section.

1.1 Research background

NFRP biocomposites have increasingly become of interest for industrial applications. Fundamental research studies seek to establish their renewability, and recyclability with a competitive price [1]. The European Union has decided to regulate sustainability concerns and reduce landfill materials by encouraging industries to invest in biodegradable materials, prompting research studies on NFRP biocomposites [2].
Natural fibres (e.g., flax fibres) were the immediate choice for research on renewable reinforcements since their environmental friendliness and availability in fibrous form were well-known [3]. Thus, composites with NF reinforcement are now amongst the most promising sustainable materials [4].

Low cost and relatively high mechanical properties are also other advantages of NFRP biocomposites [1]. For example, a number of non-complex manufacturing techniques for NFRP composites have been introduced and all allow fast production rates with relatively acceptable quality and reasonable price [5]. Physical, chemical and mechanical properties (such as low weight, corrosion resistance, specific-strength and -stiffness) of NFRP biocomposites can also be competitive with conventional engineering materials such as aluminium or steel [6].

Degradation and deterioration of NF properties are the chief barrier in applying NF in high-temperature or moisture-related environments[7]. For example, flax which is one of the most widely used natural fibres, degrades at high temperatures (e.g., 200-600 °C) due to the degradation of its components - cellulose, hemicellulose and lignin [3]. Typically, each of these components may degrade in certain ranges of temperatures during the manufacturing process, or in various moisture-related environments (e.g., water immersion, humidity, and freeze-and-thaw) during use [3]. Additional information regarding the degradation process of flax fibre is provided in the following chapters.

Degradation of biomatrix polymers is an additional obstacle as biomatrices are sensitive to high temperatures, and deteriorate in some environmental conditions. PLA, in particular, is a common and relatively new degradable biopolymer which can be derived from corn [8]. In the standard of food waste management system, PLA is expected to degrade and release CO₂ and water without emitting any harmful toxins [9-11]. Further, PLA can be hydrolysed with water to form lactic acid, which is then purified and polymerized to remake prime polymer [11]. Polymer hydrolysis recovery is the preferred method for the recycling of PLA which, thus can be polymerised and processed into new valuable products [11].
PLA is a suitable biothermoplastic for short-term applications or where high mechanical properties at high temperatures are not required since PLA cannot stand high temperatures [12]. Apart from high temperature required applications, PLA is usually reinforced with natural fibres to increase its mechanical properties while keeping its excellent and valuable biodegradability characteristic. In the course of manufacturing, PLA easily becomes viscous and impregnates into the fibres but degrades over time at the manufacturing temperatures. However, PLA degradation in moisture-related environments can rapidly separate the fibre/PLA bonding, which causes significant reduction of the mechanical properties of the fibre/PLA biocomposites [3]. PLA has one of the smallest gaps between Tg and Tm, meaning it can be used at ambient temperature in the elastic state yet processed at a temperature sufficiently low as to not degrade natural reinforcements. Further information regarding the degradation process of PLA fibre is provided in the following chapters.

Overall, both NF and biopolymers are very likely to degrade during and after a manufacturing process. NFRP biocomposites which use both of these biodegradable materials are sensitive to the required high temperatures in composite processing and to moisture related environments. In spite of many papers reporting the mechanical property changes of NFRP biocomposites under various environmental conditions, there is still scope for a systematic study on the biocomposites’ degradation mechanism and potential models for degradation progress rates over time at various temperatures. An in-depth study and discussion on degradation of NFRP biocomposites during and after the manufacturing process may prompt research directions for those who are interested in exploring the capabilities of NFRP biocomposites.

1.2 Research objectives
The study was conducted to address the above research goals. The primary objectives of this PhD project include, but are not limited, to:

- understanding the various characteristics in degradation of flax fibre due to temperatures during a manufacturing process;
- understanding the various characteristics in the degradation of PLA due to temperatures experienced during a manufacturing process;
developing a new analytical approach to simplify the complex model for thermo-chemical degradation of biopolymers;

- understanding the effect of transient temperature variations on the degradation process during the manufacturing process;

- establishing a method to estimate the tensile strengths of a biocomposite after exposure to high temperature; investigating the mechanical property performance of the flax/PLA biocomposites when exposed to moisture related environments.

1.3 Research method overview

There were five main phases to the research:

- knowledge acquisition,
- constructing an optimum processing window for a biocomposite,
- simplifying and revising a complex model,
- estimating mechanical property degradation, and
- evaluating mechanical properties in the moisture related environments.

Each of these phases included numerous research stages that contained unique methods. Each key phase and associated stages of the research method are presented in Figure 1-1. Additional details on specific research methods are discussed in relevant chapters, which are reformatted and extended from published peer-reviewed journal papers. A summary description for the key research phases are presented below.

1.3.1 Phase 1: Knowledge acquisition

Published literature addressing all the topics relevant to natural polymers and their compositions were studied. Then, PLA production methods and compositions, flax and PLA mechanical properties were carefully reviewed. Thereafter, thermal degradation of flax and its compositions and of PLA were investigated. Next, thermo-chemical degradation of flax and PLA due to chain-scission was also explored. Finally, moisture related degradations of NFRP biocomposites were critically reviewed. All these topics were reviewed to develop the required background knowledge and to formulate research
objectives. Additionally, models which are associated with the degradation process of natural fibre reinforced biopolymer composites are considered. Overall, this phase of the investigation contributes significantly to the thesis through the definition and outline of several necessary unstudied gaps in degradation of NFRP biocomposites.
Chapter 1: Introduction

Phase 1: Knowledge acquisition

Stage 1a: Literature review
Chapter 1: Introduction
Stage 1b: Set research objective
Chapter 2: Literature review

Phase 2: Constructing an ideal processing window for a biocomposite

Stage 2a: Thermal penetration and melting point
Chapter 3: Consolidation process boundaries of the degradation of mechanical properties in compression moulding of natural-fibre bio-polymer composites
Stage 2b: Impregnation of matrix
Published version DOI:
http://dx.doi.org/10.1016/j.polymdegradstab.2017.03.004
Stage 2c: Pyrolysis and TGA data of matrix and fibre
Stage 2d: Thermo-chemical degradation of matrix and fibre
Stage 2e: Manufacturing of flax/PLA biocomposite
Stage 2f: Tensile properties analysis
Stage 2g: Comparison with model (generating a manufacturing window)

Phase 3: Simplifying and revising a complex model

Stage 3a: Revising the complex model for the chain-scission degradation of biopolymers
Published version DOI:
http://dx.doi.org/10.1016/j.polymdegradstab.2016.09.033
Stage 3b: Determining the effect of the temperature history on the degradation progress and effects on the tensile strength
Chapter 4: Technical Note: On modelling thermo-chemical degradation of poly(lactic acid)
Published version DOI:
https://doi.org/10.1007/978-3-319-64641-1_6
Chapter 4: Effect of time dependent process temperature variation during manufacture of natural-fibre composites
Published version DOI:
https://doi.org/10.1007/978-3-319-64641-1_6
**Chapter 1: Introduction**

**Phase 4: Estimating mechanical property degradation**

- Stage 4a: Mechanical property in relation to degree of polymerisation
- Stage 4b: Modelling and prediction of the tensile properties of PLA
- Stage 4c: Calculation and prediction of the tensile strength of fibres
- Stage 4d: Proposed model to predict the tensile strength of NFRP bio-composites

Chapter 5: Estimation of mechanical property degradation of poly(lactic acid) and flax fibre reinforced poly(lactic acid) bio-composites during thermal processing

Published version DOI: https://doi.org/10.1016/j.measurement.2017.11.031

**Phase 5: Evaluating mechanical property in moisture related environments**

- Stage 5a: Composites samples preparation
- Stage 5b: Degradation in water immersion tests
- Stage 5c: Degradation in humidity tests
- Stage 5d: Degradation in freeze and thaw tests
- Stage 5e: Moisture absorption and physical changes
- Stage 5f: Mechanical properties evaluation
- Stage 5g: Effect of exposure time and moisture concentration on degradation

Chapter 6: The mechanical properties of flax fibre reinforced poly(lactic acid) bio-composites exposed to wet, freezing and humid environments

Published version DOI: 10.1177/0021998317714857

Chapter 7: Conclusion, contributions and suggestions

Figure 1-1 Research methods overview
1.3.2 Phase 2: Constructing an optimum processing window for a biocomposite

The key goal of Phase 2 was to gain an in-depth understanding of the degradation processes of natural fibre biocomposites during thermal processing with a view to setting practical upper and lower limits to consolidation temperature and processing time. The thermal moulding process itself is a complex balance between processes that must occur for the composite to successfully consolidate before the onset of thermal degradation of the natural fibre and/or matrix materials. With this in mind, each sub-process occurring during compression moulding was modelled as a function of time and temperature and expressed in the form of a progress variable/parameter having values between zero and one indicating the progress from start to ultimate finish.

The properties and processes considered in defining the processing window were melting temperature, thermal penetration, impregnation of matrix into fibres, pyrolysis of matrix and fibre, and thermochemical degradation of matrix and fibre. To set lower limits to the processing time, critical studies and calculations were performed on the thermal penetration as a result of heating the platens of the compression moulding machine to higher than the melting point of the PLA, and on the impregnation of matrix into flax fibres. Upper limits to the processing temperature were achieved by comparing reaction process in terms of pyrolysis and thermochemical degradation. Evaluations on the pyrolysis degradation of PLA, flax fibres and their main compositions (including cellulose, hemicellulose and lignin) were conducted based on TGA data from the literature. Moreover, assessments on the thermo-chemical (chain-scission) degradation of PLA, flax fibres and natural fibres’ main compositions were conducted; and by bringing them all together an optimum processing window for a biocomposite was constructed.

The proposed processing window was tested experimentally. Several tests measuring changes in the tensile properties of a flax/PLA biocomposite were performed to examine the validity of the concept within and outside the borders for the optimized window.
1.3.3 Phase 3: Simplifying and revising a complex model

The results of the previous phase demonstrate that calculation of the extent of the chain-scission degradation of biopolymers is the key consideration for monitoring degradation of mechanical properties during compression moulding. Moreover, models in the current literature for biopolymer degradation require simultaneous solution of at least three chemical rate equations making the analysis somewhat complex and cumbersome. To facilitate the calculation, a simplified and revised model was proposed which no longer requires solution of simultaneous differential equations; and, for isothermal conditions, an analytical solution is readily available. The model was examined and validated against the more complex model and experimental results for PLA degradation reported in the literature. Additional work performed in this phase was to calculate degradation progress parameters, defining experiment process maps for identifying the effect of the temperature history on the degradation progress and effects on the tensile strength.

1.3.4 Phase 4: Estimating mechanical property degradation

Models and knowledge acquired at previous phases demonstrate that there is a relationship between the degree of polymerisation of natural fibres and biopolymers and the tensile strength of a biocomposite. In other words, thermal degradation and chemical degradation are among the key issues affecting mechanical properties and ultimately utilization of natural fibre reinforced polymer (NFRP) biocomposites. Thus, in this phase, a correlation relating the tensile strength of flax/PLA bio-composite to the processing temperature history is proposed using the concept of rule of mixtures for NFRP biocomposites. It was found that the existing linear model, which corresponds to the tensile strength of natural polymers and their degree of polymerization (DP), is not applicable for predicting the tensile strength of NFRP biocomposites as a function of processing temperature history at longer periods of times. Thus, a non-linear model has been proposed which is capable of predicting the tensile strength of the biocomposite.
1.3.5 Phase 5: Evaluating mechanical properties in moisture related environments

To have a more complete understanding of the degradation of a biocomposite after manufacturing, a set of experiments were performed at controlled conditions for temperatures much lower than those encountered during manufacture. The findings were critically discussed and compared with the previous studies on NFRP biocomposites. Flax/PLA bio-composite samples were exposed to moisture related environments (wet, freezing and humid) which can be the most detrimental of environments. With respect to moisture absorption and physical changes of samples, the flexural and tensile properties were evaluated periodically to determine the detrimental effect of each exposure condition on the mechanical performance of biocomposites. Valuable discussions on the mechanisms and reasons for the degradation of the properties of green composites are presented as the result of this phase. The conclusion and recommendation of the thesis is also performed at this phase.

1.4 Thesis layout

This thesis is presented in a form of a contemporary thesis layout that comprises both traditional thesis chapters and reformatted peer reviewed publication chapters. By publishing research outputs from high quality journals, the PhD study has then the advantage of international expert review of the main body chapters thereby ensuring their quality. The academic and practical elements of any thesis can definitely be strengthened by using ‘thesis by publication’ approach. With this benefit in mind, the traditional introductory chapters are presented in order to highlight the research backgrounds, methods and context of the study; and the remaining chapters are presented in a form of extended reformatted published or accepted peer reviewed papers. Each of the reformatted peer reviewed papers has literature review, methodology, results and discussion sections which are specifically prepared for that particular publication. Finally, the thesis is summarised by overall research conclusions, contributions and suggestions in the last chapter.

There are five distinct components of peer reviewed publications within this thesis being:
(i) Article paper: consolidation process boundaries for compression moulding of natural-fibre biopolymer composites
(ii) Technical Note: On modelling thermo-chemical degradation of poly(lactic acid)
(iii) Book chapter: effect of time-dependent process temperature variation during manufacture of natural-fibre composites
(iv) Article paper: estimation of mechanical property degradation of poly(lactic acid) and flax fibre reinforced poly(lactic acid) bio-composites during thermal processing
(v) Article paper: the sensitivity of mechanical properties of flax fibre reinforced poly(lactic acid) bio-composites to wet, freezing and humid environments

In its entirety, the thesis consists of seven chapters. This chapter (Chapter 1) introduces the research through a discussion on the research motivation and background, a summarised overview of the research method and the ‘thesis by publications’ layout. More importantly, the chapter presents the study’s broad research objectives, which were developed from the knowledge acquired through the literature review and the established research gaps. Further, the research objectives directed the design of the research method and underpinned the investigations for the acquisition of results to meet the objectives.

Chapter 2 provides a detailed discussion and review topics including a historical overview of NFRP bio-composites, advantages and disadvantages of NFRP bio-composites, natural fibres types, natural fibre polymer biocomposites, flax fibres, PLA, thermal processing (NFRP composites), and general degradation of NFRP biocomposites. General degradation process includes degradation of natural fibres and PLA due to pyrolysis and chain scission. Moreover, the chapter explores earlier research covering fields of green composite degradation during and after the manufacturing process. The chapter concludes through a research persuasion, which summarises the reviewed literature and presents the key gaps that currently exist in the body of knowledge. Additional critical reviews of the literature are detailed within Chapters 3 through to 7.
Chapter 3 details the general knowledge of the chemical and physical changes occurring in the molten PLA and flax fibres during the consolidation process. This chapter, which is a peer-reviewed published journal paper, includes theoretical background and measures of consolidation progress to express thermal penetration and melt infusion as a function of time and temperature. The chapter also contains theoretical background and measures of thermal degradation and chemical degradation of natural fibres and biopolymers to construct an optimum processing window for a biocomposite. All processes are mapped in terms of normalized consolidation progress parameters making it easier to identify critical processes and process boundaries. Validation of the concept is achieved by measuring changes in the mechanical properties of flax/PLA biocomposites formed over a range of processing conditions within and outside of the optimized window.

Chapter 4 includes the second peer reviewed published journal paper and a peer reviewed book chapter published by Springer. In the published journal paper, a well-established model for simulation of the chain-scission process of polylactic acid (PLA) during thermal processing has been simplified and revised. The key assumption in the new model is that the total number of monomer units is invariant as reactions progress. Surprisingly, this seemingly obvious assumption appears to have been previously overlooked. The revised model no longer requires solution of simultaneous differential equations and, for isothermal conditions, an analytical solution is readily available. The paper concludes with using the proposed model to check its validity with previous studies. The present model is in excellent agreement with the more complex model and experimental results for PLA degradation reported in the literature. In the published book chapter, the focus was to calculate for effect of time-dependent process temperature variation during manufacture of green composites. Kinetic data are used to calculate degradation progress parameters, defining experiment process maps for identifying the effect of the temperature history on the degradation progress and effects on the tensile strength. The model can also express the tensile strength changes in comparison with other degradation parameters. The paper concludes with simulating the effect of heating and cooling rates on the degradation of NFRP biocomposites at three distinct rates (slow, medium and fast), which demonstrates the model is a useful tool for predicting the degradation effect of any temperature history to which the composite is subjected during manufacture.
Chapter 5, which is a published paper in a high impact journal, proposes a methodology to estimate the tensile strength of flax/PLA bio-composite to the processing temperature history. For the first time, an existing linear model, which corresponds to the tensile strength of natural polymers and their DP, has been combined with reaction kinetics to predict the tensile strength of NFRP bio-composites as a function of processing temperature history. In addition, the chapter contains a non-linear model which shows a significant improvement of prediction for degradation of NFRP biocomposites for longer periods of time, compared with the linear model. Furthermore, the model is based on the underlying thermo-chemical degradation processes occurring during manufacture of NFRP bio-composites.

Chapter 6, which is a peer-reviewed published journal paper, focuses predominantly on the performance of flax/PLA biocomposites performance when exposed to environments similar to those found outdoors such as wet, freezing and humid conditions. Moisture absorption and physical changes to specimens were periodically examined. Flexural and tensile properties were evaluated periodically to determine the detrimental effect of each exposure condition on the mechanical performance of biocomposites. Then, mechanisms and reasons involved in the degradation of the properties of green composites are discussed. The chapter concludes by comparing and discussing the findings with those of previous works which have been produced for potential applications.

Finally, Chapter 7 summarises the key research outcomes, disseminates the contributions made by the existing research for the current body of knowledge and presents the implications of the results for the green composite manufacturing field. The chapter also presents recommendations for the implementation within the NFRP biocomposite manufacturing industry, as well as the need for future research in this field to address all limitations identified in the current research.
Chapter 2: Literature Review

This chapter presents an overview of previous work and studies on related literature along with key concepts and theories which were provided by the previous researchers for the purpose of this research.

2.1 Historical overview of NFRP bio-composites

Human beings have been developing and using natural fibres for thousands of years. Flax fibres and cords of flax were used in textiles and tool making in Egypt in the prehistoric period [13]. Additionally, natural fibres were used in other applications such as clothes, papers, and riggings for naval ships [13].

Although natural fibres have been used from the prehistoric period, the applications of NFRP composites were introduced to the world by the electronics industry in the early 20th century. Before the Second World War, Henry Ford used compressed soybeans composites as natural materials for body panels [14]. At the end of the 20th century, NFRP composites were used in the airplane industry for seats and fuel tanks [15].

Once environmental issues became a priority in the developed countries, NFRP composites re-emerged as potential alternatives of glass or aramid fibres (AF), which had decades of developments in their properties and subsequently in their applications [16]. For example, the European car companies have fabricated dashboards, door panels and handles using NFRP composites [16]. The market was 4,000 tonnes of manufactured biocomposites in 1996. Recent statistics collected by the German Nova-institute shows that European car makers and the construction industries have used more than 300,000 tonnes of composites reinforced by natural fibres, and this is expected to reach above 800,000 tonnes by 2020 [17]. These figures indicate there is a greatly increasing interest in using biocomposites. Car manufacturers, especially in Germany, are the main reason for this growth as they prefer to produce parts which are either recyclable or biodegradable.
2.2 Advantages and disadvantages of NFRP bio-composites

The main compelling benefits of using NFRP composites in comparison with synthetic fibre reinforced composites are [18-24]:

i. weight savings (≈30%)
ii. cost savings (raw materials)
iii. low cost of manufacturing
iv. safer manufacturing (no severe risk of processing e.g. skin irritation or dust inhalation)
v. reduced wear of mould tools and equipment
vi. highly renewable resource and less dependency on oil resources
vii. recyclability with very low cost.

On the other hand, there are serious obstacles in applying NFRP biocomposites for various applications:

i. the scattering or variability of fibre properties,
ii. the dimensional instability,
iii. degradation at moderate temperatures,
iv. and high moisture absorption

To extend the application of NFRP biocomposites, several studies have been performed to highlight critical factors or boundaries associated with fast degradation of NFRP biocomposites [3, 24-29]. However, more research is needed to confidently use NFRP biocomposites in various conditions.

2.3 Natural Fibre Types

Natural fibres are categorised by the source, including animals, minerals or vegetable as shown in Figure 2-1[7, 30, 31]. These have different characteristics due to the fact that their compositions are completely different. For example, cellulose and protein are the main compositions in vegetable fibres and animal fibres, respectively [30]. Vegetable or
cellulosic fibres have been shown to be the most suitable natural fibres for reinforcement in polymeric composites [32].

Bast fibres (BFs) are potential reinforcements for polymer matrix composites and are found as structural elements in the stems of dicotyledonous plants (flowering plants with net-veined leaves) [19, 33-36]. The principal BFs used to date as reinforcements are flax fibre (FF), hemp fibre (HF), jute fibre (JF), kenaf fibre (KF), nettle fibre (NF) and ramie fibre (RF). They are classified as mechanically strong fibres [19, 34, 37, 38] making them an ideal choice for natural fibre reinforced polymer matrix composite (NFRP). Not only are their mechanical properties good, but as with most natural fibres, BF have potential for easier end-of-life disposal in the form of biodegradable composites [6, 39, 40]. Recyclable BF can provide unique biodegradable composites [6, 39, 41-43] for use in the automotive [16, 44-47], marine [48, 49], construction [50, 51] and especially packaging industries [40, 52-55].

Figure 2-1 Categorization of natural fibres and some samples named at various studies.

2.4 Structure of natural fibres
‘Elementary fibre’ is the practical term used for the smallest strand of vegetable fibre easily identifiable with an optical microscope. These fibres possess various characteristics and nature associated to their cultivation and extraction locations [13,
These fibres are usually naturally bonded together into ‘technical fibres’, which include 10-40 elementary fibres. The average length and diameter of the technical fibres can reach up to a meter and 50-100 µm, respectively [56]. To illustrate the structure, Figure 2-2 shows the physical form of flax stem fibres as an example of natural fibres. For composite manufacturing, technical fibres have been used as reinforcement owing to the simple extraction techniques, combined with their overall properties [57].

Figure 2-2 Physical form of the flax stem as an example of natural fibres [57].

2.4.1 Cellulose

Cellulose is the main component of natural fibres and its percentage is in the range 40-70%, contingent on the type of fibre [58]. At the molecular level, cellulose is a homopolysaccharide, which is composed solely of β-D-glucopyranose units, linked to (1→ 4)- glycosidic bonds to form cellulose units. Figure 2-3 shows the smallest repeating unit in cellulose [59].

Macromolecular structure, chemical and physical properties are the results of the molecular structure of cellulose. In addition, cellulose is the load-bearing component of natural fibres and its degradation leads to a reduction of mechanical properties (strength, stiffness, and stability) [58]. There is no clearly-defined value for the length of the chain (DP) of cellulose in the living natural fibres; however, the size of native molecules is ≈5000-10000 glucopyranose units [59]. Strong hydrogen bonds between the three hydroxyl groups in each unit and their position are responsible for the connection of the end-to-end chains [18, 56].
2.4.2 Hemicellulose

Hemicellulose is any of the several heteropolymers (matrix polysaccharides) which exist in every natural fibre [56, 58]. Similar to cellulose, the majority of hemicelluloses function as supporting material in the cell wall and they are extremely hydrophilic [56, 58, 60]. The chemical structure of hemicellulose contains xylan, glucuronoxylan, arabinoxylan, glucomannan and xyloglucan (Figure 2-4) [56]. The molecular weights (MW) of hemicellulose are lower than those of cellulose and they have a DP of ≈50-300 [30].

2.4.3 Lignin

Lignin is a complex three-dimensional (aromatic hydrocarbon polymer) molecule with an amorphous structure, that provides the natural fibre’s rigidity. In other words, natural plants cannot be tall without lignin (Figure 2-5)[58]. The chemistry of lignin is not precisely defined because of the technological difficulties in isolating lignin in its native state. Mohanty et al. [56] reported that lignin can be considered as a thermoplastic polymer which melts at 170 °C. It acts as a chemical adhesive within and between fibres in the stem and also increases resistance of natural fibres to microorganisms [59]. Lignin has a high MW and is less polar than cellulose [58], and hence regarded as having a hydrophobic nature.
2.5 **Natural fibre polymer biocomposites**

There has been significant interest in improving the properties of natural fibre reinforced composites at laboratory scale [62, 63], but these bio-composites still have major limitations preventing their widespread use in industrial applications [62]. Degradation and resistance to deterioration in dry and wet environments are of considerable concern for bio-composite materials [64]. The lack of data regarding their deterioration progress and the mechanisms which govern this has resulted in the focus on these aspects of bio-composites [27].

The literature suggests that BFs degrade at ~200°C. Given that stressed composites should be designed to work below the glass transition temperature, and that \( T_g = T_m - 200(\pm50)\)°C, the options for matrix systems that perform sensibly at ambient temperature are limited to thermosets (where the Tg is of a similar value to the maximum cure temperature) or a very limited set of thermoplastics as discussed below.
2.6 Thermoplastic composites

NFRP biocomposites have considerable potential to be used as lightweight products in various industries. Polymeric materials are categorised into: thermoplastics and thermosets. While thermosets have conventionally been used in biocomposites, the thermoplastics have also been selected for various applications due to their less stressed processing than thermosets and satisfactory mechanical properties [65]. Thermosets become permanently hard after processing due to chemical reactions during curing and cross linking of the polymer molecules. However, thermoplastics can be repeatedly reshaped according to their proposed application by applying heat at high-temperature (e.g. 100-300 °C), as their molecules are associated with physical intermolecular forces and are able to move under stress [66]. Additionally, thermoplastics require a short and easier processing cycle, which means lesser processing time [67].

Various manufacturing techniques are available to fabricate NFR thermoplastic biocomposites such as injection moulding [68, 69] and compression moulding [70-73], which are the most widely used processes in industry. For the last three decades, NFR thermoplastic biocomposites have been generally manufactured by using compression moulding [71]. In these manufacturing techniques, by applying heat, the polymer (matrix) melts and impregnates the reinforcement (fibres). Then, the composite is consolidated for a period of time to allow the matrix to completely cover/infuse to fibres. Finally, through the cooling process the system is transformed into a rigid biocomposite [74]. To maximise the efficiency of NFRP biocomposites manufacturing process, the process parameters need to be studied to avoid any possible malfunctions.

2.7 Flax fibres

Flax is a high yielding industrial vegetable, which can supply global demand for biodegradable fibres [3]. The low cost of cultivation of flax is the main reason for high-global demand [3]. Additionally, FFs have high specific mechanical properties which are close to GFs, though flax is more flexible [3, 75]. Some general characteristics of FFs and more detailed information are provided in the following sections.
2.7.1 Flax fabric production

Flax cultivation is not too difficult and it can be cultivated in either a cool, humid climate or within moist soil. It has been cultivated in many countries such as Austria, Belgium, Canada, China, Denmark, France, Germany [3] or Ulster. In addition, the quality of FF varies between the growth location and many think that Belgium produces the finest-quality flax fibers in the world [76, 77]. The common steps in producing flax fabrics are [76]:

i. seed planting to harvesting of the flax plant which usually takes ≈ 100 days; the leaves become whiter, the stem turns yellow and the seeds turn brown after ≈ 90 days, thus representing that it is harvest time;

ii. rippling process which is the removal of the seeds and leaves from the plant; this is achieved by passing stems through coarse combs;

iii. water or chemical retting is used to decompose the woody bark surrounding the flax fibre;

iv. squeezing and allowing time to dry out for the breaking process;

v. combing and straightening the fibres for the spinning process at which the short fibres (called tow, which are used for making more coarse, sturdy goods) are separated from the longer (fine) fibres.

vi. putting long fibres through a machine (called a spreader) for combining fibres of the same length, laying the fibres parallel so that the ends overlap, creating a sliver, which passes through a set of rollers, making a roving which is ready for spinning;

vii. putting the rovings on a spinning frame and drawing out into thread and ultimately these are wound on bobbins or spools;

viii. transferring these moist yarns from bobbins on the spinning frame to large take-up reels to dry, weave or wind into yarn spools of varying weight and cutting flax yarn. The higher the cut, the finer the yarn becomes. The yarn is now ready to transport to the loom for weaving into fabrics.

2.7.2 Flax physical and chemical properties

Flax is mass-produced into yarn for thread or woven (linen) fabrics. The general characteristics of FFs are softness, flexibility, attractiveness and the cloth is now in
fashion [3, 78-80]. To have an overview of flax characteristics, several well-known physical and chemical properties of FF are summarised in Table 2-1.

Table 2-1 Physical and chemical properties of flax fibres [3, 78-80].

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Chemical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Length</strong></td>
<td><strong>Physical Properties</strong></td>
</tr>
<tr>
<td>450-750 mm (≈18-30 inch)</td>
<td><strong>Chemical Properties</strong></td>
</tr>
<tr>
<td><strong>effect from heat</strong></td>
<td>withstands only weak acids</td>
</tr>
<tr>
<td>excellent resistance to environmental heat</td>
<td>excellent resistance to alkalis</td>
</tr>
<tr>
<td><strong>hygroscopic nature</strong></td>
<td>resistant of common solvents (acetone, alcohol,…</td>
</tr>
<tr>
<td>very absorbent</td>
<td><strong>bleaching actions</strong></td>
</tr>
<tr>
<td><strong>dimensional stability</strong></td>
<td>cool chlorine and hypo-chlorine bleaching agent does not affect it</td>
</tr>
<tr>
<td>Good, but tends to crease easily</td>
<td><strong>effect of insects</strong></td>
</tr>
<tr>
<td><strong>resiliency</strong></td>
<td>resistant to moth, grubs and bacteria</td>
</tr>
<tr>
<td>very poor</td>
<td><strong>dye ability</strong></td>
</tr>
<tr>
<td><strong>abrasion</strong></td>
<td>has not a good affinity to dyes</td>
</tr>
<tr>
<td>good abrasion resistance</td>
<td><strong>lustre</strong></td>
</tr>
<tr>
<td>slightly silky</td>
<td></td>
</tr>
</tbody>
</table>

*additional information regarding the thermal properties of flax fibres is provided in the following sections.

Table 2-2 shows the main chemical compositions of FFs and the general information regarding the chemical and physical characteristics of natural fibres are provided in section 2.3.
Table 2-2 The main chemical compositions of flax fibres as weight percentages [1, 15, 81-83].

<table>
<thead>
<tr>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>62-75</td>
<td>11-20</td>
<td>2-2.5</td>
</tr>
</tbody>
</table>

2.7.3 Flax mechanical properties

Tensile properties of FFs are important for investigation of fibre reinforced polymer composites (FRP) [3, 15, 84]. Tensile properties of natural fibres have significant variations and each sample of FF reinforced biocomposite may show a different tensile deformation, even when cultivation location and test parameters are identical [3]. The tensile properties changes are caused because of the field conditions or the potential damages during harvesting, extraction, supplying, handling, treating and measuring processes that the fibres have experienced [3, 85, 86]. The tensile properties of FFs are not also uniform in length; and generally the fibres in the stem base are stronger and stiffer and the mid-span or the tip of the fibre has moderate mechanical properties [3]. Moreover, the biochemical analyses on the natural fibres show that the tensile variations in the tensile properties of the fibre extracted at different locations are associated with the variations in the cellulose contents [15, 87]. Thus, Charlet et al. [87] concluded that cellulose contents of the natural fibres are responsible for the ultimate value of tensile properties.

One issue causing the variation is that many authors have assumed the fibres have circular cross section and derived cross-sectional area (CSA) from measurement of an apparent fibre diameter. Virk et al. [88] demonstrated that the coefficient of variation for moduli and strengths based on the foregoing assumption was greater than for the elongation at break (a parameter independent of the CSA). Virk et al. [89] then introduced a Fibre Area Correction Factor (FACF) to correct moduli and strength based on a scaling factor derived from the ratio of the apparent area to the true area.
In addition, FFs are very hydrophilic and their tensile moduli are weakly associated with the environmental relative humidity (RH) [3, 15, 84, 90]. Davies et al. [91] have reported $\approx35\%$ and $\approx19\%$ reduction in static and dynamic moduli of FFs, for RH values from 30% and 90% respectively. Also, moisture absorption and swelling (or poor dimensional stability) of the natural fibres can significantly deteriorate the composites’ tensile properties. The main reason for this is the incompatibility between the hydrophilic natural fibres and the hydrophobic matrices [3, 15, 84, 90]. In general, the adhesion of fibre and matrix is reduced because of the hydrophilic features of the natural fibres, which can seriously lower the tensile properties of the fibres themselves, and thus lower the mechanical performance of biocomposites [3, 15, 84, 90].

### 2.7.4 Environmental impact of flax

Environmentalists encourage governments to subsidise natural fibre cultivation as natural fibres contribute to the sequestration of CO$_2$ by absorbing it from the atmosphere [92]. To highlight this, nearly 1.5 tonnes of CO$_2$ is needed to produce 1 tonne of natural fibres [92]. Moreover, it has been reported that 1 hectare of natural fibres can consume the released CO$_2$ of 20 cars over a year [92]. 85% of the world’s production of FFs comes from Europe, and France is the world leading country for flax production [93]. In addition, flax is perceived to be the most environmentally friendly fibre for composites (but see the next paragraph), which is widely available in Europe since no water is used for irrigation and only reduced amounts of chemicals are used in its cultivation process [93]. Moreover, FFs require 5 times less energy compared to GFs and 20 times less compared to carbon fibres (CFs) [93].

However, a thorough Life Cycle Assessment (LCA) by Dissanyake et al. [94, 95] suggested that, even for best practice agriculture, the high embodied energy in agrochemicals and spinning fibre into yarn, left FFs with similar environmental burdens to glass fibres (GFs).
2.7.5 Flax’s practical application
There are many applications for FFs and fabrics in various industrial sectors. FFs or fabrics can be used in clothing, decorative fabrics, table and wall coverings, curtains, luggage fabrics, filtration, automotive industry, reinforced plastics and composite materials [3, 78, 80].

Many automobile parts are currently being manufactured using FF reinforced biocomposites [30, 40, 96, 97]. However, their degradability at high temperatures and in wet environments need more studies. The above mentioned reasons and the high trend in using degradable biocomposites have led to the selection of FFs as a reinforcement material in this doctoral research. Moreover, some governments want to subsidise FFs to support non-food agriculture and are now also considering new policies for future development in biocomposite applications [80, 98, 99].

2.8 PLA
PLA is a biomaterial with highly desirable properties which are comparable to many petroleum-based polymers [100]. PLA has several environmental benefits such as:

i. low energy consumption during the manufacturing process,

ii. reduction in greenhouse gas production, capability to recycle back to lactic acid by hydrolysis/alkalolysis,

iii. decline in land fill volume due to degradability [101].

Degradable PLA plastics are used for bio-waste bags, disposal table wares, carrier bags, and rigid packaging of products [102-104].

2.8.1 PLA Production
In 1780, a Swedish chemist Scheele isolated lactic acid from sour milk for the first time; however lactic acid was commercialised by early 1882 [105]. The biochemical route (formation) is the common method for manufacturing lactic acid which is the basic building block of PLA [105]. To produce high MW PLA (>10^5 g/mol), methods such as polymerization through lactide formation, azeotropic dehydrative condensation or direct
condensation polymerization, can be applied [106]. Figure 2-6 shows synthesis of PLA using these methods.

In ring-opening polymerization through the lactide formation technique, Lactide, the cyclic dimer of lactic acid, can be produced by two lactic acid molecules as: L-lactide (two L-lactic acid molecules), D-lactide (two D-lactic acid molecules) and meso-lactide (an L-lactic acid and an D-lactic acid molecule) (see Figure 2-7). Lactide formation technique is used for producing any commercially available high MW PLA [102, 106, 107].

![Diagram showing different techniques for synthesis of PLA from l- and d-lactic acids](image)

Figure 2-6 Different techniques for synthesis of PLA from l- and d-lactic acids (concept reproduced from [106]).

![Chemical structures of lactides](image)

Figure 2-7 Chemical structure of a) LL-lactide, b) Meso-lactide, and c) DD- lactide (m.p. is melting point) (concept reproduced from [102]).
In the azeotropic dehydrative condensation of lactic acid, high MW PLA is produced without using adjuvants or chain extenders. To perform this, first the distillation pressure of lactic acid reduces for 2–3 h at 130 °C. Then, most of the condensation water is removed and a catalyst is added concurrently with diphenyl ester. Next, the solvent is returned to a vessel for an additional 30–40 h at 130 °C. Lastly, PLA is isolated or is sent to further purification if required [108].

In the direct condensation technique, high vacuum and temperature are applied in the system to remove water produced by the condensation at the last stage of polymerisation. This technique results in polymers with low to intermediate $M_w$. This technique is the least expensive one although the disadvantage is the difficulty in producing a solvent-free high MW PLA. To solve this problem, external coupling agents can be used to grow its chain length which bring additional costs [108, 109].

Overall, after the synthesis process, as shown in Figure 2-8, the residual monomers separate and return back to the polymerization process.

![Diagram of PLA synthesis process](image)

Figure 2-8 Non-solvent process to prepare polylactic acid (concept reproduced from [104]).

### 2.8.2 PLA physical properties

To determine the thermal characteristics of PLA, DSC and TGA are typically utilised. An example of DSC for PLA is shown in Figure 2-9. As PLA properties are shown in
Table 2-3, commercialised PLA has amorphous glassy grades with $T_g \approx 55-65 \, ^\circ C$, followed by $T_m \approx 160-180 \, ^\circ C$ and melting enthalpy $\approx 40-50 \, J/g$ [102, 106]. $T_g$ is a key characteristic of polymers as it outlines the practical temperature range for many applications [102]. It has been reported that $T_g$ may be reliant on the specimen thermal history, $M_w$, and presence of plasticizers [102, 106]. $T_m$ is the essential temperature for manufacturing at which chain scission reaction results in lowering $M_w$ or thermal degradation [102, 106]. PLA thermal properties can be improved by adding D-lactide to the L-lactide units. As a final point, PLA decomposes at $\approx 215-285 \, ^\circ C$ [102, 106].

![DSC result of PLA](image)

Figure 2-9 A typical DSC result of PLA (reproduced from [110]).

PLA properties are usually compared with those of polystyrene, poly (ethylene terephthalate) (PET) and poly (propylene) PP. PLA has lower melt strength than polystyrene and also has lower melting temperature than polyethylene terephthalate ($\approx 250 \, ^\circ C$), resulting in limited applications [111, 112]. In comparison with PP which has a $T_g \approx -20\, ^\circ C$. The $T_g$ of PLA is $\approx 55-65 \, ^\circ C$, meaning that PLA is brittle at room temperature because this is lower than its $T_g$ while PP is leathery at a similar temperature due to its $T_g$ being below ambient temperature. On the other hand, these properties of PLA result in lower $T_m$ in comparison with other polymers, and subsequently lower hydrolysis and chain scission degradations [111, 112].
2.8.3 Mechanical Properties of PLA

Mechanical properties can vary by alteration of MW, orientation of molecular chain and crystallinity of polymers in the course of the manufacturing process [102, 106]. During thermal processing, the mechanical properties of PLA show variations over a great range from soft, elastic plastic, to stiff and high strength plastic [102, 106]. In addition, at higher $M_w$, higher mechanical properties can be achieved [113]. For example, tensile and flexural strengths of PDLA increased from 49 MPa to 53 MPa and 84 MPa to 88 MPa, respectively when $M_w$ was increased from 47500 g/mol to 114000 g/mol [113].

In general, as mentioned above, PLA cannot be used where toughness is needed (such as for screws and car parts) because of its brittleness resulting from $T_g \approx 55\text{-}65\, ^\circ C$. To tackle this problem, toughening preparations, plasticisers and improved composites can be used.

Table 2-3 Physical, mechanical and thermal properties of commercially available PLA [114].

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>NatureWorks® PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt flow rate (g/10 min)</td>
<td>$^a$</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>1.25</td>
</tr>
<tr>
<td>Haze</td>
<td>2.2</td>
</tr>
<tr>
<td>Yellowness index</td>
<td>20-60</td>
</tr>
</tbody>
</table>

**Mechanical properties**

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>NatureWorks® PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength at yield (MPa)</td>
<td>53</td>
</tr>
<tr>
<td>Elongation at yield (%)</td>
<td>10-100$^b$</td>
</tr>
<tr>
<td>Flexural Modulus (MPa)</td>
<td>350-450</td>
</tr>
</tbody>
</table>

**Thermal properties**

<table>
<thead>
<tr>
<th>Thermal properties</th>
<th>NatureWorks® PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat distortion temperature (HDT, °C)</td>
<td>40-45, 135$^d$</td>
</tr>
<tr>
<td>VICAT Softening point (°C)</td>
<td>$^c$</td>
</tr>
<tr>
<td>Glass transition temperature (GTT) (°C)</td>
<td>55-65</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>120-170</td>
</tr>
</tbody>
</table>
Due to PLA’s moisture sensitivity, a more accurate test RV t-test method 4.3- 2.4; 
Oriented and sheet respectively, non-blended; close to GTT; amorphous and crystalline respectively.

2.8.4 Biodegradation and environmental impact of PLA

Biodegradability is “an event which takes place through the action of enzymes and/or chemical decomposition associated with living organisms (bacteria, fungi, etc.) and their secretion products”, according to Albertsson et al. [115]. Biodegradability also can be an answer to waste-disposal difficulties.

Degradability of PLA after its life-cycle has been proven through disintegration by bacteria in nature. There are two phases in biodegradation of PLA [116]:

i. hydrolysis or chain scission which results in lower $M_w$,
ii. digestion of macromolecules by soil bacteria and converting them to carbon dioxide and water.

Degradability of PLA can be accelerated in high humidity and temperatures of 50-70 °C. However, PLA is stable at room temperature [116].

Key characteristics of “sustainable material” are [117, 118]:

i. resource efficiency (ability to manufacture from renewable resources)
ii. energy efficiency (an equivalent function to the product it replaces)
iii. water conservation (no negative impact on water or food supply)
iv. affordability (availability at a competitive or lower price)
v. safe to both humans and the environment

Not all nature-derived materials are sustainable. For example, cultivation of cotton requires massive deforestation since cotton entails special weather conditions, much fertiliser, pesticides and water (almost 9000 and 20000 L/kg seed and lint cotton, respectively) to grow [119].

Energy usage and CO$_2$ production of PLA, high-density polyethylene, polyethylene terephthalate and PLA were compared by Rudnik [120] in Table 2-4. PLA- year 1 is compared to all production stages from corn growing to the polymerization stage. PLA- year 5 refers to the environmental impact of PLA produced by high-technology
machines and those for which power is provided from clean energies. This indicates that PLA production will significantly be more efficient and cheaper for novel applications [120].

Table 2-4 Cradle-to-factory gate energy use and CO₂ production of PLA and polymers [120].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Process energy from fossil sources</th>
<th>Feedstock energy from fossil sources</th>
<th>Total fossil energy</th>
<th>Fossil CO₂ from process energy</th>
<th>CO₂ absorption at plant growth</th>
<th>Net CO₂ *</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA - Year 1</td>
<td>54 [GJ/10³ kg plastic]</td>
<td>0 [GJ/10³ kg plastic]</td>
<td>54 [GJ/10³ kg plastic]</td>
<td>3450 [kg/ 10³ kg plastic]</td>
<td>-2190 [kg/ 10³ kg plastic]</td>
<td>1260</td>
</tr>
<tr>
<td>PLA – Target year 5</td>
<td>7 [GJ/10³ kg plastic]</td>
<td>0 [GJ/10³ kg plastic]</td>
<td>7 [GJ/10³ kg plastic]</td>
<td>520 [kg/ 10³ kg plastic]</td>
<td>-2280 [kg/ 10³ kg plastic]</td>
<td>-1760</td>
</tr>
<tr>
<td>high-density polyethylene</td>
<td>31 [GJ/10³ kg plastic]</td>
<td>49 [GJ/10³ kg plastic]</td>
<td>80 [GJ/10³ kg plastic]</td>
<td>1700 [kg/ 10³ kg plastic]</td>
<td>0 [kg/ 10³ kg plastic]</td>
<td>1700</td>
</tr>
<tr>
<td>polyethylene terephthalate</td>
<td>38 [GJ/10³ kg plastic]</td>
<td>39 [GJ/10³ kg plastic]</td>
<td>77 [GJ/10³ kg plastic]</td>
<td>4300 [kg/ 10³ kg plastic]</td>
<td>0 [kg/ 10³ kg plastic]</td>
<td>4300</td>
</tr>
<tr>
<td>(bottle grade)</td>
<td>81 [GJ/10³ kg plastic]</td>
<td>39 [GJ/10³ kg plastic]</td>
<td>120 [GJ/10³ kg plastic]</td>
<td>5500 [kg/ 10³ kg plastic]</td>
<td>0 [kg/ 10³ kg plastic]</td>
<td>5500</td>
</tr>
</tbody>
</table>

*Equals the sum of "Fossil CO₂ from process energy" and "CO₂ absorption at plant growth".

2.8.5 PLA’s practical applications

To fabricate PLA-based products on an industrial scale, blow moulding, thermoforming, injection moulding and extrusion machines which have reliable thermal stability can be used [121, 122]. Thermal stability of these machines is important to maintain MW and properties and to avoid undesired degradation. A maximum of 200 °C is suggested by Garlotta et al. [107] for the processing of PLA to prevent thermal degradation by hydrolysis or chain-scission of PLA during the manufacturing process.

There are versatile opportunities for PLA applications such as plastic films and biodegradable medical devices (e.g. plates that are expected to biodegrade in vivo within
6-12 months). Since PLA contracts under heat, it is also useful for shrink wrap applications. In fact using PLA in various applications is popular due to the desire to create cost-efficient, non-petroleum plastic production. However, its applications are limited for products which require high temperatures (e.g. plastic cups which are required to hold hot liquid) due to its low glass transition temperature. As PLA’s life cycle in environmental conditions is low, it can be beneficial for short lifespan applications where biodegradability is highly valuable such as a plastic water bottle. Although the PLA bottle can be degraded in the ocean after 0.5 to 2 years while other conventional plastics may take several hundred years to be degraded, a more responsible attitude to plastics waste disposal must be encouraged to leave a sustainable planet for future generations! In spite of this degradation speed, PLA is a reliable and robust substance for applications such as plastic electronic components.

To practically compare the technical capability of PLA to other polymers, Wolf et al. [114] reported the findings of an interview with three polymer materials experts, Cargill Dow, Hycaill and Biomer about potential substitution of PLA. As shown in Table 2-5, PLA can be partly substituted for PMMA, PA and polyethylene terephthalate or even can be possibly substituted for PP. However, it cannot substitute for polycarbonates (PC), polyoxymethylene and non-polymeric materials (e.g. as wood, leather).

There are some constraints in the usage of PLA. For example, composites with a PLA-matrix still cannot be used in building applications due to the requirement of 20 years operational time and the relatively higher price compared with PP, polyethylene terephthalate and high-density polyethylene, which have conventionally been used for that purpose. Although there was a significant drop in the price of PLA (∼40%) by 2007, it is still more expensive than those conventional polymers for which production machines and technologies have already been developed. In August 2017, the average cost of PP, high-density polyethylene and polyethylene terephthalate (conventional polymers) was 1.2-1.7 USD/kg, 1.5-1.8 USD/kg and 1.5-2.5 USD/kg and, respectively, in comparison with the PLA price (a biodegradable polymer) which was 2.8-3 USD/kg [123].
Table 2-5 Technical substitution potential for PLA according to Cargill Dow, Hycail and Biomer[114].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Cargill Dow</th>
<th>Hycail</th>
<th>Biomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(vinyl chloride)</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>high-density polyethylene</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>low-density polyethylene</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>polypropylene</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>crystal clear polystyrene</td>
<td>-</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>poly(methyl methacrylate)</td>
<td>+/-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>polyamide</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>polyethylene terephthalate</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>polybutylene terephthalate</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>polycarbonates</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>polyoxymethylene</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>polyurethane</td>
<td>+/-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>high impact polystyrene</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>acrylonitrile butadiene styrene</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

++ full substitution, + partial substitution, - no substitution

2.9 Pre-process drying of NFRP biocomposites
The water in natural fibres is often stated as a concern when natural fibres are being considered for the reinforcements of biocomposites. Baley et al. [124] reported that FFs contain almost 6 to 10 wt. % water at room temperature depending on the retting and growth conditions; they also stated that the contained water performs as a cell wall plasticizer.
The contained water may potentially initiate defects (e.g. porosity) during the manufacturing process. Summerscales and Grove [125] recommended that fibres should be conditioned (dried) before composites manufacture to minimise the effects of moisture release which are primarily manifest as voids within the composite. Yan et al. [3] have reported that the preheating (drying process) of FF prior to fabrication has a positive effect on the mechanical properties of flax/polymer reinforced biocomposites. In the Yan et al. review paper [3], each author suggested different temperatures and times for the drying process, and they highlighted that this might help to increase the mechanical performance of the biocomposite by removing the intrinsic moisture of FFs [3].

On the other hand, removing the contained water by increasing storage temperature causes the tensile strength reduction since the plant layers are sensitive to thermal exposure [126, 127]. Van et al. [128] reported that drying process at 120 °C for tens of minutes (15, 30, 60 and 120 min) removed the water along with surfaces waxes of the fibre; and they also reported that higher temperatures also are more detrimental by deteriorating other compositions of flax such as cellulose, hemicellulose and lignin [124, 126]. Stamboulis et al. [129] also reported that exposing FFs to high temperature causes defects inside the cell walls and subsequently reduction in the fibre strength. To conclude the effect of drying process, Baley et al.[126] conducted a comprehensive research on the influence of drying on the mechanical behaviour of FFs and their unidirectional (UD) composites. They found that the initial drying process did not lead to an improvement in the mechanical properties of FFs. In fact, drying process (e.g. 24h at 105 °C) causes reduction in the desirable mechanical properties (failure strength and failure strain) of FFs.

2.10 Thermal processing (NFRP composites)
Temperature, during the bio-composite manufacturing process, has a significant effect on fibre/matrix interaction [130]. Because of the differences in the coefficients of thermal expansion between fibres and matrix, the matrix tends to flow around the fibres [65, 131].
Moreover, if this temperature is high enough and optimum, all of the moisture can be removed from the bio-composite [132]. This removal of intrinsic moisture may be desirable for the final characteristics of high quality bio-composites.

Process temperature and pressurisation of mat layers in the course of curing may positively improve the fibre/matrix interaction [65]. Therefore evaluation of the effects of process conditions is desirable to create useful, comprehensive and productive process-controlling schemes for bio-composite fabrication industries. The optimum or effective process parameters are currently difficult to determine for various bio-composite-production processes. Thus comprehensive investigations into the effect of process parameters during biocomposite manufacture are desired for each fibre/matrix combination.

In addition to controlling the temperature during consolidation of the composite, it has been shown that it is important to control the cooling rate, since for FRP fabrication, time and cost are vital for industrial sectors [133]; and, the cooling rate is significant for final bio-composite properties regarding crystallization and the fibre/matrix bond strength [65, 134, 135]. If the cooling is high, the bond strength of the composites will decrease. Conversely, if it is at a very low rate, the high crystallinity will lead to a strong interface bond which is important in the mechanical performance of composites [135-138].

NFRP biocomposites need thermal processing which can be performed through various manufacturing processes such as injection moulding and compression moulding processes. Compression moulding is the most accepted and productive technique for manufacturing NFRP composites. These days, compression moulding has been used in automated manufacturing, particularly for the house furniture industry. The manufacturing process begins with placing fibres and matrix layers in the designed mould, and then the temperature of the system will be raised to a certain value. After that, the viscosity of the matrix reduces under heat and pressure, resulting in the matrix impregnating on/into fibres [139].

A number of studies have indicated that the moulding time has a significant effect on the mechanical properties of compression-moulded PLA-based bio-composites [132,
However, there is not a general consensus as to the most suitable length of time that the composite should remain at high temperature and pressure and few studies quantify the effect on the mechanical properties. In terms of characterizing the effect of the moulding time, Alimuzzaman et al. [144] considered the effect of the moulding time on the mechanical properties of flax and PLA bio-composites using a novel air-laying process followed by hot pressing, to form a prepreg for the bio-composite. After drying the prepgregs, the composites were consolidated using compression moulding. The results from their study showed small decreases in tensile and flexural strength with increasing moulding time and no measurable change to the tensile and flexural moduli. The best mechanical properties were achieved for the shortest moulding time (5 min). Neat PLA showed the same trends that were observed for the composites for strength and moduli [140].

A certain consolidation time is needed to make sure that the matrix is totally impregnated but not over consolidated which will cause the properties deterioration of the biocomposite [139, 145]. The impregnation is a process where a polymeric matrix flows through the fibre reinforcement and completely encloses it. The dual scale impregnation process can be divided into two stages – macro impregnation (inter-tow) and micro impregnation (intra-tow) [146]. Micro-impregnation is the rate determining step where the molten thermoplastic polymer enters into the fibre yarn (or tow in the case of synthetic reinforcement) and completely wets each technical fibre. For compression moulding, by applying pressure the liquid polymer enters the yarns of twisted reinforcement fibres.

This highlights the significance of consolidation-time investigation in the manufacturing of NFRP bio-composites [147]. Once a matrix completely flows into all pores, the machine employs a cooling system to cure the composite while the mould is closed. Finally, the mould opens and the composite is ready for further steps such as cutting, painting and so on.

2.11 General degradation of NFRP biocomposites
Degradation or deterioration of NFRP bio-composites is the main obstacle in expanding/developing the range of their applications [27, 83, 148-150]. The reason for
degradation of any kind of (fibre or matrix) polymeric materials is found to be predominantly pyrolysis and chain-scission reactions [7, 115, 144, 151-158]. These reactions can also occur during and after the manufacturing of combined polymeric materials (NFRP biocomposites). Thus, while ‘end-of-life’ degradation is a major merit for biocomposites, in-service degradation can be a significant problem.

There is not a complete record of research on the effect of thermochemical degradation reactions on NFRP biocomposites. There are however, data available on the effect of each of these reactions on the individual polymers from other studies in chemistry or in chemical engineering. The fundamental data are summarised in this section along with their relationship to practical/mechanical properties and applications of flax/PLA biocomposites. This information has opened a new window of research on the degradation of NFRP biocomposites during and after the manufacturing process, which are elaborated in the following chapters.

2.11.1 Pyrolysis degradation

Pyrolysis is the thermal decomposition of materials normally in an inert atmosphere (e.g., N₂, CO₂ or vacuum) and can be measured by mass loss at high temperatures [159]. Pyrolysis degradation occurs in natural fibres and polymers associated with changes in physical and mechanical properties, demonstrating the importance of studying the thermal stability of natural fibres such as flax and their biocomposites [160-162]. In addition, early weight loss takes place at low temperatures (50-100 °C) due to moisture evaporation [163]. The further weight losses take place at higher temperatures (>200 °C) which probably corresponds to the decomposition of hemicellulose, cellulose and lignin [163]. The weight loss at low temperatures demonstrates less thermal stability of NFRP biocomposites in comparison with other synthesised composites [164, 165].

Thermogravimetric analysis/Derivative thermogravimetry (TGA/DTG) test is a common approach to evaluate the thermal stability of natural fibres and their biocomposites when subjected to heat [29, 132]. The TGA curve gives mass changes in milligrams or micrograms as a function of time or temperature subjected to heating; and the DTG gives the percentage and peak temperature of sample mass change. In other
words, TGA/DTG measure the weight change of the sample subjected to heating. The TGA curve shows a slight weight drop, and then a rapid drop over a short time period, leading to zero slope, which demonstrates the reactant is exhausted. Figure 2-10 shows an example of TGA/DTG graphs of flax/PLA.

![TGA/DTG Graphs of Flax/PLA](image)

Figure 2-10 Typical a) TGA and b) DTG graphs of flax and PLA (reproduced from[144]).

Practically, there is no significant difference in TGA/DTG of lignocellulosic fibres since their properties are similar. For example, the thermal decomposition happens in a range of 215-310 °C for almost 60% of natural fibres [29]. Thus these temperatures can be used to determine the thermal degradation behaviour of NFRP biocomposites. Beg et al. [166] stated that the degradation of natural fibres begins at 260 °C by dehydration and emission of volatile components, following a fast weight loss as a result of oxidative decomposition, showing char formation at high temperatures. Furthermore, three main
The stages of weight loss are defined for natural fibres in the course of increasing temperature [144]:

i. the release of absorbed moisture in the fibres at 30–150 °C;

ii. the degradation of cellulosic substances such as hemicelluloses and cellulose at 150–375 °C;

iii. the degradation of non-cellulosic materials in the fibre at 375–600 °C.

Typically, published papers used Arrhenius rate equations for the theoretical calculations of pyrolysis [144, 151-156]:

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$

(1)

Where $k$ determines the thermal-degradation rate, $A$ is the pre-exponential factor (s$^{-1}$), $E_a$ is apparent activation energy, $R$ is universal gas constant (8.3136 J/mol K) and $T$ is temperature (K).

Thermal degradation of NFRP biocomposites can be studied using data extracted from TGA and the findings can be used to determine the degree of degradation which can be critical for the manufacturing process. For example, it has been reported by [25, 144, 167, 168] that the processing temperatures of polymeric materials overlap with the main decomposition range of natural fibres; and consequently these temperatures affect their mechanical properties and the life-cycle of biocomposites.

### 2.11.1.1 PLA Pyrolysis

Thermal degradation and stability of PLA is the subject of many studies because PLA is very sensitive to heat [169]. These studies [164, 169-172] reported that several factors (such as moisture, hydrolysed monomer and oligomer, and residual metal catalyst) are responsible for the poor stability of PLA. PLA’s thermal degradation is a single process which includes the non-radical decomposition, radical alkyl-oxygen homolysis, and radical acryl-oxygen homolysis and causes formation of an intermolecular transesterification, which experiences ester pyrolysis, and unzipping depolymerisation/random chain scission [170, 172-175].
The depolymerization mechanism can occur at high temperature in which monomeric units split off from the end of the polymeric chain [176]. Indeed, this is the reverse mechanism of the polymerization. Active polymers can be depolymerized until the equilibrium between monomer and polymer at a given temperature is reached [176, 177]. Degree of polymerisation quantifies the number of monomers remaining after the chain scission process and can be calculated using Eq. (2) [176, 177]:

\[ DP_n = \frac{M_n}{M_0} \]  

(2)

Where \( DP_n \) is the number-average degree of polymerization, \( M_n \) is the molecular number average, \( M_w \) is the molecular weight, \( M_0 \) is the molecular weight of monomer unit.

Various values of activation energy (\( E \)) were found for PLA dependent on the test condition and the scheme of calculation of the \( E \) value (see Table 2-6). Zou et al. [178] defined the thermal degradation kinetic of PLA as multi-step degradation mechanisms. Hantao et al. [178] used different methods to calculate \( E \) of PLA and reported that the obtained values are in good agreement with each other (their findings are 177.5 kJ mol\(^{-1}\), 183.6 kJ mol\(^{-1}\) and 181.1 kJ mol\(^{-1}\) for \( E \) values calculated using Ozawa-Flynn-Wall, Friedman and Kissinger methods, respectively). Kopinke et al. [172] also stated that PLA pyrolysis is a multi-step process and the pyrolysis behaviour would be different if it contains some metals (impurities) such as Sn, Zn, Al or Fe; and they found \( E \) was 119 kJ mol\(^{-1}\) for PLA [172]. Liu et al. [179] studied the kinetics of thermo-oxidative and thermal degradation of PDLLA at processing temperatures and concluded that there were three stages. In the first stage, oxygen and nitrogen had negligible influence on the degradation process due to a large amount of oligomers containing carboxylic acid groups and hydroxyl groups, resulting in almost the same \( E \) values. In the second stage, oxygen played an important role in the thermo-oxidation process, causing a significant decline in \( E \) value. In the third stage, PDLLA was degraded under nitrogen over 200 °C due to the appearance of a carboxylic acid substance.
In summary, although there are several studies on the pyrolysis of PLA, there is no study to highlight the degradation progress during processing time. Comprehending the PLA stability during the heating process may provide valuable information about the degradation properties of manufactured products. As stated above, TGA has been widely utilised to characterise the decomposition behaviour and the kinetic factors of PLA. Thermal degradation and the stability of PLA are significant for introducing a time frame for processing PLA without triggering thermal decomposition.

Table 2-6 Available activation energy ($E$) for PLA

<table>
<thead>
<tr>
<th>Material</th>
<th>Atmosphere</th>
<th>Temperature ($^{\circ}$C)</th>
<th>Activation Energy($E$) Overall Avg. (kJ/mol)</th>
<th>Technique (heating rate)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>nitrogen</td>
<td>30 to 800 $^{\circ}$C</td>
<td>215</td>
<td>10 $^{\circ}$C/min</td>
<td>[171]</td>
</tr>
<tr>
<td>PLA</td>
<td>nitrogen</td>
<td>30 to 600 $^{\circ}$C</td>
<td>177-183</td>
<td>5-40 $^{\circ}$C/min</td>
<td>[178]</td>
</tr>
</tbody>
</table>

2.11.1.2 Flax Pyrolysis

The degradation of FFs also needs to be investigated at high temperatures since the fabrication of biocomposites needs a high temperature. TGA analysis can give the necessary factors of a kinetic model to determine the degradation rate. Several studies reported the value of these factors for flax and its components [151, 152]. In this regard, the pyrolysis of cellulose, hemicellulose and lignin were also investigated [180, 181] and are explained in the following sections.

To have a better understanding of natural fibre decomposition kinetics, scholars have measured various reaction approaches. For example, Koufopanos et al. [182] established a multi-step reaction mechanism for wood and wood components. Several years later, Diebold [183] introduced an elaborate seven-step global kinetics of cellulose pyrolysis. Additionally, Orfao et al. [184] employed a three independent parameter reaction model for some lignocellulose materials, while Di Blasi [185] employed a three parallel reaction model for the pyrolysis of wood. Velde et al. [151] and Arbelaitz [152]
investigated the thermal degradation of FF with the use of TGA and achieved $E$ values of 121.7 kJ mol$^{-1}$ and 138 kJ mol$^{-1}$, respectively (see Table 2-7). Gronli et al. [185] have concluded that the basic and simplified characteristics of natural fibres are adequate for essential calculations in practical engineering applications. Thus, it is more practical to comprehend and predict the thermal decomposition or pyrolysis of FFs with the use of simplified kinetic approaches for specific processing temperatures of NFRP biocomposites. However there are few fundamental studies on the pyrolysis of natural fibres during the manufacturing process.

2.11.1.2.1 Cellulose Pyrolysis

In investigating thermal decomposition of flax, cellulose has been by far the most frequently studied component due to its high proportion in flax composition. In the literature, there is various information (various values of $E$) for cellulose due to variation in sample characteristics, equipment parameters and the methods of analysing data. For example, Antal et al. [186, 187] investigated the pyrolysis of pure (ash free) cellulose and concluded that it is a single-step and irreversible process which follows a first-order law with $E$ value of 228-238 kJ mol$^{-1}$. Milosavljevic and Suuberg [188] reviewed various cellulose kinetic polymers and concluded that $E$ value would be 140-155 kJ mol$^{-1}$, if cellulose was rapidly heated above 600 K. Capart et al. [189] utilised dynamic and isothermal methods to determine kinetic parameters of micro-angular cellulose and achieved two $E$ values (202 kJ mol$^{-1}$ and 255 kJ mol$^{-1}$). Gašparovič et al. [190] and Burhenne et al. [191] studied the pyrolysis of the main components of plant fibres and reported $E$ values of cellulose to be 175.6 kJ mol$^{-1}$ and 236 kJ mol$^{-1}$ (see Table 2-7).

Sergeeva and Vaivads[162] examined and measured the degradation of birch cellulose in air using differential thermal analysis (DTA). DTA measures the heat flow during temperature changes and gives changes in temperatures per mg. As mentioned above, DTG measures the weight loss of the sample during the heating process and usually it decreases when exothermic reaction occurs. Thus both curves from DTA and DTG are usually overlapping each other, in order to explain what's going on during the thermal
processes. Sergeeva and Vaivads [162] described the various endothermic and exothermic peaks and plateaus of the resulting DTA curve as:

i. endotherm: at 95 °C to 100 °C, evaporating hydrosopic water;
ii. plateau: at 155 °C to 259 °C, heating cellulose without bond breaking;
iii. exotherms: at 259 °C to 389 °C, splitting of cellulose macromolecules;
iv. plateau: at 452 °C to 500 °C, forming stable substances;
v. endotherm: at 500 °C to 524 °C, completing the reaction.

Moreover, Domansky and Rendos [160] examined four different sources of cellulose (Whatman paper, spruce sulphite cellulose, spruce sulphate cellulose, and beech sulphate cellulose) in nitrogen. They concluded that the exothermic reaction began at 230 °C for all samples and became endothermic at 315 to 320 °C.

### 2.11.1.2.2 Hemicellulose Pyrolysis

The second major component of FF is hemicellulose which decomposes in the range of 200-260 °C, meaning that it is less stable and chars more easily than cellulose [159]. It has also been reported that hemicellulose begins to decompose at a lower temperature than cellulose. Mohan et al. [159] reported that hemicellulose pyrolysed in the range of 130-194 °C and major loss occurred at higher than 180 °C. In a fast pyrolysis process, the decomposition of hemicellulose occurred in only a few seconds but its relevance against cellulose is still unknown [159]. Gašparovič et al. [190] and Burhenne et al. [191] reported $E$ values of 132.9 kJ mol$^{-1}$ and 100 kJ mol$^{-1}$ for hemicellulose (see Table 2-7).

### 2.11.1.2.3 Lignin Pyrolysis

The third major component of FF is lignin and several research works were conducted on its pyrolysis either alone or mixed with other polymers [159, 192]. A main objective of these studies was to find a temperature range at which lignin shows significant decomposition. It was concluded that lignin decomposes over a broader range when heated at 280-500 °C [159, 192]. Brebu [192] described the DTA results as:

i. moisture evaporation at 100-180 °C and resulting in an endothermic peak;
ii. a broad exothermal peak at 280-390 °C;
iii. the second broad exothermal peak at ≈420 °C
iv. and a long tail beyond 500 °C.

Pyrolysis of lignin has been investigated for a range of different thermal conditions [190-195]. Varhegyi et al. [161] reported a low range of $E$ values (34-65 kJ mol$^{-1}$) for wood lignin decomposition. Gašparovič et al. [190] and Burhenne et al. [191] reported $E$ values of 101 kJ mol$^{-1}$ and 46 kJ mol$^{-1}$ for lignin. Thus, thermal degradation of lignin is generally influenced by heat and mass transfer processes, which significantly affect the activation energy of the process (see Table 2-7).

In summary, the thermal decomposition of lignin takes place in a broad temperature range and is strongly influenced by parameters such as its nature (functional groups), degradation atmosphere and moisture content (MC). These parameters can have a considerable effect on conversion and product yields, as well as on the physical properties and quality of the products. Figure 2-11 shows TGA and DTG curves of cellulose, hemicellulose and lignin as three main components of natural fibres [192].

![Figure 2-11 TGA/DTG curves of cellulose, hemicellulose and lignin (reproduced from [192]).](image)

Table 2-7 Available activation energy ($E$) for flax and its components.
2.11.2 Thermo-chemical degradation

Thermo-chemical degradation is a process which characteristically contains the breaking down of long/high MW chains to shorter/lower MW molecules. This kind of degradation can happen at high temperatures through chemical reactions in polymeric materials, resulting in changes in their physical or mechanical properties. Although there were many attempts in the past to stabilize these chemical reactions, newly developed technologies use these reactions to convert waste polymers into higher value chemical products or quickly return them back to nature.

In general, when the thermal energy is adequate to overcome bond dissociation energies and cause chain scissions, thermo-chemical degradation takes place [196]. Chain scissions arbitrarily happen at weak bonds along the polymer chain and consequently
result in bond cleavages or depolymerisations. Moreover, these chain scissions cause a fast reduction in the MW of the polymers.

Previously, there were many efforts to avoid or minimise degradation of materials; however recent research studies have also focused on the degradation progress of polymers for recycling applications or sustainability concerns.

### 2.11.2.1 PLA chain-scission

Chain scission is the main type of degradation in polymeric materials. This begins with the breaking down of the long/high MW polymers to short/low MW polymers through heat and chemical reactions. Chain scission eventually results in changes in mechanical properties of the polymeric materials. Gupta et al. [197] stated that the thermal degradation is a chain-scission reaction which follows a first-order model. Chain scission reactions can involve hydrolysis, depolymerisation, oxidation degradation or intramolecular or intermolecular reactions. Thus degradation of PLA exposed to heat is due to a combination of several reactions which are broadly described as chain scission. For example, an intermolecular transesterification reaction eventuates in cyclic oligomers of lactide acid and lactide [164, 172, 174, 198, 199]. Concurrently, a recombination of the cyclic oligomers with linear polymers occurs through insertion reactions [164, 174, 198-200] and hydrolytic ester splitting is associated with water content [199]. The pyrolytic elimination, resulting in molecules with acrylic end groups, has lesser influence on the degradation progress than other reactions [199]. Moreover, radical degradations are only important when temperatures above 250 °C are employed [199]. Doi et al. [201] also stated that the thermal degradation and hydrolysis of microbial polymers take place through the chain scission process, regardless of the type of involved reactions and chemical compositions.

Wachsen et al.[153, 199] explained the alteration of MW during thermal processing with the use of a statistical process. They simulated the alteration of MW by using a two-parameter model which included a statistical degradation and a recombination step; and the concentration of a polymer of length $n$ in their model is governed by:
where $P_n$ is the polymer with a degree $n$ of polymerization, and indexes $d$ and $c$ are the degradation and (re)combination rate indices, respectively. Yu et al. [156] further developed this statistical method and performed an experimental test, concluding that the results are in good agreement with the experimental data. They re-expressed Equation (3) in terms of moments ($\lambda_i$) of different orders which are defined according to Eq. (4) as:

$$\lambda_i = \sum_{n=0}^{\infty} n^n [P_n] i = 0, 1, 2, 3 \ldots$$

### 2.11.2.2 Flax chain scission

The influence of temperature on the mechanical properties of fibre is critical for the practitioners as this is closely linked to overall mechanical properties of fibre reinforced composites. In this regard, Gassan et al. [202] found that the major weak point of natural fibres is their thermal instability at temperatures higher than 180 °C. Due to this fact, thermoplastics with a melting point less than that are being used in the manufacturing of NFRP bio-composites [202]. For example, Brushwood [203] reported little loss of strength when heating cotton for 20 min at 160 °C, but rapid strength reduction when exposing cotton to higher temperatures. Burger et al. [204] also reported a reduction in the tenacity of FFs when held at a temperature of 200 °C for 12 minutes and concluded that the degradation rate is also dependent on the period of heating. Herrmann et al. [205] reported that tenacity of ramie fibres was also significantly reduced when the fibre was exposed to longer times (≈4hrs) at 150 °C.

Some scholars have reported that the progress of degradation of natural fibres is dependent on their composition. For example, Ramiah et al. [193] stated that the order of degradation is hemicellulose<lignin<cellulose. Additionally, it has been demonstrated that cellulosic fibres show alteration in either physical or chemical properties such as depolymerisation or hydrolysis when exposed to manufacturing temperatures [206]. For example, Zeronian[206] found that the value of $DP$ of cotton fibres reduced from 5360 to 320 after a heating process at temperatures 165-240 °C for
six hours. He also reported that there was damage to crystallites at a temperature above 230 °C.

The rate of degradation can be measured through the changes of the intrinsic fluidity \((1/\eta)\) or it can be called the inverse of the average degree of polymerisation \((1/DP)\) [207]. The random scission of bonds in a linear chain polymer follows a first-order kinetics rate law [207]:

\[
\frac{dN}{dt} = K \times N
\]  

(5)

where \(N\) is the total number of bonds between monomer units, \(t\) is the time and \(K\) is the observed rate constant. This relationship may also be expressed in terms of the fraction of the total number of available bonds \((1-1/DP_n)\) where \(DP_n\) is the number-average degree of polymerization [207]:

\[
\frac{d}{dt}(1 - \frac{1}{DP_n}) = K(1 - \frac{1}{DP_n})
\]

(6)

This equation can be simplified when only a small fraction of the bonds have been broken:

\[
\left(\frac{1}{(DP_n)_t} - \frac{1}{(DP_n)_0}\right) = \alpha \times K' \times t
\]

(7)

where \(\alpha\) is a measure of the bonds’ accessibility and \(K'\) is the rate constant for the rate of bonds being broken in the anhydroglucose chains [207]. The chain breaking rate follows simple zero-order kinetics.

2.12 Moisture-related degradation

Water or moisture absorption is the main deteriorative parameter of the degradation of biocomposites in practical applications [208-210]. Absorbed water in NFRP can be categorised as free water and bound water. Free water is defined as water molecules which are relatively free to travel through the micro voids and pores, while bound water is defined as that dispersed within the polymer matrix or attached to the polar groups of the polymer (see Figure 2-12) [7, 211, 212].
Moisture absorption causes NFRP biocomposites to have very low stability in moist environments. When NFRP composites are exposed to moist conditions, water molecules enter the composite through micro-cracks. This phenomenon causes a reduction in interfacial adhesion between fibres and matrix, as highlighted in the review by Azwa et al. [7]. Moisture promotes swelling of the fibres and leads to micro-cracks [213]. Following this, micro-cracks may also appear in the matrix, which ultimately causes debonding between fibres and matrix (see Figure 2-13) [7, 211].
Moisture diffusion, and the consequent water absorption (WA), in polymer composites is directed and controlled by various mechanisms:

i. diffusion of water molecules into the free volume between polymer chains [214],

ii. diffusion of water molecules into the structure of fibres (resulting in hydrogen bonding with hydroxyl group of cellulose molecules) [215],

iii. movement of water molecules into gaps and flaws at the fibre/matrix interface as a result of capillary action [214, 215], and

iv. capillary flow into micro-cracks in the matrix caused by swelling of fibres [213].

Thirmizir et al [216] investigated the influences of ~10-40 w/o fibre loadings on the mechanical properties, WA and dimensional stability of kenaf/PBS composites. Moisture absorption increased in proportion to the KF loading, which is attributable to the increase in hydrophilic sites in the composites. Additionally, an increment in the diffusion coefficient occurred with increased fibre loading, conforming to Fick’s Law of Diffusion (Eq.8) [216].
\begin{equation}
F = -D \frac{\partial C}{\partial x}
\end{equation}

where $F$ is the rate of transfer in the $x$ direction per unit area of a section, $C$ is the concentration of the diffusion substance, $x$ is the space coordinate measured normal to the section, and $D$ is the diffusion coefficient of the solid.

From the point of view of the components of FF, hemicelluloses (plant cell wall material associated with cellulose) are largely responsible for moisture absorption in plant fibres [7, 60] because they are amorphous with higher free volume than the crystalline cellulose and hence facilitate easier water transport and access to hydrophilic groups. Increased hemicellulose content may result in greater moisture absorption, leading to faster biodegradation in plant fibres [7, 60, 217].

Wang et al [218] investigated the water uptake and mechanical properties of RF reinforced composite immersed in distilled water. Owing to the strong hydrophilic characteristics of RF, the saturated water uptake and the coefficient of diffusion of the RF reinforced composite were found to have higher values (compared with synthetic FRP such as CF, GF or basalt fibres) [218]. Additionally, a significant reduction of flexural modulus and strength was observed after 1 day of immersion in water. In spite of a slight restoration of flexural properties after drying, lower values for flexural properties were observed compared with the values before immersion. This is a clear indication of permanent damage. Wang et al [218] categorised mechanical property as a function of the water uptake into three stages:

\begin{enumerate}
  \item an initial dramatic reduction,
  \item a levelling off period, and
  \item a subsequent quick decrease.
\end{enumerate}

These effects could be attributed to con/subsequent occurrence of degradation of fibre, hydrolysis of fibre and resin, and fibre debonding [218].

Alam et al [219] demonstrated that the WA of 32 w/o jute/PC or jute/PP composites was found to be less significant compared to that of bleached jute Hessian cloth/PC or PP composite. A very small amount of WA was observed at the edges of these composites where fibre ends exist. Encapsulation by the polymer and good fibre/matrix
bonding caused reductions in the fibre moisture absorption, which led to decreases in the rate and amount of water absorbed in the interface region of the composite [219]. Digital Neutron Radiography revealed hidden defects (such as voids, cracks, or inhomogeneity) in the composite [219, 220].

Interestingly, Nosbi et al [221] found that immersion in water causes higher failure strain than that observed for non-immersed samples. Their findings for 70 w/o pultruded kenaf/UP composites agreed with the findings of Akil et al [222] for pultruded jute/UP composites. Both attributed this decrease in compressive behaviour of composites to the plasticisation of composites after exposure to ambient moisture [221, 222]. Nosbi et al [221] added that composites immersed in distilled water have higher compression strength (40.7 MPa) than those immersed in seawater (32.7 MPa) or in an acidic solution (32.4 MPa).

Takemura [223] conducted static test for a jute/PP composite under both dry and wet conditions. Composites were prepared at 30 or 50 w/o and two pellet lengths (4 mm and 12 mm) were used. The results clearly showed that:

i. water absorption decreased the static modulus and strength for jute/PP.
ii. the strength of the re-dried samples did not appear to be the same as that for the non-absorption samples.

The mechanical properties and operational characteristics of composites are reduced by the moisture absorption and swelling of NFRP composites [213, 215, 224-230]. Madsen et al. [231] evaluated MC and dimensional changes at five levels of ambient humidity (65%, 80%, 85%, 90% and 95%) for 24, 39, 43 or 49 w/o UD hemp/PET composites. The principal conclusions [355] from their experiments were:

i. the moisture content of the composites increased linearly as a function of the fibre weight fraction, in agreement with a simple weight-based mixture relationship;
ii. the dimensional changes of the composites, being transversely isotropic, have relatively large and nearly equal hygral strains in the two transverse (radial) directions despite showing very low hygral strains in the fibre axial direction.
The application of micro-mechanical models (of axial and transverse hygral strains of composites) is in accordance with the experimental data;

iii. from a practical point of view, this work demonstrates values for the relative moisture content and dimensional changes of the composites with reference to a particular humidity level of 65% RH. For a collective span of ambient humidity conditions between 33% and 85% RH, and for composites with a high (49 w/o) fibre weight fraction, the relative moisture content ranged from -0.9-1.6%, which eventually resulted in transverse relative hygral strains in the range from -0.007 to 0.011, and zero axial hygral strain;

iv. generally, the experiments confirmed that the composites have low moisture adsorption capacity and low dimensional changes.

The relative magnitudes of the movements in the axial and radial directions (point ii above) is consistent with the elastic properties and especially Poisson’s ratios of anisotropic materials [232, 233]: the stiff covalent bonds in the cellulose molecules are aligned along or close to the fibre axis while the transverse direction primarily meets intermolecular bonding.

Temperature also plays an important role in promoting the degradation process. Humidity or hygrothermal environments can accelerate the damage to biocomposites due to the presence of both moisture and temperature. Hu et al [234] studied the moisture absorption and microstructure of uncoated and coated 30%, 40% and 50% v/o short jute/PLA composites set in a hygrothermal environment (at 70 °C). The moisture absorption process of the uncoated sample consisted of three different stages [234]:

i. a quick moisture absorption stage;

ii. a slow but steady increasing of moisture uptake stage;

iii. and a very rapid moisture absorption stage.

The entire moisture absorption process (up to the completion of the relaxation of the samples) showed no occurrence of moisture saturation after eight days. As suggested by Hu et al [234], a reliable procedure should be in place to isolate jute/PLA composites during exposure to a hygrothermal and moist environment. In the course of the aging process, the most significant defects were the presence of pores, micro-cracks,
delamination and complete structure relaxation [234]. The tensile strength of the samples appeared to decrease after four days in a hygrothermal environment [234]. Thus, it is important to investigate the degradation process of NFRP biocomposites at moisture-related environments.

2.13 Applications

As mentioned above, a lot of research has been performed on biobased materials and biocomposites, resulting in developed science implementing various applications such as packaging, biomedical, civil and automotive sectors. For example, nearly all big car companies including Audi, Mercedes, BMW, Ford and Volkswagen fabricate parts using NFRP biocomposites. Audi, for instance, uses flax or sisal fibre reinforced biocomposites in their A2, A3, A4, A6, A8 and Roadster models for door panels, seat backs and boot lining [13]. Mercedes also uses jute and banana fibre reinforced biocomposites for the door panels of the E-class and A-class, respectively [23]; the green composites which are utilised for several parts for the C-class are shown in Table 2-8. In addition, Daimler-Chrysler and Lotus also use NFRP biocomposites in the manufacturing of parts, such as bumpers and interior trimmings made of flax and sisal fibre reinforced composites, respectively [23]. However, fully sustainable products give rise to high manufacturing cost, largely due to recycling processes, which composes the chief obstacle of consumers and manufacturers of environmentally friendly products [235]. Apart from the automobile industries which are able to pay for those high costs of manufacturing, there are other small industries such as musical instrument and furniture manufacturers which have begun to introduce their products made of flax/PLA biocomposites to the market. These potential products of flax/PLA biocomposites are listed in Table 2-8.
Table 2-8 Application of NFRP biocomposites.

<table>
<thead>
<tr>
<th>Applications in</th>
<th>Products/Materials</th>
<th>Samples</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive</td>
<td>Mercedes C-class components/NFRP biocomposites</td>
<td><img src="image" alt="Mercedes C-class components" /></td>
<td>[236]</td>
</tr>
<tr>
<td>Biomusical instruments</td>
<td>Guitar/ flax/PLA biocomposites</td>
<td><img src="image" alt="Guitar" /></td>
<td>[237]</td>
</tr>
<tr>
<td>Biosports</td>
<td>Skating board/ flax/PLA biocomposites</td>
<td><img src="image" alt="Skating board" /></td>
<td>[238]</td>
</tr>
<tr>
<td>Biofurnitures</td>
<td>Cabinet/ flax/PLA biocomposites</td>
<td><img src="image" alt="Cabinet" /></td>
<td>[235]</td>
</tr>
</tbody>
</table>
## 2.14 Chapter Summary

Various commercial areas such as automobile, music, sport and furniture have been increasingly interested in using NFRP biocomposites. Recently, non-structural interior components have partially succeeded in occupying the biocomposite markets. However, NFRP biocomposites seem to have a long future research journey to pass intrinsic constraints in order to eventually be used for structural interior components or for outdoor applications. Poor thermal stability and degradation in moisture-related environments are the main causes of the restrictions. The restrictions are significant for the research since both fibre and matrix are here intended to be fully sustainable and biocompatible. FF and PLA matrix, which are in this category and thus have considerable benefits for both biocomposite manufacturers and consumers, need more investigations into their stability and degradation. Further studies may unlock some of the remaining problems or may help to understand the issues regarding the degradation mechanisms, which may subsequently inform still further studies for the extended use of flax/PLA biocomposites.

In the literature, flax and PLA have been studied for their production methods, physical and chemical properties, mechanical properties, environmental impacts and practical applications. Although there have been several positive signals (e.g., price and biocompatibility) regarding the usage of flax and PLA, the stability during the thermal processing, which is a common manufacturing process of NFRP biocomposites, has not been carefully studied to understand the degradation rate. More precisely, there is no

<table>
<thead>
<tr>
<th>Bioautomobile parts</th>
<th>multi-position trunk load floor or a structural floor/ flax/PLA biocomposites</th>
</tr>
</thead>
</table>

[237]
methodology to construct a map or window for setting practical upper and lower limits to consolidate temperature and processing time.

Thermal and thermo-chemical degradations have been accounted as the main degradation mechanism for both flax and PLA during the manufacturing process. TGA has been used to find the necessary kinetic data of the pyrolysis of flax or PLA, and the Arrhenius rate equation has been used for the theoretical calculation of pyrolysis. Thermo-chemical degradation has mainly been studied by means of the chain-scission process. A very complex statistical equation has been used by the literature for the theoretical calculations or simulations of the chain-scission degradation rate. To calculate and simulate the chain-scission process of PLA during a thermal processing, there is a need to simplify or revise the existing statistical model. In addition, there is no record of any attempt to calculate the effect of transient temperature or the temperature history on the degradation of flax/PLA biocomposites.

Few research papers have studied the changes in MW during thermal processing and reduction in molar mass at high temperatures. Their conclusion was that the reduction of mechanical properties of individual fibre or biopolymer can be due to decline in molar mass. However, there is no particular research study to explain or describe the degradation rate of NFRP biocomposites at high temperature in association with molar mass changes or degree of polymerisation. Currently, there are no attempts to correlate these molar mass changes with the tensile strength of flax/PLA biocomposite, or to use the thermo-chemical degradation concepts to predict the tensile strength of flax/PLA biocomposites.

The water immersion test is the main tool for recognizing the sensitivity of biocomposites to outdoor environments. The above papers have discussed the effect of water immersion on various natural fibre reinforced biocomposites. However, for a better understanding of the degradation behaviour of flax/PLA biocomposites, the quality of the biocomposite can be explained by using a range of environments, from a fully wet environment to an environment where the WA level changes due to freezing and thawing. Moreover, the characteristics of the biocomposites exposed to only moisture related environments such as water, humidity and freeze/thaw (F/T) is not discussed for the flax/PLA biocomposites. Therefore, knowledge or a complete
discussion on the sensitivity of mechanical properties of flax/PLA biocomposites to wet, freezing and humid environments is essential since the information can be valuable for practitioners who are considering using flax/PLA biocomposites as serviceable products.

In general, the degradation of flax/PLA biocomposites has many unknown points that need to be studied. The produced information may be used for the betterment of the quality of the manufactured flax/PLA biocomposites and an increase in the trust of users in sustainable/biodegradable biocomposites. As a result, this study has focused on the degradation of flax/PLA biocomposites during and after manufacture.
Chapter 3: Constructing an Optimum Processing Window for a Biocomposite

Statement of contribution to co-authored published paper

This chapter includes a published journal paper.

The bibliographic details of the paper, including all authors, are:


My contribution to the paper involved: undertaking literature review, classifying the necessary theoretical backgrounds and models, performing the experimental tests, analyzing and discussing data, drawing figures, preparing tables, writing and editing the manuscript according to my supervisors’ comments.

________________________________ (Date)___ 15/Mar/2018___________

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Co-supervisor: John Summerscales (co-supervisor and co-author)
Chapter 3: Constructing an Optimum Processing Window for a Biocomposite

Consolidation Process Boundaries of the Degradation of Mechanical Properties in Compression Moulding of Natural-Fibre Bio-Polymer Composites

Abstract: In spite of the volume of literature on natural fibres, bio-matrix materials and their composites, the choices of optimum process parameters such as moulding temperature, pressure and compression time are still largely based on experience, rules of thumb and general knowledge of the chemical and physical processes occurring in the melt during consolidation. The moulding process itself is a complex balance between processes that must occur for the composite to successfully consolidate and the onset of thermal degradation of the natural fibre and/or matrix materials. This paper brings together models of thermal penetration, melt infusion, thermal degradation and chemical degradation of natural polymers to construct an optimum processing window for a bio-composite. All processes are mapped in terms of normalized consolidation progress parameters making it easier to identify critical processes and process boundaries. Validation of the concept is achieved by measuring changes in the mechanical properties of a flax/PLA bio-composite formed over a range of processing conditions within and outside of the optimized window.

Keywords: Bio-polymer composites; Chemical degradation; Natural fibres; Mechanical properties; and Thermal processing degradation
3.1 Introduction

The use of natural fibres as the reinforcement for composites has been comprehensively reviewed by the authors of this paper [19, 34, 37, 239, 240] and others. One of the key challenges for the use of natural fibres for reinforcing thermoplastics and thermosets is minimizing the thermal degradation of the cellulosic material that can occur during hot processing of the composite [128]. For bio-composites, plant-derived resins such as poly (lactic acid) (PLA) and poly(L-lactic acid) (PLLA) also suffer from thermal degradation for temperatures that typically occur during the compression moulding process [153, 155, 156, 241]. Thus the temperature and time are the key process parameters for controlling thermal degradation in both the natural fibre and the bio-based matrix material. The temperature of the hot press should be sufficiently above the melting point of the matrix to lower its viscosity and the time sufficiently long for penetration of the melt into the fibres achieving a strong bond between matrix and fibre. In competition with these requirements, the melt temperature should be as low as possible to slow the rate of thermo-chemical degradation and the time as short as possible to limit the progress of these undesired chemical reactions [241, 242]. This leaves a narrow window of opportunity to achieve a well-consolidated bio-composite without compromising the mechanical properties of matrix and fibre.

A number of studies have indicated that the moulding time has a significant effect on the mechanical properties of compression-moulded PLA-based bio-composites [132, 140-144]. However, there is not a general consensus as to the most suitable length of time that the composite should remain at high temperature and pressure and few studies quantify the effect on the mechanical properties. Indicative process conditions from the literature are given in Table 3-1.
Chapter 3: Constructing an Optimum Processing Window for a Biocomposite

Table 3-1 Indicative process conditions for pressing bio-composites.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Matrix</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Time (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>kenaf</td>
<td>PLA</td>
<td>160 °C</td>
<td>10 MPa</td>
<td>10</td>
<td>[140]</td>
</tr>
<tr>
<td>cotton, lyocell, hemp, kenaf</td>
<td>PLA</td>
<td>180 °C</td>
<td>4.2 MPa</td>
<td>20</td>
<td>[141]</td>
</tr>
<tr>
<td>Hemp, lyocell, lyocell</td>
<td>PLA/PP</td>
<td>195 °C</td>
<td>1.7 MPa</td>
<td>20</td>
<td>[132]</td>
</tr>
<tr>
<td>jute</td>
<td>PLA</td>
<td>185-195 °C</td>
<td>1.33 MPa</td>
<td>8</td>
<td>[142]</td>
</tr>
<tr>
<td>hemp</td>
<td>PLA</td>
<td>185 °C</td>
<td>2 MPa</td>
<td>5</td>
<td>[143]</td>
</tr>
<tr>
<td>40-60% nonwoven flax</td>
<td>PLA fibres</td>
<td>160 °C</td>
<td>0.4 MPa</td>
<td>5</td>
<td>[144]</td>
</tr>
<tr>
<td></td>
<td>Drying</td>
<td>80 °C</td>
<td>Ambient</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>prepreg</td>
<td>180-200°C</td>
<td>5 MPa</td>
<td>5, 10 or 15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Moulding</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In terms of characterizing the effect of the moulding time, Alimuzzaman et al. [144] considered the effect of the moulding time on the mechanical properties of flax and PLA bio-composites using a novel air-laying process followed by hot pressing, to form a prepreg for the bio-composite. After drying the prepregs, the composites were consolidated using compression moulding. The results from their study showed small decreases in tensile and flexural strength with increasing moulding time and no measurable change to the tensile and flexural moduli. The best mechanical properties were achieved for the shortest moulding time (5 min). Neat PLA showed the same trends that were observed for the composites for strength and moduli [140].

Longer moulding times have been employed for FFs in other matrix materials. For example, Kumar and Anandjiwala [243] had a compression moulding time of 2 h at 170
°C for their flax – polyfurfuryl alcohol (PFA) bio-composites. Zhang et al. [244] studied the effect of process parameters on the tensile strength of FF reinforced PP composites; they found a maximum strength for 181 °C and 45-50 min moulding time. In contrast, the effect of moulding times in excess of 30 minutes for PLA-based bio-composites does not appear to have been quantified in the literature.

While practitioners working with bio-composites are no doubt aware of the issues, there have been surprisingly few attempts to quantitatively map out the process boundaries for successful compression moulding of bio-composites. The aim of this study is to highlight the key considerations and propose a quantitative guide for moulding time limits based on the available literature and a practical study of a representative flax/PLA bio-composite.

3.2 Theoretical background and measures of consolidation progress

The processes occurring during manufacture of the composite can be conveniently discussed using normalized progress parameters, $\kappa_i$, where $\kappa_i = 0$ implies the process has just started and $\kappa_i = 1$ implies the process is completed or has reached a maximum or desired state. Each process parameter needs to be expressed as a function of time and temperature.

3.2.1 Thermal penetration and melting point

The first process after starting the hot press is to heat all the matrix to at least its melting point. Here $\kappa_{\text{heatup}} = 0$ implies the laminate is at room temperature and $\kappa_{\text{heatup}} = 1$ indicates the centre of the matrix is a melt at the set-point temperature. To achieve these limits, the progress parameter can be defined in terms of the specific enthalpy $h(T)$:

$$
\kappa_{\text{heatup}} \equiv \frac{h(T_{\text{cen}}) - h_s(T_0)}{h_l(T_{\text{platen}}) - h_s(T_0)}
$$

(1)

where $T_{\text{cen}}$ is the temperature in the centre of the composite (i.e. half way between the two heated plattens), $T_0$ is the initial temperature of the composite and $T_{\text{platen}}$ is the temperature of the platen. $h_l(T)$ is the specific enthalpy of the liquid while $h_s(T)$ is the specific enthalpy of the solid.
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Evaluating $h(T_{cen})$ in Eq. (1) as a function of time requires numerical integration of the unsteady heat conduction equation including any phase change. Since this may be inconvenient, it is useful to consider two limiting cases which have analytical solutions. First, if specific heat capacity is approximately constant and the latent heat of melting can be neglected, $\kappa_{\text{sensible}}$ may be approximated from a solution to the transient heat conduction equation [245]:

$$\kappa_{\text{heatup}} \approx \kappa_{\text{sensible}} = \frac{T_{cen} - T_0}{T_{\text{platein}} - T_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} e^{-\frac{(2n+1)^2 \pi^2 a t}{L^2}}$$

(2)

where $a$ is the effective thermal diffusivity of the composite, $L$ is the distance between the platens (i.e. the thickness of the composite) and $t$ is time. For $\kappa_{\text{heatup}} = 0.9$, Eq. (2) gives the Fourier number:

$$\frac{\alpha t}{L^2} \bigg|_{\kappa=0.9} \approx 0.26$$

(3)

Alternatively, if the latent heat dominates the time required for all of the matrix material to melt (i.e. the sensible heat capacity of the material is small compared with latent heat), then a second useful approximation is:

$$\kappa_{\text{latent}} \approx \sqrt{\frac{8k_{\text{cond}}(T_{\text{platein}} - T_m)}{(1-V_f)\rho h_f L^2}}$$

(4)

where $\kappa_{\text{latent}} = 0$ indicates all of the material is in the solid phase and $\kappa_{\text{latent}} = 1$ indicates that all of the matrix material is liquid. In Eq. (4), $T_m$ is the melting point, $k_{\text{cond}}$ is the effective thermal conductivity of the composite, $\rho$ is the density of the matrix material, $V_f$ is the volume fraction of fibre and $h_f$ the latent heat of fusion (melting). Combining Eqs. (3) and (4) a suitable approximation for the total heat up time would be:

$$t_{\text{heatup}} \approx t_{\text{sensible}} + t_{\text{latent}}$$

(5)
where \( t_{\text{sensible}} \) is the time determined from Eq. (3) for sensible heating and \( t_{\text{latent}} \) is determined from Eq. (4) by selecting appropriate values for \( \kappa_{\text{sensible}} \) and \( \kappa_{\text{latent}} \). To obtain meaningful results from Eq. (4), the set-point for the platen temperature must be equal to, or greater than the melting temperature. In the literature this temperature is often identified when an endothermal peak appears in differential scanning calorimetry (DSC) curves [246]. While the melting point is usually assigned a single value, the peak normally shows some breadth which is primarily related to the size and degree of perfection of the polymer crystals [246]. The manufacturing temperature of polymeric composites is usually 20-30 °C above the melting temperature (e.g. [132, 141-144, 243, 244]). This is to ensure that the viscosity of the melt is low enough to allow the PLA to flow into the pore space between the fibres during production and it allows for some variation in the melting temperature. The melting temperature of PLA is reported to be in the range of 146-152 °C in the literature [155, 247, 248] and that used in this study was measured at 148.6 °C by DSC.

Table 3-2 shows typical properties of PLA from previous studies [155, 247, 249] needed for evaluating the heat up and melting times from Eqs. (3) and (4). Figure 3-1 shows simulated results for the time required for the progress parameters \( \kappa_{\text{heatup}} \) and \( \kappa_{\text{latent}} \) to reach 90% for different process temperatures for a PLA/flax composite with a thickness of 1 mm and fibre volume fraction \( V_f \) of 50%. For the purpose of evaluation, the effective thermal conductivity of the composite was assumed to be approximately that of PLA.

<table>
<thead>
<tr>
<th>Material</th>
<th>( k_{\text{cond}} ) (W/m.K)</th>
<th>( \rho ) (kg/m(^3))</th>
<th>( c ) (J/kg-K)</th>
<th>( h_{fs} ) (J/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>0.26</td>
<td>1260</td>
<td>2221</td>
<td>23.2</td>
<td>[155, 247, 249]</td>
</tr>
</tbody>
</table>
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Figure 3-1 Melting temperature and temperature/time maps corresponding to necessary time for fulfilling the thermal penetration times for a 1 mm thick PLA/flax composite considering both sensible heat up and time required for melting. By selecting a process temperature on this graph, the curve shows the time at that temperature required to melt 90% of the matrix ($\kappa_{\text{heatup}} = 0.9$).

In Figure 3-1, the sensible heat up time (solid line) corresponds to Eq. (3) and the total heat up time (dash line) to Eq. (5). The definition of $\kappa_{\text{sensible}}$ leads to the heat up time from Eq. (3) being independent of the temperature while in Eq. (4) temperature gradients driving heat conduction through the melt are directly proportional to the temperature difference between the platen and the melting point. In either case, the heat up time is significantly less than one minute for a 1 mm thick sample. Eq. (4) indicates that the sensible heat up time is proportional to the square of the sample thickness $L$. This implies that a 10 mm thick composite will take 100 times longer to heat up than the case shown in Figure 3-1.

3.2.2 Impregnation of matrix melt into yarn

The impregnation is a process where a polymeric matrix flows through the fibre reinforcement and completely encloses it. The dual scale impregnation process can be divided into two stages – macro impregnation (inter-tow) and micro impregnation (intra-tow) [146]. Micro-impregnation is the rate determining step where the molten thermoplastic polymer enters into the fibre yarn (or tow in the case of synthetic reinforcement) and completely wets each technical fibre. For compression moulding, by
Chapter 3: Constructing an Optimum Processing Window for a Biocomposite

applying pressure the liquid polymer enters the yarns of twisted reinforcement fibres. In this study $\kappa_{\text{impreg}} = 0$ indicates no penetration and $\kappa_{\text{impreg}} = 1$ indicates the matrix has penetrated and completely filled the yarn, wetting each technical fibre. This model assumes the time required for macro impregnation is small in comparison to the time required for micro impregnation. To achieve these limits a progress parameter (degree of impregnation [250]) can be defined:

$$
\kappa_{\text{impreg}} = \frac{A_{\text{impreg}}}{A_{\text{yarn}}}
$$

where $A_{\text{yarn}}$ is the cross-sectional area of a single yarn (i.e. fibre and inter-fibre porosity) and $A_{\text{impreg}}$ is the instantaneous area within the yarn wetted by the melt. The penetration velocity can be described by Darcy’s Law Eq. (7) [251]:

$$
\phi \vec{v} = -\frac{K_p}{\mu} \nabla P
$$

where $\nabla P$, $\mu$, $\phi$ and $K_p$ are the pressure gradient, viscosity of the liquid polymer matrix, the void fraction inside the tow prior to penetration and the permeability of the fibre, respectively. To obtain an estimate of the penetration time, we assume the yarn cross section is circular in shape and the unwetted region in the centre of the tow is at atmospheric pressure. In reality, the tow will be flattened out of round during compression, but this can be accounted for by using an effective radius [252]. Using these assumptions, the Darcy equation gives [252, 253]

$$
\ln\left(\frac{r}{r_0}\right) \frac{dr}{dt} = \frac{K_p}{\mu \phi} (P_m - P_{in})
$$

where $P_m$ is the pressure in the matrix outside of the yarn, $P_{in}$ is the pressure in the unwetted region inside the yarn (assumed to be atmospheric pressure), $r_0$ is the radius of the yarn, $r$ is the radius of the unwetted region inside the yarn. Integrating Eq. (8) and applying Eq. (6) gives the time required for reaching a required degree of impregnation as:
$t = \frac{\phi \mu}{4K_p \rho_m \left( r_0^2 K_{\text{impreg}} + 2(1-K_{\text{impreg}}) r_0^2 \ln \left( \frac{1-K_{\text{impreg}}}{1-K_{\text{impreg}}} \right) \right)^{1/2}}$ \hfill (9)

$K_p$ in Eqs. (8) and (9) is a function of the microstructure of the unwetted yarn including size and connectivity of voids and technical fibre diameter. If surface wettability is neglected, $K_p$ will be independent of fluid that passes through the porous medium [254]. Bates et al. [255] used the Carman–Kozeny equation to calculate the permeability of fibre bundles for different kinds of fibres using:

$$K_p = \frac{D_f^2}{16k_{\text{Kozeny}}(1-\phi)^2}$$ \hfill (10)

where $D_f$ and $k_{\text{Kozeny}}$ are fibre diameter and the Kozeny constant (which accounts for capillary, tortuosity and shape effects). Bates et al. [255] reported a range of values for $k_{\text{Kozeny}}$ and $\phi$. Moreover, in compression moulding $\phi$ changes with pressure [253] adding considerable uncertainty in predicted values for $K_p$. In this study, to test the sensitivity of the model to the void fraction of the unwetted tow values, values for $\phi$ between 0.05 and 0.3 were used and $k_{\text{Kozeny}}$ was assumed to be 10 as a typical value [25] (see Figure 3-2). The diameter of the yarn was found using optical microscopy to be 170 µm prior to composite manufacturing.

The viscosity $\mu$ of the polymer in a molten state also plays a key role in determining the impregnation process time. A number of studies have evaluated the viscosity of PLA at various temperatures in the range 170-190 °C [256-260]. The viscosity not only changes with temperature but also with the average length of the polymer molecule, i.e. with average MW. However, for simplicity we have assumed that the viscosity is only a function of temperature and have fitted Eq. (11) to experimental data extracted from the study of Piyamanocha et al. [256].

$$\mu = Ce^{b/T}$$ \hfill (11)

where $C$ and $b$ are empirical constants that were determined by using viscosities at two temperatures ($\mu = 1700\text{Pa.s}$ at 170 °C and 540 Pa.s at 190 °C). Eq. (11) was used for
data interpolation and extrapolation to the melting temperature line as shown in Figure 3-2. Different void fractions were considered. Figure 3-2 gives the time required for the penetration process to reach 90% completion ($\kappa_{\text{impreg}} = 0.9$) for any given melt temperature. Clearly, from Figure 3-2, the impregnation process is sensitive to the void fraction. The temperature dependence of the penetration time is due to the temperature dependence of viscosity as defined by Eq. (11). Dot points in Figure 3-2 show extrapolation values at various temperatures.

![Figure 3-2 Melting temperature border and temperature/time maps corresponding to necessary time for fulfilling the impregnation process time ($\kappa_{\text{impreg}} = 0.9$) with various void fractions.](image)

**3.3 Theoretical background and measures of thermal degradation**

Reaction progress variables $\alpha_i$ for degradation processes such as pyrolysis (i.e. mass-loss due to heating) are defined such that $\alpha_i = 0$ for the initial state and $\alpha_i = 1$ for the completely degraded state. Since degradation is a negative process, for meaningful comparison with positive (i.e. desired) consolidation processes, it may be useful to express the progress of degradation using $\kappa_i = 1 - \alpha_i$, where the desired state is $\kappa_i = 1$.

**3.3.1 Pyrolysis and TGA data**

Pyrolysis or mass loss due to high temperature heating is a common measure of thermal degradation and corresponds to a major degradation of the mechanical properties of bio-
composites [171, 261]. TGA data also gives a measure of the temperature ($T_{max}$) at which peak loss occurs for a given heating rate. While the manufacturing temperature for compression moulding of bio-composites typically is not as high as that required for significant pyrolysis, degradation measured by mass loss can define an ultimate upper boundary for processing using data available in the literature. Moreover it is typically published using Arrhenius rate equations which are convenient for the calculations required in this study. For TGA data, the degradation progress variable $\alpha_{pyrol}$ is defined as:

$$\alpha_{pyrol} = \frac{m_0 - m_t}{m_0 - m_f}$$  (12)

where $m_0$, $m_t$ and $m_f$ are the initial, at time $t$, and final mass of the material. Thus $\alpha_{pyrol} = 0$ indicates that no material is lost and $\alpha_{pyrol} = 1$ indicates that all potentially volatile material has gone from the material.

$$\frac{d\alpha_{pyrol}}{dt} = k(1 - \alpha_{pyrol})^n$$  (13)

$$k = A \exp\left(\frac{-E_a}{RT}\right)$$  (14)

where $k$ determines the thermal-degradation rate, $n$ is the order of reaction, $A$ is the pre-exponential factor ($s^{-1}$), $E_a$ is apparent activation energy, $R$ is universal gas constant (8.3136 J/mol K) and $T$ is temperature (K). Eqs. (13) and (14) can be integrated numerically if temperature varies with time or analytically if the temperature is constant. For the special case where $n = 1$ and $T$ is constant:

$$\alpha_{pyrol} \Big|_{n=1, T=constant} = 1 - e^{-kt}$$  (15)

Table 3-3 lists various values of the $A$ and $E_a$ available in the literature for PLA, flax, cellulose, hemicellulose and lignin.
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Table 3-3 Available pre-exponential constant $A$, energies of activation $E_a$, and $n$-order for pyrolysis.

<table>
<thead>
<tr>
<th>Material</th>
<th>$A$ (s$^{-1}$)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$n$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>6.17×10$^{17}$</td>
<td>215</td>
<td>0.9</td>
<td>[171]</td>
</tr>
<tr>
<td>Flax</td>
<td>2.02×10$^{10}$</td>
<td>138</td>
<td>1</td>
<td>[152]</td>
</tr>
<tr>
<td>Flax*</td>
<td>3.50×10$^{98}$</td>
<td>121.7</td>
<td>1</td>
<td>[151]</td>
</tr>
<tr>
<td>Cellulose</td>
<td>3.41×10$^{12}$</td>
<td>175.6</td>
<td>1**</td>
<td>[190]</td>
</tr>
<tr>
<td>Cellulose</td>
<td>10$^{17.43}$</td>
<td>236</td>
<td>1</td>
<td>[185, 191]</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>1.25×10$^{10}$</td>
<td>132.9</td>
<td>1**</td>
<td>[190]</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>10$^{6.4}$</td>
<td>100</td>
<td>1</td>
<td>[185, 191]</td>
</tr>
<tr>
<td>Lignin</td>
<td>2.22×10$^{96}$</td>
<td>101</td>
<td>1**</td>
<td>[190]</td>
</tr>
<tr>
<td>Lignin</td>
<td>10$^{0.58}$</td>
<td>46</td>
<td>1</td>
<td>[185, 191]</td>
</tr>
</tbody>
</table>

* Pre-exponential $A$ calculated from [151] (G2 trend in Fig. 4 of Ref. [151])

** Not given explicitly in original publication but assumed that the authors’ intention was first order

Since Eq. (14) is very sensitive to the value of $E_a$, large variations in the pre-exponential (e.g. as can be observed in Table 3-3) do not always imply large inconsistencies in mass-loss predictions over a given temperature range. Therefore, for comparing kinetic data, it is often better to calculate $k$ and apply it to the problem of interest rather than simply compare the values of the kinetic parameters from different authors. Figure 3-3 shows the time required for 10\% of the volatile mass to be lost for PLA [171], flax [152], cellulose [190], hemicellulose [190] and lignin [190] at any given constant temperature. The kinetic parameters were taken from Table 3-3. These lines form an ultimate upper boundary for selecting a temperature for compression moulding of biocomposites.

Figure 3-3 shows that hemicellulose and cellulose of natural fibre are the most sensitive and insensitive components of bio-composites respectively. Lignin requires slightly higher temperatures than hemicellulose to produce the same mass loss. Flax behaves similarly to hemicellulose and lignin for $\alpha = 0.1$, which might be because the more
volatile components of the flax will be lost first. For the data in Table 3-3, PLA requires a higher temperature than flax to achieve significant mass loss and therefore is not the main concern for the production process.

Figure 3-3 Temperature/time maps corresponding to 10% mass loss ($\alpha_{\text{pyrol}} = 0.1$ (i.e. $\kappa_{\text{pyrol}} = 0.9$)) for PLA, flax, cellulose hemicellulose and lignin. This figure shows the time taken for a sample of the material to lose 10% of its volatile mass for any given constant temperature.

### 3.3.2 Thermo-chemical degradation of matrix (depolymerisation via chain scission)

At temperatures lower than required for significant mass loss, chemical reactions occur within the matrix material leading to a decrease in the average length of polymer chains tending towards an equilibrium value [153, 155, 156]. Since there is strong correspondence between mechanical properties and polymer length it is appropriate to define another degradation progress parameter as:

$$
\alpha_{\text{chem-mat}} = \frac{M_{n-\text{avg}} |_{t=0} - M_{n-\text{avg}}}{M_{n-\text{avg}} |_{t=0} - m_0}
$$

(16)

where $M_{n-\text{avg}}$ is the number-average molar mass of polymers in the matrix and $m_0$ is the molar mass of a single monomer unit. Eq. (16) is defined such that the completely degraded state ($\alpha_{\text{chem-mat}} = 1$) corresponds to the polymers entirely broken into monomer
units. The phenomenon of random chain scission is a main mechanism for polymer thermal degradation at high temperature and is prominent in polymers with acidic end groups such as PLA [197, 262]. Here a statistical method proposed by Wachsen et al. [153] and modified by Yu et al. [156] is used to simulate changes of molar mass as a function of temperature and time. The model considers both degradation reactions and recombination reactions which occur within the polymer during the thermal processing [153, 155, 156]. Eqs. (17) and (18) describe the degradation and recombination processes respectively [156]:

\[ P_n \rightarrow P_{n-r} + P_r \]  \hspace{1cm} (17)

\[ P_r + P_{n-r} \rightarrow P_n \]  \hspace{1cm} (18)

where \( P_n \) is the polymer with a degree \( n \) of polymerization. The influence of temperature is defined using an Arrhenius law (Eqs. (19) and (20)):

\[ k_d = A_d \exp \left( \frac{-E_{ad}}{RT} \right) \]  \hspace{1cm} (19)

\[ k_c = A_c \exp \left( \frac{-E_{ac}}{RT} \right) \]  \hspace{1cm} (20)

where \( d \) and \( c \) are the degradation and recombination rate indices, respectively. It is assumed that the same rate coefficients apply to polymers of any length. As expressed by Wachsen et al. [153], the concentration of a polymer of length \( n \) will be governed by (see Appendix A-1):

\[ \frac{d[P_n]}{dt} = -(n-1)k_d[P_n] + 2k_d \sum_{i=n+1}^{\infty}[P_i] + \frac{1}{2}k_c \sum_{i=n}^{\infty}[P_i][P_{n-i}] - k_c [P_n] \sum_{i=n}^{\infty}[P_i] \]  \hspace{1cm} (21)

Rather than solve Eq. (21) simultaneously for a large number of polymer chains of different lengths, Yu et al. [156] re-expressed the equations in terms of moments \( (\lambda_i) \) of different orders which are defined according to Eq. (22) as:

\[ \lambda_i = \sum_{n=1}^{\infty} n^i [P_n] \]  \hspace{1cm} (22)
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The low-order moments \( \lambda_0 \) and \( \lambda_1 \) (mol/L) can be interpreted as the total number of molecules per unit volume and the total number of monomer units per unit volume (counting all monomers in all polymers), respectively. Neglecting higher-order moments, the differential equation system (Eq. (21)) reduces to [156]:

\[
\frac{d\lambda_0}{dt} = k_d (\lambda_1 - \lambda_0) - \frac{k_e \lambda_0^2}{2}
\] (23)

\[
\frac{d\lambda_1}{dt} = k_d (\lambda_1 - \lambda_0)
\] (24)

\[
\frac{d\lambda_2}{dt} = \frac{k_d (\lambda_1 - \lambda_0)}{3} + k_e \lambda_1^2
\] (25)

To close Eqs. (23)-(25), the following approximation is used [156]:

\[
\lambda_3 = \frac{\lambda_2}{\lambda_1} \left[ 2\lambda_2 \lambda_0 - \lambda_1^2 \right]
\] (26)

Eqs. (23) to (25) require initial conditions and a means of linking the values of \( \lambda \) to \( M_{n-\text{avg}} \) in Eq. (16). The number and weight average molar mass can be described as:

\[
M_{n-\text{avg}} = m_0 \sum_{n=1}^{\infty} n[P_n] \frac{\lambda_1}{\lambda_0}
\] (27)

\[
M_{w-\text{avg}} = m_0 \sum_{n=1}^{\infty} n^2[P_n] \frac{\lambda_2}{\lambda_1}
\] (28)

where \( m_0 \) (g/mol) is the mass of an individual monomer unit. Using Eqs. (27) and (28), the polydispersity index \( (Q) \) is:

\[
Q = \frac{M_{w-\text{avg}}}{M_{n-\text{avg}}} = \frac{\lambda_2 \lambda_0}{\lambda_1^2}
\] (29)
Appropriate values of the above variables for PLA are extracted from the literature and listed in Table 3-4. The degradation rate is also known to be influenced by the presence of moisture [242]. Since this is not considered in the present study, the data shown in Table 3-4 correspond to dry PLA.

Table 3-4 Kinetic parameters and initial conditions for modelling polymer degradation of PLA.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>( A_c ) (L/mol/s)</th>
<th>( E_{ac} ) (kJ/mol)</th>
<th>( A_d ) (s(^{-1}))</th>
<th>( E_{ad} ) (kJ/mol)</th>
<th>( m_0 ) (g/mol)</th>
<th>( M_{n-start} ) (g/mol)</th>
<th>Start ( Q )</th>
<th>Density (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Le Marec et al. [155]</td>
<td>121.6</td>
<td>37.7</td>
<td>1600</td>
<td>87.2</td>
<td>72.07</td>
<td>8.29×10(^4)</td>
<td>1.425</td>
<td>1260</td>
</tr>
<tr>
<td>Yu et al. [156]</td>
<td>2200</td>
<td>49</td>
<td>7.1×10(^6)</td>
<td>120</td>
<td>72.0</td>
<td>1×10(^5)</td>
<td>1.5</td>
<td>1260</td>
</tr>
</tbody>
</table>

Noting the physical meanings of \( \lambda_0 \) and \( \lambda_1 \) given above, the initial conditions for the differential Eqs. (23) to (24), can be determined from the data in Table 3-4 using:

\[
\begin{align*}
\lambda_{0-initial} &= \frac{\rho}{M_{n-start}} \\
\lambda_{1-initial} &= \frac{\rho}{m_0}
\end{align*}
\]

(30)  
(31)

where \( \rho \) is the density of the PLA. Using the results from Eqs. (30) and (31), the initial values for \( \lambda_2 \) and \( \lambda_3 \) can be found from Eqs. (25) and (26) respectively.

For the present study, the differential Eqs. (23)-(25) were solved using a fourth-order Runge-Kutta method as recommended by Yu et al. [156] (see Appendix A-2). After obtaining \( \lambda_0 \), \( \lambda_1 \) and \( \lambda_2 \), values of \( M_{n-average} \) and \( M_{w-average} \) (and subsequently \( \alpha_{chem-mat} \)) were determined using Eqs. (27), (28) and (16) as a function of time for different processing temperatures. The results were compared with the experimental data on molar mass degradation of PLA reported by Le Marec et al. [155] and Yu et al. [156] (not shown) to confirm that the model had been formulated correctly. Khanlou et al. [241] proposed a revised formulation of the model by Yu et al. [156] which does not require the differential Eqs. (23)-(25) and, for isothermal conditions an analytical solution is readily available.
In relation to defining process boundaries for PLA as the matrix for a bio-composite, Figure 3-4 shows the time required for 10% thermo-chemical decomposition ($\alpha_{\text{chem-mat}} = 0.1$) of PLA (or PLLA in the case of Yu et al. [156]) due to thermal processing and the chain scission mechanism at various temperatures. The kinetic data by Yu et al. [156] indicates faster degradation than the data by Le Marec et al. [155] and gives a safer border to limit the zone of manufacturing process. Both degradation lines maintain a similar trend after a 100 minute interval. Since these borders are very close to melting temperature line, the chain scission mechanism for the matrix is an important consideration in the manufacturing process.

![Figure 3-4 Melting temperature border and temperature/time maps corresponding to 10% chain scission ($\alpha_{\text{chem-mat}} = 0.1$ (i.e. $\kappa_{\text{chem-mat}} = 0.9$)) for PLA due to thermal processing. This figure shows the time taken for the number-average PLA polymer size to decrease by about 10% for any given constant temperature]

3.3.3 Thermo-chemical degradation of natural fibres

(degree of polymerization of natural fibres)

Natural fibre cellulosic chains also show scission behaviour when they are exposed to a high temperature, in a similar way to polymeric matrices. To find a quantitative value for chain scission, the degree of polymerization ($DP$) (or an average number of monomeric units in a macromolecule) has been used to evaluate the degradation of natural fibres [202, 207, 263, 264]. This is actually a dimensionless equivalent of the number-averaged molar mass ($M_{n-\text{avg}}$) since for a single polymer type, $DP$ is the
number-averaged molar mass divided by the molar mass of a monomer unit. Gassan et al. [202] investigated the $DP$ behaviour of jute and flax fibres at various temperatures and its relationship with mechanical properties (tenacity) of fibre.

In this study, a degradation progress parameter ($\alpha_{\text{chem-fibre}}$) is proposed to identify the chemical reaction or chain scission progress in the natural fibres with the use of $DP$ as:

$$
\alpha_{\text{chem-fibre}} = \frac{DP|_{t=0} - DP}{DP|_{t=0} - 1}
$$

Eq. (16) will have the same form as Eq. (32) if numerator and denominator are divided by $m_0$. The degree of polymerization can be determined empirically by measuring the viscosity of a natural polymer solution extracted from the fibre using a cellulose solvent [202]. Chemical rate equations are usually expressed using concentrations. For this purpose, $1/DP$ is proportional to the number of molecules per unit volume. For chain scission of cellulosic materials, Testa et al. [207] expressed their chemical rate equation in terms of $N$ as defined in Eq. (33):

$$
N = 1 - \frac{1}{DP}
$$

For their model, a first-order kinetic rate law corresponds to the random chain scission of bonds in a linear chain polymer:

$$
\frac{dN}{dt} = K \times N
$$

Here, we have followed a similar strategy except that we have assumed that $K$ is temperature-dependent according to the Arrhenius law:

$$
K = A \exp\left(\frac{-E_a}{RT}\right)
$$

For a given temperature, Eqs (34) and (35) may be solved to give:
where \( N_0 \) and \( N \) are \( 1 - (1/DP_0) \) and \( 1 - (1/(\kappa)DP_0) \), respectively, \((\kappa=1-\alpha)\) is the progress of degradation as mentioned above, and \( DP_0 \) is the initial \( DP \).

Unfortunately, the necessary kinetic data for chemical degradation of flax fibre is difficult to find in the literature. In a study by Gassan et al. [202], \( DP \) was measured after heating flax fibre for different periods of time for three different temperatures as listed in Table 3-5. The initial value given for \( DP_0 \) was 1505.

Table 3-5 \( DP \) of flax fibre heat treated for three time periods and at three temperatures [202].

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>170 °C</th>
<th>190 °C</th>
<th>210 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>866</td>
<td>509</td>
<td>387</td>
</tr>
<tr>
<td>120</td>
<td>511</td>
<td>360</td>
<td>261</td>
</tr>
</tbody>
</table>

For the present study, a least-squares fitting procedure was used to determine the pre-exponential factor \((A = -0.178 \text{ s}^{-1})\) and the apparent activation energy \((E_a = 50.5\times10^3 \text{ J/mol})\) to fit Eqs. (33) to (35) to the data given in Table 3-5. Finally, Figure 3-5 shows temperature/time maps corresponding to 10% to 90% chain scission \((\kappa_{\text{chem-fibre}} = 0.9 \text{ to } 0.1)\) and was drawn in relation to defining process boundaries for flax fibre as the reinforcement for a bio-composite. This boundary corresponds to the chemical-thermal degradation of the fibre which occurs during thermal processing. This border significantly limits the zone of manufacturing process and gives a caution to the bio-composite manufacturer that the mechanical properties of bio-composite will inevitably degrade during the manufacturing process. This process boundary is of high importance to the manufacturing process in order to prevent the initial degradation during the manufacturing process.
3.4 Experiment for validation of concept

Ultimately we are interested in the effect that the overall process has on the mechanical properties of the composite. For this purpose, mechanical properties of a flax/PLA biocomposite were measured for different processing conditions.

3.4.1 Materials and methods

Unidirectional (UD) flaxply fabric (180 g/m² flax) manufactured by Lineo Company (France) was used in this study. PLA film (25 microns thick) was supplied by Magical Film Enterprises Co. Ltd. (Taiwan).

Thermal transition temperatures of the PLA were measured for four samples using differential scanning calorimetry (DSC). The average glass transition temperature \( T_g \) was 61.9 °C and the corresponding melting temperature \( T_m \) was 146.2 °C.

A flat aluminium plate (3 mm thick) was treated with high temperature release agent (Aliphatic Hydrocarbones, Marbocote Ltd, UK) and used as the lower moulding surface. Two layers of PLA film were placed directly on the bottom mould surface followed by a single layer of fibre and two further layers of PLA. This pattern was repeated for four composite layers. There are four layers of PLA between each
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reinforcement layer. The bio-composite plate was moulded with a total thickness of approximately 1 mm with a planar area of approximately 300 × 300 mm.

The compression moulding machine (Carver Inc, Wabash, USA) was set to a temperature of 170 °C which is above the melting temperature of the PLA. The bottom moulding surface and the composite layup were not introduced to the moulding machine until the top mould surface temperature reached the set point value. The composite was compressed to a pressure of 300 kPa and held at the set temperature for a set consolidation time (15, 30, 45, 60 or 120 minutes). The pressure was maintained as the top and bottom platens of the compression moulder were cooled. The cooling process was manually controlled by a supply of cold water to the platens. The temperatures of the upper and lower platens were recorded during the entire process using a data logger (USB TC-08, Pico Tech, UK) sampling at a rate of 1 Hz (Figure 3-6).

![Figure 3-6 Processing temperature histories for different consolidation times](image)

Tensile test specimens were laser cut from the composite plates (parallel to the fibre direction). Sixteen samples were cut from each plate. The test specimen dimensions were 250 × 15 × 1 mm. Tensile testing was carried out using an Instron 3367 testing machine with an Instron 30 kN load cell (serial no. 68296). Gripping end tabs were used during tensile testing as recommended by ASTM D3039/D3039 M. A standard crosshead displacement rate was set at 2mm/min. The tensile strain in the specimens
was measured with a 50 mm Instron extensometer attached to the surface of the material. Modulus was calculated over the axial strain range of 1000 micro-strain to 3000 micro-strain. To determine the advance estimate of the standard deviation for the flax/PLA composites, 16 tensile test specimens cut from a single plate were used.

3.4.2 Mechanical properties analysis
The mean mechanical properties and standard deviations for each of these times are shown in Table 3-6. The moduli can be seen to be fairly independent of consolidation time (means range from 20.0 to 27.0 GPa), but the tensile strength and fracture strain reduce significantly as the consolidation time increases (from 308 to 132 MPa and 2.1 to 1.2 % respectively).

<table>
<thead>
<tr>
<th>Consolidation time [min]</th>
<th>Tensile Modulus [GPa] (std/CoV)</th>
<th>Tensile strength [MPa] (std/CoV)</th>
<th>Failure strain [%] (std/CoV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>21.1 (2.9/13%)</td>
<td>308 (11/3%)</td>
<td>2.1 (0.22/10%)</td>
</tr>
<tr>
<td>30</td>
<td>22.9 (1.5/6%)</td>
<td>280 (28/10%)</td>
<td>2.0 (0.22/11%)</td>
</tr>
<tr>
<td>45</td>
<td>27.4 (4.8/17%)</td>
<td>235 (32/13%)</td>
<td>1.2 (0.29/24%)</td>
</tr>
<tr>
<td>60</td>
<td>22.0 (1.8/8%)</td>
<td>132 (24/18%)</td>
<td>0.9 (0.42/46%)</td>
</tr>
<tr>
<td>120</td>
<td>20.1 (3.2/16%)</td>
<td>132 (12/9%)</td>
<td>1.2 (0.45/37%)</td>
</tr>
</tbody>
</table>

The coefficient of variation (CoV) for both modulus and failure strain increases as the consolidation time lengthens. The mean tensile strengths and fracture strains at 15 mins and 30 mins consolidation are fairly consistent (308 and 280 MPa, and 2.1 and 2.0% respectively), but decrease markedly at 60 mins and 120 mins. The tensile strength and fracture strain approximately halves when the consolidation time is ≥ 45 mins.
3.4.3 Comparison with Model

Figure 3-7 shows the completed process map corresponding to the PLA/flax composite. Positive consolidation processes are assigned a value of $\kappa = 0.9$ and degradation processes $\alpha = 0.1$. The experimental data for tensile strength of the composite is shown as symbols. The shaded region corresponds to the recommended processing window based on the various models. In this case, the kinetic data indicate that the upper and lower bounds for the time under the hot press are defined by thermochemical fibre degradation and melt penetration into the yarn, respectively.

![Completed temperature/time maps corresponding to $\kappa = 0.9$ or $\alpha = 0.1$ and experimental data for flax/PLA bio-composite. The only exception to this is for thermo-chemical degradation of the fibre where $\kappa = 0.6$ is assigned as a compromise due to the rapid degradation of the flax fibre. The shaded region shows the range of favourable process conditions for compression moulding of this composite.](image)

3.5 Conclusion

In this study, we have mapped out a window of suitable temperatures and consolidation times for compression moulding of a flax-PLA bio-composite using kinetic data and available models from the literature for thermal penetration, melt-fibre impregnation and thermochemical degradation of both fibre and matrix. By expressing each of the processes using dimensionless progress variables, convenient temperature/time maps can be constructed enabling manufacturers to have an overview of degradation processes during the manufacturing process. Thus making it possible to optimize the
manufacturing time, ensuring that degradation in properties of the bio-composite is minimized.

The map derived for flax/PLA composite suggests that the most important processes are penetration of the melt into the yarn which defines the minimum consolidation time and thermochemical degradation of the natural fibres which defines the maximum consolidation time allowed to avoid major degradation of the composite mechanical strength. Consistent with the model, experimental data showed a considerable reduction in tensile strength for the composite for consolidation times greater than 45 min.

Acknowledgments: The authors are grateful to Adam Parsons who worked as intern with Dr Michael Heitzmann at University of Queensland for their help in DSC characterization of PLA.
Chapter 4: Simplifying, Revising and Demonstrating a Complex Model

Statement of contribution to co-authored published paper

This chapter includes a published journal paper and a published book chapter.

The bibliographic details of the paper, including all authors, are:


And


My contribution to the paper involved: undertaking literature review, classifying the necessary theoretical backgrounds and models, performing the experimental tests, analyzing and discussing data, drawing figures, preparing tables, writing and editing the manuscript according to my supervisors’ comments.
Chapter 4: Simplifying, Revising and demonstrating a Complex Model

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Co-supervisor: John Summerscales (co-supervisor and co-author)
A- Technical Note: On modelling thermo-chemical degradation of poly(lactic acid)

Abstract: A well-established model for simulation of the chain-scission process of polylactic acid (PLA) during thermal processing has been simplified and revised. The key assumption in the new model is that the total number of monomer units is invariant as reactions progress. Surprisingly, this seemingly obvious assumption appears to have been previously overlooked. The revised model no longer requires solution of simultaneous differential equations and, for isothermal conditions, an analytical solution is readily available. The present model is in excellent agreement with the more complex model and experimental results for PLA degradation reported in the literature. This simplified model has potential to be applied to other thermoplastics.

Keywords: Modelling; Thermal Degradation; Polymeric Material; Chain-scission; PLA.
4.1 Introduction and theoretical backgrounds

In 1997, a statistical model was proposed by Wachsen et al. [153] to simulate changes of molar mass of poly (L-lactic Acid) (PLLA) as a function of temperature and time. This model was later modified by Yu et al. [156] who proposed a more convenient form to estimate molecular properties of PLLA after thermal processing. Recently, Le Marec et al. [155] fitted the Yu et al model to experimental data for PLA. The statistical model for the polymer considered both degradation and recombination reactions which occur during the thermal processing. As a result, the average length of polymer chains decreases towards an equilibrium value [153, 155, 156]. Eqs. (1) and (2) describe the degradation and recombination processes respectively [156]:

\[ P_n \rightarrow P_{n-r} + P_r \]  

(1)

\[ P_r + P_{n-r} \rightarrow P_n \]  

(2)

where \( P_n \) is the polymer with a degree of polymerization, \( n \), and a change in that parameter, \( r \).

The effect of temperature on degradation and recombination is expressed using the Arrhenius equation (Eqs. (3) and (4)):

\[ k_d = A_d \exp\left(\frac{-E_{ad}}{RT}\right) \]  

(3)

\[ k_c = A_c \exp\left(\frac{-E_{ac}}{RT}\right) \]  

(4)

where \( k_d \) is the degradation rate and \( k_c \) is the recombination rate, \( A_d \) and \( A_c \) are the pre-exponential factors, \( E_{ad} \) and \( E_{ac} \) are apparent activation energies, \( R \) is the universal gas constant and \( T \) is the temperature.

It is assumed that the same values of \( k_d \) and \( k_c \) apply to polymers of any length. As expressed by Wachsen et al. [153], using these assumptions, the rate of change of concentration of a polymer of length \( n \) will be given by:
\[
\frac{d[P_n]}{dt} = -(n-1)k_d[P_n] + 2k_d \sum_{n=1}^{\infty} [P_n] + \frac{1}{2} k_c \sum_{i=1}^{\infty} [P_i] [P_{n-i}] - k_c [P_n] \sum_{i=1}^{\infty} [P_i]
\]  

(5)

where \([P_n]\) is the concentration of \(P_n\), \(i.e\) the number of moles of the polymer (of length \(n\)) per unit volume.

Eq. (5) should be solved concurrently for a large number of polymer chains of different lengths, which is inconvenient for practical analysis. The major contribution of Yu et al. [156] was to re-express these equations in terms of moments (\(\lambda_i\)) of different orders defined by:

\[
\lambda_i = \sum_{n=1}^{\infty} n^i [P_n], \quad i = 0, 1, 2, 3 \ldots
\]  

(6)

Considering only the first three moments, the differential equation system (Eq. (5)) was reduced to [156]:

\[
\frac{d\lambda_0}{dt} = k_d (\lambda_1 - \lambda_0) - \frac{k_c \lambda_0^2}{2}
\]  

(7)

\[
\frac{d\lambda_1}{dt} = k_d (\lambda_1 - \lambda_0)
\]  

(8)

\[
\frac{d\lambda_2}{dt} = \frac{k_d (\lambda_2 - \lambda_1)}{3} + k_c \lambda_1^2
\]  

(9)

To close Eqs. (7)-(9), the following approximation was made:

\[
\lambda_3 = \frac{\lambda_2}{\lambda_1} \left[ 2 \lambda_2 \lambda_0 - \lambda_1^2 \right]
\]  

(10)

Equation (5) or Eqs. (7) to (10) have been used successfully to model the thermo-chemical degradation of PLLA, PLA and PP [12, 154-156, 265, 266].
4.2 The proposed model and its logic

An important point, that appears to have been overlooked in studies that have made use of the Yu et al model (Eq. (7)-(10)) [156] is that \( \lambda_1 \) can be considered to be a constant. This parameter can be interpreted as the total number of moles of monomer units per unit volume (see Eq. (6)). The key to the model developed in this chapter is an unwritten assumption in the model by Wachsen et al. [153] (Eq. (1)-(5)) that no degradation of the basic monomer unit occurs, and hence the total number of monomer units should not change as the reactions progress. This note rectifies this omission. A constant \( \lambda_1 \) decouples Eq. (7) from Eqs. (8) and (9) and makes it unnecessary to solve Eq. (8). Moreover, if the temperature is also constant then Eq. (7) can be solved analytically by separating the variables to give (see Appendix C):

\[
\lambda_0 = -\frac{k_d}{k_c} + \frac{\sqrt{2} k_c k_d \lambda_1 + k_d^2}{k_c} \tanh \left( \frac{(t + C) \sqrt{2} k_c k_d \lambda_1 + k_d^2}{2} \right)
\]

(11)

where \( C \) is defined by the initial condition for \( \lambda_0 \) as:

\[
C = \frac{2}{\sqrt{2} k_c k_d \lambda_1 + k_d^2} \tanh^{-1} \left( \frac{\lambda_{0\text{, initial}} + \frac{k_d}{k_c}}{k_c \sqrt{2} k_c k_d \lambda_1 + k_d^2} \right)
\]

(12)

This analytical result is in a convenient form for prediction of degradation of polymeric materials such as PLA during melt processing [12, 122, 154, 265-272] under isothermal conditions.

As Eq. (6) defines \( \lambda_0 \) as the total number of moles of molecules per unit volume, the initial condition may be specified as:

\[
\lambda_{0\text{, initial}} = \rho / M_{n\text{-start}}
\]

(13)

and \( \lambda_1 \) as:

\[
\lambda_1 = \rho / m_0 = \text{constant}
\]

(14)
where $\rho$ is the density of the polymer, $M_{n\text{-start}}$ is the initial number-averaged molar mass for the polymer and $m_0$ is the molar mass of a monomer unit.

For all of the models, the number-averaged molar mass $M_{n\text{-avg}}$ can be specified at any time as:

$$M_{n\text{-avg}} = m_0 \sum_{n=1}^{\infty} p[P_n] \frac{\lambda_1}{\lambda_0}$$

(15)

### 4.3 Validation of the proposed model

Since enforcing Eq. (14) rather than using Eq. (8) will in principle lead to different results for $\lambda_1$, it is important to consider the impact of the simplified model on predictions of thermo-chemical degradation of PLA. The present model (Eqs. (11) and (12)) was used to calculate results for comparison with the model of Yu et al. [156] (Eqs. (7) to (10)) using kinetic data for PLA degradation from Le Marec et al. [155] (Table 4-1). This comparison is shown in Figure 4-1 which also includes the experimental data on molar mass degradation of PLA reported by Le Marec et al. [155]. The present model is in excellent agreement with the Yu et al model for the range of available data with a maximum deviation of less than 0.1% for $\lambda_0$. For the data shown, the Yu et al model also predicts a maximum of only 0.1% change in the value of $\lambda_1$.

Table 4-1 Kinetic parameters and initial conditions for modelling polymer degradation of PLA.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>$A_c$ (L/mol/s)</th>
<th>$E_{ac}$ (kJ/mol)</th>
<th>$A_d$ (s$^{-1}$)</th>
<th>$E_{ad}$ (kJ/mol)</th>
<th>$m_0$ (g/mol)</th>
<th>$M_{n\text{-start}}$ (g/mol)</th>
<th>Start Polydispersity (g/L)</th>
<th>Density (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Le Marec et al. [155]</td>
<td>121.6</td>
<td>37.7</td>
<td>160</td>
<td>0</td>
<td>72.07</td>
<td>8.29 $\times 10^4$</td>
<td>1.425</td>
<td>1260</td>
</tr>
</tbody>
</table>
Figure 4-1 Confirmation of the experimental data extracted from Yu et al. [156] or Le Marec et al [155] model with the present model.

To sum up, the model for thermo-chemical degradation of PLLA proposed by Yu et al. [156] can be simplified significantly by assuming that the total number of monomer units is invariant as reactions progress. The present model accurately simulates the experimental data of Le Marec et al. [155] for PLA in Figure 4-1, without the need to recalculate the original activation energies or pre-exponentials.
B- Effect of time-dependent process temperature variation during manufacture of natural-fibre composites

Abstract: One of the key issues in compression molding of natural fibre reinforced polymer (NFRP) bio-composites is the thermochemical degradation of the fibre and matrix during manufacture. In the previous work, models of thermal penetration, melt infusion, thermal degradation and chemical degradation of flax/PLA bio-composite were used to propose the degradation boundaries for bio-composite manufacturing. This study proposes a thermal degradation model which accounts for the effect of time-dependent process temperature variation during manufacture of green composites. Kinetic data are used to calculate degradation progress parameters, defining experiment process maps for identifying the effect of the temperature history on the degradation progress and effects on the tensile strength. The model also can express the tensile strength changes in comparison with other degradation parameters.

Keywords: Bio-polymer composites; Natural fibres; Thermo-chemical degradation; Heating and cooling rate, Mechanical properties
4.4 Introduction and theoretical background

Thermal and chemical degradation occur during thermal processing of natural fibre reinforced polymer (NFRP) bio-composites and are key processes influencing the mechanical properties of the composite. To quantify the extent of degradation, in the earlier study [241, 273], degradation progress parameters (α) and consolidation progress parameters (κ) were defined, where κ = 1 - αi = 0 for the completely degraded state and κ = 1 - αi = 1 for the initial or desired state. To estimate the progress of PLA melting, heat up and PLA impregnation process, Eqs. (1-5) were proposed [273]:

\[ \kappa_{\text{heatup}} \equiv \frac{h(T_{\text{cen}}) - h_i(T_0)}{h_i(T_{\text{platen}}) - h_i(T_0)} \]  
\[ \kappa_{\text{heatup}} \approx \kappa_{\text{sensible}} \approx \frac{T_{\text{cen}} - T_0}{T_{\text{platen}} - T_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \left( \frac{(-1)^n}{2n+1} \right)^2 e^{-\left(\frac{2n+1}{2}\right)^2 \pi^2 \alpha/t} \]  
\[ \kappa_{\text{latent}} \approx \sqrt{\frac{8k_{\text{cond}} (T_{\text{platen}} - T_m)}{(1-V_f) \rho h_f L^2}} \]  
\[ I_{\text{heatup}} \approx I_{\text{sensible}} + I_{\text{latent}} \]  
\[ \kappa_{\text{impreg}} = \frac{A_{\text{impreg}}}{A_{\text{yarn}}} \]  

where \( T_{\text{cen}} \) is the temperature in the centre of the composite (i.e. half way between the two heated platens), \( T_0 \) is the initial temperature of the composite and \( T_{\text{platen}} \) is the temperature of the platen, \( h_l(T) \) is the specific enthalpy of the liquid while \( h_s(T) \) is the specific enthalpy of the solid, \( a \) is the effective thermal diffusivity of the composite, \( L \) is the distance between the platens (i.e. the thickness of the composite) and \( t \) is time, \( T_m \) is the melting point, \( k_{\text{cond}} \) is the effective thermal conductivity of the composite, \( \rho \) is the density of the matrix material, \( V_f \) is the volume fraction of fibre and \( h_f \) the latent heat of fusion (melting), \( A_{\text{yarn}} \) is the cross-sectional area of a single yarn (i.e. fibre and inter-fibre porosity), \( A_{\text{impreg}} \) is the instantaneous area within the yarn wetted by the melt; and where \( \kappa_{\text{latent}} = 0 \) indicates all of the material is in the solid phase and \( \kappa_{\text{latent}} = 1 \) indicates that all of the matrix material is liquid.
The thermochemical degradation progress of the fibre and matrix are defined as Eq. (6-8) [241, 273]:

\[ \kappa_{\text{pyrol}} = 1 - \frac{m_0 - m_f}{m_0 - m_f} \]  

(6)

\[ \kappa_{\text{chem-fibre}} = 1 - \frac{DP|_{t=0} - DP}{DP|_{t=0} - 1} \]  

(7)

\[ \kappa_{\text{chem-matrix}} = 1 - \frac{M_{n-\text{avg}}|_{t=0} - M_{n-\text{avg}}}{M_{n-\text{avg}}|_{t=0} - u_0} \]  

(8)

Where \( m_0 \), \( m_t \) and \( m_f \) are the initial, at time \( t \), and final mass of the material, \( DP \) is degree of polymerisation, \( M_{n-\text{avg}} \) is the number-average molar mass of polymers in the matrix and \( u_0 \) is the molar mass of a single monomer unit.

\( DP \) and \( M_{n-\text{avg}} \) are calculated as a function of the temperature history of the melt using first-order Arrhenius rate kinetics [155, 156, 202]. For the fibre, the degradation rate is expressed as:

\[ \frac{dN}{dt} = K \times N \]  

(9)

where

\[ N = 1 - \frac{1}{DP_{\text{fibre}}} \]  

(10)

A parameter \( N \) related to the molecule concentration can be predicted using a first-order chemical rate equation as shown by Testa et al. [207] to estimate the chain scission of cellulosic materials. Their model corresponds to the random chain scission of bonds in a linear chain polymer. Besides, \( K \) is defined using the Arrhenius equation:

\[ K = A \exp\left(-\frac{E_a}{RT}\right) \]  

(11)

For the thermo-chemical degradation of the PLA matrix,
\[
\frac{d\lambda_0}{dt} = k_d \left( \frac{\rho}{m_0} - \lambda_0 \right) - \frac{k_c \lambda_0^2}{2}
\]  

(12)

where

\[
\lambda_0 = \rho / M_p = \frac{\rho}{m_0 D_{p_{\text{matrix}}}}
\]  

(13)

and \( k_d \) and \( k_c \) are degradation and recombination Arrhenius rate coefficients, respectively as given by

\[
k_d = A_d \exp\left(\frac{-E_{ad}}{RT}\right)
\]  

(14)

\[
k_c = A_c \exp\left(\frac{-E_{ac}}{RT}\right)
\]  

(15)

The activation energies and pre-exponentials for Eqs. (11), (14) and (15) are available in page 87 (Table 4-1) or [155, 241].

4.5 Experiments

An experimental program was carried out using unidirectional flax fibre and PLA to fabricate 1 mm thick bio-composite plates in a compression moulding machine. The details of the experiment are described elsewhere [241, 273]. The volume fraction of fibre was 50% and the plates were cut into tensile test specimens using a laser cutter. Tensile properties were measured for high temperature (set temperature: 170 °C) consolidation times of 15 minutes, 30 minutes, 45 minutes, 60 minutes and 120 minutes. K-type sheathed thermocouples and a data logger were used to record the temperature history during compression moulding.

4.6 Results

Figure 4-2a shows measured temperatures of the upper and lower plates of the compression moulding machine, which are recorded during the manufacturing process for 120 min. The bottom moulding plate and the composite layup were not introduced to the moulding machine.
until the top mould surface temperature reached the set point value. It is clear that the temperature history deviates somewhat from the ideal model of instantly rising to the set temperature, staying at a constant temperature for 120 min and then instantly cooling to room temperature. The largest deviation from the ideal model occurs during the first 20 minutes of consolidation where the temperature overshoots to about 185 °C. There are also differences between the temperature of the upper and lower plate. This is particularly apparent during heat up where the temperature of the upper plate rises slowly before pressure is applied. During this stage (-27 min to 0 min on Figure 4-2a) the composite is not in contact with the upper plate.

Figure 4-2b shows the findings from the models for degradation progress resulting from various factors and experimental data for the tensile strength of the flax/PLA bio-composite with different processing times (further discussion regarding this are provided in Chapter 5, section 5.8 and 5.9). Comparing the dotted lines with the solid lines shows the effect of including the actual temperature history on the predicted degradation of flax and PLA. The thermochemical degradation for the dotted lines was found by numerically integrating Eqs. (9) and (12) using the measured temperature history in Eqs. (11), (14) and (15). It can be seen that the differences between constant temperature and non-ideal temperature history are within 10% error.

By non-dimensionalizing the tensile strength against the maximum measured strength, it is possible to obtain an additional experimental measure of degradation of the composite during processing. The scale of the experimental data shown in Figure 4-2b for tensile strength has been selected so that vertical scale on the left hand side (κ) shows the degradation of the tensile strength (Eq. (16)). The trend line of experimental results also shows a similar trend to the changes of κ associated with thermal-chemical degradation of the fibre. The model shows that a processing time of less than about 20 min is desired to limit thermal degradation of the fibre and greater than about 10 min to allow for penetration of the matrix into the fibre.

\[
\kappa = \frac{\sigma_{\text{experiment}}}{\sigma_{\text{max}}} \quad (16)
\]
Figure 4-2  a) Measured processing temperature history for 120 min consolidation times, b) Consolidation $\kappa$-time maps and experimental data for flax/PLA bio-composite. A value of $\kappa = 1$ or $\alpha = 0$ corresponds to the desired state of complete consolidation and no thermochemical degradation. The solid lines show optimum processing (isothermal) while dashed lines show calculations based on the actual temperature history of the melt for PLA and flax fibre.

4.7 Simulation and conclusion

To realize the effect of heating and cooling rate on the degradation of NFRP bio-composites, three various rates (at 1.5 K/min, 5 K/min, 20 K/min as slow, average and fast, respectively,) were selected (see Figure 4-3a). In addition, the $\kappa$ changes of PLA and flax fibre, which resulted from the simulated heating and cooling rate to a processing temperature of 170 °C, are shown in Figure 4-3b. PLA shows insignificant reactions to the rate changes while flax fibre shows notable additional degradation during the heat up period for slow heating. In case of PLA, two processes (degradation and recombination) are responsible for the degradation progress at high temperature during the thermal processing [241, 273]. For PLA the final state of degradation (>150 min) is almost identical even though the slower heating/cooling case shows slightly lower values for $\kappa$ during consolidation. The slight recovery (increase of $\kappa$ for the slower cooling case) after 120 min for PLA can be due to monomer recombination factor (Eq. (12), 2nd term on the right) which is considered in the calculation of the
degradation progress of PLA. However, there is not such a factor in the degradation progress model of the flax fibre (Eq. (9)), resulting in continuous degradation of the flax fibre. Moreover, the slow rate of heating and cooling represents a negative effect on the mechanical properties of flax fibre and consequently on the bio-composite; as fibre is mostly responsible for the mechanical properties of composites, according to the rule of mixtures [89]. Thus we have demonstrated that the present model is a useful tool for predicting the degradation effect of any temperature history to which the composite is subjected during manufacture.

Figure 4-3 a) three various rates of heating and cooling as slow, average and fast, b) \( \kappa \)/time maps for PLA and flax at the various rates.
Chapter 5: Estimating Mechanical Property Degradation

Statement of contribution to co-authored published paper

This chapter includes a published journal paper.

The bibliographic details of the paper, including all authors, are:


My contribution to the paper involved: undertaking literature review, classifying the necessary theoretical backgrounds and models, performing the experimental tests, analyzing and discussing data, drawing figures, preparing tables, writing and editing the manuscript according to my supervisors’ comments.

_________________________________
(Date) 15/Mar/2018

Hossein Mohammad Khanlou
Chapter 5: Estimating Mechanical Property Degradation

Estimation of mechanical property degradation of poly(lactic acid) and flax fibre reinforced poly(lactic acid) bio-composites during thermal processing

Abstract: Thermal degradation and chemical degradation are among the key issues affecting mechanical properties and ultimately utilization of natural fibre reinforced polymer (NFRP) bio-composites. In previous work, mathematical models were used to identify thermal processing boundaries and to recognize an optimized window for NFRP bio-composites. In this study, a correlation relating the tensile strength of flax/PLA bio-composite to the processing temperature history is proposed. For the first time, an existing linear model, which corresponds to the tensile strength of natural polymers and their degree of polymerization, has been combined with reaction kinetics to predict the tensile strength of NFRP bio-composites as a function of processing temperature history. In addition, a non-linear model has been proposed which shows a significant improvement for longer periods of time, compared with the linear model. The model is based on the underlying thermo-chemical degradation processes occurring during manufacture of NFRP bio-composites. The model is capable of predicting the tensile strength of the bio-composite within 10% error.

Keywords: Bio-polymer composites; Chemical degradation; Degree of polymerization; Natural fibres; Mechanical properties; Thermal degradation
5.1 Introduction

Thermal degradation is one of the main challenges in the manufacture of NFRP bio-composites, when a thermal processing method is used [69, 70]. Unlike carbon and glass fibre composites where the fibre is robust to composite manufacturing temperature, natural fibres degrade quickly when exposed to temperatures as low as 160°C [274], 180°C [141], 180-190°C [70] or 180-200°C [144]. Bio-matrices also suffer a similar problem in comparison with synthetic polymers [69, 132, 241, 275]. Compression molding is a common method in which setting an appropriate temperature (e.g. 170-200°C) and consolidation time play an important role in achieving the ultimate mechanical properties of the produced bio-composite. Many studies have manufactured bio-composites at various temperatures (e.g. 160-220°C) and various consolidation times (e.g. 2-20 min) and as a result have demonstrated the sensitivity of the mechanical properties to the thermal history during manufacture of NFRP bio-composites [69, 70, 132, 141, 144, 274, 276]. In particular, the effects of chemical reactions (molar mass changes) are responsible for degradation of mechanical properties of both matrix and fibre during the thermal processing [202, 277-280]. Indicative process conditions from the literature are given in Table 5-1, which shows the effect of temperature and other factors on freshly manufactured bio-composites.

An important gap in the literature is in connecting the degradation of mechanical properties of bio-materials to the thermochemical degradation that occurs during manufacture. There are a few works in the literature which have tried to investigate the relationship between mechanical properties and the number-average MW of polymers or fibres [202, 277-280]. In 1945, Flory [277] demonstrated a linear relationship between the number average MW and the tensile strength of a blend composed of a mixture of cellulose acetate fractions. In 2014, Rasselet et al. [278] also tried to link the molar mass of oxidised PLA polymer to its mechanical properties. They concluded that the reduction of mechanical properties is linked to molar mass reduction during the oxidation process. In addition, mechanical properties (tenacity) of fibres have been shown to reduce along with decline in molar mass [202]. To fill the gap, this paper considers molar mass degradation or reduction in degree of polymerisation as a critical indicator of the extent of thermochemical degradation making it possible to determine the rate of deterioration of mechanical properties for both matrix and fibre. Data produced from the proposed models can be used in prediction or optimising mechanical
properties of bio-composites. For the first time, this study has brought the thermochemical degradation concepts together with the models which have been used for composites to predict the tensile strength of NFRP bio-composites after thermal processing.
Table 5-1 Indicative process conditions for pressing bio-composites.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Fibre Orientation</th>
<th>Fibre fraction (%)</th>
<th>Matrix</th>
<th>Pressure (MPa)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Young modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile strain at failure (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ramie</td>
<td>-</td>
<td>35 w/o</td>
<td>PP</td>
<td>2</td>
<td>185</td>
<td>10</td>
<td>-</td>
<td>42.8</td>
<td>-</td>
<td>[281]</td>
</tr>
<tr>
<td>ramie</td>
<td>-</td>
<td>30 v/o</td>
<td>PLA</td>
<td>20</td>
<td>170</td>
<td>4</td>
<td>-</td>
<td>52</td>
<td>3.2</td>
<td>[276]</td>
</tr>
<tr>
<td>jute</td>
<td>-</td>
<td>40 w/o</td>
<td>PP</td>
<td>0.5</td>
<td>180</td>
<td>2</td>
<td>≈3.5</td>
<td>≈27</td>
<td>-</td>
<td>[22]</td>
</tr>
<tr>
<td>jute</td>
<td>UD</td>
<td>40 w/o</td>
<td>PLA</td>
<td>3.3</td>
<td>180-220 and 60</td>
<td>3-10 and 1</td>
<td>-</td>
<td>≈100</td>
<td>1.6</td>
<td>[70]</td>
</tr>
<tr>
<td>kenaf</td>
<td>UD</td>
<td>40 w/o</td>
<td>PLA</td>
<td>4.2</td>
<td>180</td>
<td>20</td>
<td>7.1 and 4.2</td>
<td>52.9 and 24.1</td>
<td>1.05 and 0.76</td>
<td>[141]</td>
</tr>
<tr>
<td>kenaf</td>
<td>UD</td>
<td>70 v/o</td>
<td>PLA</td>
<td>10</td>
<td>160</td>
<td>10</td>
<td>≈23</td>
<td>≈220</td>
<td>-</td>
<td>[140]</td>
</tr>
<tr>
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<td>NW</td>
<td>30 w/o</td>
<td>PP</td>
<td>5</td>
<td>250</td>
<td>15</td>
<td>≈1.6</td>
<td>≈40</td>
<td>-</td>
<td>[282]</td>
</tr>
<tr>
<td>flax</td>
<td>-</td>
<td>10-30 w/o</td>
<td>PLA</td>
<td>18</td>
<td>170</td>
<td>5</td>
<td>3.9-6.3</td>
<td>42-54</td>
<td>-</td>
<td>[69]</td>
</tr>
<tr>
<td>flax</td>
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<td>PLA</td>
<td>5</td>
<td>180</td>
<td>5</td>
<td>≈8-10</td>
<td>≈65-80</td>
<td>≈77-60</td>
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<tr>
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<td>60 w/o</td>
<td>AESO</td>
<td>4</td>
<td>160</td>
<td>5</td>
<td>32</td>
<td>280</td>
<td>-</td>
<td>[274]</td>
</tr>
<tr>
<td>Hemp</td>
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<td>40 w/o</td>
<td>PP</td>
<td>0.4</td>
<td>180</td>
<td>2</td>
<td>≈7</td>
<td>≈52</td>
<td>-</td>
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<td>Hemp</td>
<td>-</td>
<td>30-64 w/o</td>
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<td>200</td>
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<td>-</td>
<td>15-26</td>
<td>3.6-9.3</td>
<td>[283]</td>
</tr>
<tr>
<td>Hemp</td>
<td>UD</td>
<td>40 w/o</td>
<td>PLA</td>
<td>4.2</td>
<td>180</td>
<td>20</td>
<td>8</td>
<td>57</td>
<td>1.24</td>
<td>[141]</td>
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<tr>
<td>Hemp</td>
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<td>PLA</td>
<td>1.7</td>
<td>195</td>
<td>20</td>
<td>6</td>
<td>45</td>
<td>-</td>
<td>[132]</td>
</tr>
<tr>
<td>Hemp</td>
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<td>PP</td>
<td>1.7</td>
<td>195</td>
<td>20</td>
<td>4</td>
<td>25</td>
<td>-</td>
<td>[132]</td>
</tr>
</tbody>
</table>
5.2 Theoretical Background and considerations

This section reviews degradation and mechanical property models that are appropriate for composite manufacturing and can potentially be used to account for thermochemical degradation of NFRP bio-composites.

5.2.1 Temperature/time dependent mechanical properties

To manufacture composites by compression moulding, the temperature of the hot press should be sufficiently above the melting point of the polymer to lower the matrix viscosity and the time sufficiently long for penetration of the melt into the fibres achieving a strong bond between matrix and fibre [273]. However, mechanical properties of natural fibres and thermoplastic matrices are degraded even at low temperatures and short holding times [128, 273]. In particular, poly (lactic acid) (PLA) suffers from thermal degradation for temperatures that typically occur during the compression moulding process [153, 155, 156]. A number of studies have also indicated that the moulding time has a significant effect on the mechanical properties of compression-moulded PLA-based bio-composites [132, 140-144, 284]. Thus, in this study the purpose is to determine the tensile strength and modulus of the matrix, fibre and composite as a function of processing temperature history.

5.2.2 Thermo-chemical degradation of matrix (depolymerisation via chain scission)

The temperature of the hot press causes chemical reactions within the matrix material leading to a decrease in the average length of polymer chains tending towards an equilibrium value [153, 155, 156]. A reduction of the degree of polymerization (DP) is a main indicator for polymer thermal degradation at high temperature and is prominent in polymers with acidic end groups such as PLA [197, 262]. Since there is strong correspondence between mechanical properties and polymer length it is appropriate to propose Eqs. (1) and (2) where the mechanical properties are simply a function of the degree of polymerization which itself is a function of the temperature history:

\[ E_x = E_x(DP_x(T,t)) \]  

(1)
\[ \sigma_x = \sigma_x(DP_x(T,t)) \] (2)

where subscript \( x \) is \( m \) for matrix in this context, or \( f \) for fibre at \( \S 5.2.3 \), and \( DP \) is given by Eq. (3) [273]:

\[ DP_x = M_{n-avg}/m_0 \] (3)

where \( M_{n-avg} \) is the number-average molar mass of polymers in the matrix and \( m_0 \) is the molar mass of a single monomer unit. To estimate \( M_{n-avg} \), a statistical model for the polymer considered both degradation and recombination reactions which occur during the thermal processing as proposed by Wachsen [153] and revised by Yu et al. [156] and Khanlou et al. [241].

For the thermo-chemical degradation of the PLA matrix [241],

\[ \frac{d\lambda_0}{dt} = k_{xd} \left( \rho \frac{\lambda_0}{m_0} - \lambda_0 \right) - \frac{k_{xc}\lambda_0^2}{2} \] (4)

where \( \rho \) is the density, \( k \) is the effect of temperature on the reaction with subscript \( c \) for (re-)combination and subscript \( d \) for degradation, and \( \lambda_0 \) is the total number of moles of molecules per unit volume,

\[ \lambda_{0-initial} = \rho / M_{n-start} \] (5)

The effect of temperature on (re-)combination and degradation (\( k_{xc} \) and \( k_{xd} \) in Eq. (4)) is expressed using the Arrhenius equation (Eq. (6)) [273]:

\[ k_{xy} = A_{xy} \exp\left(\frac{-E_{asy}}{RT}\right) \] (6)

where subscript \( y \) is \( c \) for (re-)combination or \( d \) for degradation, \( A_{xy} \) are the pre-exponential factors (s\(^{-1}\)) and \( E_{asy} \) are the apparent activation energies, \( R \) is the universal gas constant (8.3136 J/mol K) and \( T \) is the temperature (K). It is assumed that the same
values of $k_{xc}$ and $k_{xd}$ apply to polymers of any length. Table 5-2 shows the values for kinetic parameters and initial conditions for modelling polymer degradation of PLA, which are calculated or extracted from the literature [155, 241]; and Figure 5-1 shows changes of $DP$ of PLA at various temperatures and times.

To calculate $\lambda_0$ for isothermal processing conditions, an analytical solution, Eq. (6), was developed by separating the variables [241]:

$$\lambda_0 = \frac{-k_d}{k_c} + \frac{\sqrt{2k_c k_d \lambda_1 + k_d^2}}{k_c} \tanh\left(\frac{(t + C)\sqrt{2k_c k_d \lambda_1 + k_d^2}}{2}\right)$$

(7)

where $C$ is defined by the initial condition for $\lambda_0$ as:

$$C = \frac{2}{\sqrt{2k_c k_d \lambda_1 + k_d^2}} \tanh^{-1}\left(\frac{\lambda_{0-initial} + k_d}{k_c \sqrt{2k_c k_d \lambda_1 + k_d^2}}\right)$$

(8)

where $\lambda_1$ is the total number of moles of monomer units per unit volume:

$$\lambda_1 = \rho / m_0 = \text{constant}$$

(9)

Table 5-2 Kinetic parameters and initial conditions for modelling polymer degradation of PLA.

<table>
<thead>
<tr>
<th>$A_c$ (L/mol/s)</th>
<th>$E_{ac}$ (kJ/mol)</th>
<th>$A_d$ (s$^{-1}$)</th>
<th>$E_{ad}$ (kJ/mol)</th>
<th>$m_0$ (g/mol)</th>
<th>$M_{n-start}$ (g/mol)</th>
<th>Start Polydispersity (g/L)</th>
<th>Density (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>121.6</td>
<td>37.7</td>
<td>1600</td>
<td>79</td>
<td>72.07</td>
<td>1.06×10$^5$</td>
<td>1.87</td>
<td>1260</td>
</tr>
</tbody>
</table>
5.2.3 Thermo-chemical degradation of natural fibres (degree of polymerization of natural fibres)

Natural fibre cellulosic chains also show scission behaviour when they are exposed to a high temperature, in a similar way to polymeric matrices. Gassan et al. correlated the mechanical (tenacity) properties of jute and flax fibres at various temperatures to DP [202]. Now assuming the fibre modulus and strength are each a function of DP, we can use Eqs. (1), (2) and (3) with subscript \( x = f \) (fibre).

A parameter \( N \) related to the molecule concentration (\( N = 1 - (1/DP) \)) can be predicted using a first-order chemical rate equation as shown by Testa et al. [207] to estimate the chain scission of cellulosic materials. Their model corresponds to the random chain scission of bonds in a linear chain polymer:

\[
\frac{dN}{dt} = K \times N
\]

and using Eq. (6) again with subscript \( x \) in the equation now being \( f \) (fibre degradation). For a given temperature, Eqs. (6) and (10) may be solved to give:

\[
N = N_0 e^{\frac{-E_A}{RT}}
\]  

Figure 5-1 \( DP \) progress of PLA at various temperatures and times.
In a study by Gassan et al. [202], $DP$ was measured after heating flax fibre for different periods of time for three different temperatures as listed in Table 5-3. The initial value given for $DP_0$ was 1505. For the present study, a least-squares fitting procedure was used to determine the pre-exponential factor ($A = -0.178 \text{ s}^{-1}$) and the apparent activation energy ($E_a = 50.5 \times 10^3 \text{ J/mol}$) to fit Eqs. (3), (6) and (10) to the data given in Table 5-3 [273]. Figure 5-2 shows changes of $DP$ progress of flax at various temperatures and times.

Table 5-3 $DP$ of flax fibre heat treated for three time periods and at three temperatures [202].

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>170 °C</th>
<th>190 °C</th>
<th>210 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>866</td>
<td>509</td>
<td>387</td>
</tr>
<tr>
<td>120</td>
<td>511</td>
<td>360</td>
<td>261</td>
</tr>
</tbody>
</table>

Figure 5-2 $DP$ progress of flax at various temperatures and times
5.3 Rule of mixture for mechanical properties prediction

The prediction of composite material properties normally uses a rule-of-mixture (RoM) to estimate the moduli and axial strength. It is a parallel spring model based on the assumption that fibres and matrix will experience equal strain under loading in the fibre direction. It is assumed that the fibres can be anisotropic with different mechanical properties in the axial and transverse (radial) directions, while the matrix is isotropic [89]. Eqs. (12) and (13) [89] have recently been developed specifically for NFRP bio-composites:

\[
E_c = \kappa \eta_f \eta_d \eta_o V_f E_f + E_m V_m \tag{12}
\]

\[
\sigma_c = \kappa \eta_f \sigma_f + V_m \sigma_m \quad \text{(for UD composites on the principal axis)} \tag{13}
\]

where \( E \) is the elastic modulus (using Eq. (1) here), \( V \) is the volume fraction, \( \kappa \) is a fibre area correction factor (FACF) (used when properties have been derived using an assumption of circular cross-sectional area (CSA) but fibres do not have circular CSA, \( \eta_d \) is the fibre diameter distribution factor, \( \eta_l \) is the fibre length distribution factor, \( \eta_o \) is the fibre orientation distribution factor, \( \sigma \) is the strength (using Eq. (2) here), \( \sigma^*_m \) is the stress in the matrix at the failure strain of the fibre and subscripts \( c, f, m \), are composite, fibre and matrix, respectively. Eqs. (12) and (13) predict that the composite properties will increase with increasing fibre volume fraction/percentage (v/o) [143, 285-287]. The fibres play an important role as carriers of load and stress, for example, stiffness and strength [276, 288-290].

5.4 Mechanical properties in relation to degree of polymerization

The objective here is to consider the connection between the chemical degradation and tensile properties of bio-composites. Thus, as discussed above, we found that mechanical properties are dependent on \( DP \), and in particular it has been reported that tensile strength is in a linear relationship with \( 1/DP \) [277]:

\[
\sigma = a_0 - a_1 \frac{1}{DP} \tag{14}
\]

where \( a_0 \) and \( a_1 \) are constants which can be determined empirically from experimental data.
5.5 Experiment

Ultimately we are interested to predict tensile properties of a flax/PLA bio-composite manufactured using the compression moulding process. For this purpose, the similar methods of manufacturing and mechanical properties examinations to our previous work were carried out [273]. Unidirectional (UD) flaxply fabric (180 g/m² flax) manufactured by Lineo Company (France) was used in this study. PLA film (25 microns thick) was supplied by Magical Film Enterprises Co. Ltd. (Taiwan) [273].

Polymer molecular weight and polydispersity were measured using gel permeation chromatography (GPC) on a Shimadzu 20A system equipped with refractive index detector (RID-10A). Analysis was performed at 35°C using a Styrage HT 4 column (7.8 mm x 300 mm) obtained from Waters, Co (Miliford, MA) in isocratic (involving a mobile phase whose composition is kept constant and uniform) conditions using tetrahydrofuran (THF) as solvent with a flow rate of 1.0 ml/min.

For manufacturing of neat PLA, a sealed mould and a vacuum bag setup were used. The sealant (Airtech AT200Y high temperature tacky tape) was utilised for its ability to withstand temperatures up to 200°C. The mechanical properties of three samples were evaluated.

To find the sensitivity of mechanical properties of the bio-composite to various processing conditions, mechanical properties of a flax/PLA bio-composite were measured at different processing times. Six consolidation times were considered with 16 samples tested for each consolidation time. Figure 5-3 shows the tensile properties of flax/PLA composite at the six consolidation times. The moduli can be seen to be sensibly independent of consolidation time (in the range from 28.2 to 29.9 GPa based on the initial slope of the stress-strain curve), but the tensile strength and fracture strain reduce significantly as the consolidation time increases (from 276 to 155 MPa and 2 to 1.2 % respectively).
Chapter 5: Estimating Mechanical Property Degradation

![Graph a)](image1)

![Graph b)](image2)
Figure 5-3 Mechanical properties of flax/PLA composites: (a) modulus; (b) tensile strength; and (c) failure strain.

5.6 Modelling and prediction of the tensile properties of PLA

Since the changes of tensile modulus are insignificant, we have considered Eq. (1) to be independent of the temperature history. To predict tensile strength of PLA Eq. (14) has been applied as:

\[ \sigma_{\text{matrix}} = a_{0\text{-matrix}} - a_{1\text{-matrix}} \frac{1}{DP} \]  

To find \(a_{0\text{-matrix}}\) and \(a_{1\text{-matrix}}\), the tensile strength is plotted against \(1/DP\) graph (Figure 5-4) resulting in \(a_{0\text{-matrix}} = 67\) MPa, and \(a_{1\text{-matrix}} = 18\) GPa. In Figure 5-4, tensile strengths of PLA were achieved through experiments in this study and \(1/DP\) values of the reported temperatures/times are calculated using Eq. (3). Moreover, the initial trend of tensile changes of PLA (Figure 5-4) is similar to the linear changes reported by Flory [277]. A better fit to the measured data could be obtained using an equation in the form:

\[ \sigma_{\text{matrix}} = A \exp(-B/DP) + C \]  

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Figure 5-4 Tensile strength vs $1/DP$ for PLA at various temperatures and times. $DP$ for PLA was measured using gel permeation chromatography (GPC).

### 5.7 Calculation and prediction of the tensile strength of fibres

To find $a_{0\text{-fibre}}$ and $a_{1\text{-fibre}}$ for Eq. (17), we need to calculate the tensile strength of fibre using a RoM (Eq. 13), when parameters are: $\kappa = 1.35$ (which is half of apparent diameter) [291], $V_f = 0.48$, $V_m = 0.52$ (assuming zero voids), experimental tensile strengths of the bio-composite, $DP$ of matrix, $DP$ of fibre, and calculated tensile strengths of matrix at various conditions, which are presented in Table 5-4. In Figure 5-5, $1/DP$ values for the fibre at various temperatures/times are calculated using Eqs. (3), (6) and (15). Subsequently, the tensile strengths of fibre using the linear model and proposed model are achieved (see Table 5-4). As a result, $a_{0\text{-fibre}} = 560$ MPa and $a_{1\text{-fibre}} = -2.1 \times 10^5$ MPa are achieved using the linear model.

$$\sigma_{\text{fibre}} = a_{0\text{-fibre}} - \frac{a_{1\text{-fibre}}}{DP}$$  \hspace{1cm} (17)

Similar to PLA, the data could be better correlated using:

$$\sigma_{\text{fibre}} = A \exp(-B/DP) + C$$  \hspace{1cm} (18)
Figure 5-5 Tensile strength vs $1/DP$ for flax fibre at various temperatures and times. $DP$ for flax was not measured but rather was calculated using data from Ref. [202] using Eqs. (3, 6, 11) and (15) with the measured temperature history.

Table 5-4 $DP$ of flax fibre heat treated for five time periods and at 170°C using proposed model.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>276</td>
<td>746</td>
<td>1183</td>
<td>39</td>
<td>385</td>
</tr>
<tr>
<td>30</td>
<td>234</td>
<td>514</td>
<td>975</td>
<td>30</td>
<td>334</td>
</tr>
<tr>
<td>45</td>
<td>206</td>
<td>404</td>
<td>829</td>
<td>24</td>
<td>300</td>
</tr>
<tr>
<td>60</td>
<td>187</td>
<td>343</td>
<td>721</td>
<td>21</td>
<td>277</td>
</tr>
<tr>
<td>120</td>
<td>166</td>
<td>252</td>
<td>474</td>
<td>16</td>
<td>239</td>
</tr>
<tr>
<td>180</td>
<td>149</td>
<td>231</td>
<td>353</td>
<td>14</td>
<td>231</td>
</tr>
</tbody>
</table>
5.8 Proposed model for the tensile strength of NFRP bio-composites

The linear relationship proposed by Flory [277] (Eq. 14) is unrealistic for longer periods of time. As shown in Figure 5-6, the trend of his model reaches to zero or negative values of the tensile strength after 180 minutes. To overcome this shortcoming, a new model is proposed here (Eqs. (16) and (18)) to predict the tensile strength for longer periods and ensure that the trend never goes below zero. The proposed model was used to predict the tensile strength of matrix and fibre (shown in Figure 5-4 and Figure 5-5 as ‘proposed model’, Eqs. (16) and (18)); subsequently it was used to predict the tensile strength of the flax/PLA bio-composite. The model results are also in agreement with our previous measurements [273] (for a different batch of materials) also shown in Figure 5-6.

Figure 5-6 Experimental data of the flax/PLA bio-composite and the prediction differences of the linear model and the proposed model
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5.9 Conclusions
In this paper we introduced a link between the chemical degradation of NFRP bio-composite during thermal processing and their subsequent mechanical properties. To achieve this goal the following processes were taken into account:

i. Mechanical properties of the bio-composite can be calculated by estimating their relationship with the changes of $DP$ over the temperature and time. This relationship has separately been proposed for both matrix and fibre.

ii. The modulus of elasticity for both the flax fibre and for PLA may be assumed to be independent of the thermal processing.

iii. A linear relationship between strength and $1/DP$, as proposed in the literature, was used to calculate the tensile strength of matrix and fibre, and for first time used to predict the mechanical properties of NFRP bio-composites.

iv. To predict the tensile strength of NFRP bio-composite, the linear model was neither reliable nor practical for extended periods of time; subsequently a new exponential model was proposed which is realistic and within 10% of errors. Thus, tensile strength of PLA can be predicted as a function of its temperature history during processing using Eqs. (4-6) and (16) and the fibre using Eqs. (3, 6, 10) and (18).

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Chapter 6: Evaluating Mechanical Properties in Moisture Related Environments

Statement of contribution to co-authored published paper

This chapter includes a published journal paper.

The bibliographic details of the paper, including all authors, are:


My contribution to the paper involved: undertaking literature review, classifying the necessary theoretical backgrounds and models, performing the experimental tests, analyzing and discussing data, drawing figures, preparing tables, writing and editing the manuscript according to my supervisors’ comments.
Chapter 6: Evaluating Mechanical Properties in Moisture Related Environments

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Chapter 6: Evaluating Mechanical Properties in Moisture Related Environments

The sensitivity of mechanical properties of flax fibre reinforced poly (lactic acid) biocomposites to wet, freezing and humid environments

Abstract: Biocomposites are increasingly being perceived as a green alternative to synthetic composites in many applications. However, the overall long-term durability of biocomposites is a major concern, particularly their ability for sustained performance under harsh and changing environmental conditions. This paper reports a detailed study on the effect of environmental conditions on the performance of flax/PLA biocomposites. Neat poly (lactic acid) PLA and bio composite samples were exposed to environments similar to those found outdoors: wet, freezing and humid. Moisture absorption and physical changes of specimens were periodically examined. Flexural and tensile properties were evaluated periodically to determine the detrimental effect of each exposure condition on the mechanical performance of biocomposites. Direct contact with liquid water is the most deteriorating environment for biocomposites. A drying process can partially restore the mechanical performance of these materials. Biocomposites can survive reliably in warm humid environments and in those that could create freeze-and-thaw cycles for short-term outdoor applications. The mechanisms and reasons involved in the degradation of the properties of green composites are discussed.

Keywords: natural fibres reinforced polymer composites; flax fibre; PLA; environmental application
6.1 Introduction

There is significant global interest in biocomposites due to their practical and potential environmental benefits. Biocomposites are commonly referred to as “sustainable composites”, but such claims are rarely supported by a full four pillars (economic, environmental, equity, governance) life cycle analysis (LCA) [292]. The attractive features of biocomposites are acceptable mechanical properties (which are now comparable to unsustainable alternatives), reasonable price, low density, biocompatibility and, subject to LCA, good sustainability [292]. These points encourage manufacturing industries (especially packaging and automotive [96]) to produce sustainable products using biocomposites. However, low durability and swift degradation of biocomposites in outdoor applications has become a chief obstacle. In particular, wet environments can cause a rapid deterioration of mechanical properties and performance of bio-composites due to moisture absorption [28] and dimensional changes [231]. Knowledge of the sensitivity of properties of biocomposites to moist environments is essential for prospective applications.

Water immersion, warm humid and freeze/thaw (F/T) tests are the main tools in recognizing the sensitivity of biocomposites to the environment [16, 39, 40, 45]. The quality of the biocomposite can be explained by using a range of environments, from a fully wet environment to an environment where the WA level changes due to freezing and thawing (F/T). Table 6-1 shows that all three types of moisture-related environments can cause major degradation in mechanical properties. Although several studies regarding the degradation of NFRP biocomposites have been published (Table 6-1), there is a need for further studies to generate a complete understanding of biocomposites in various environments for various applications. When the durability in specific environments is determined, practitioners may be able to accordingly adjust their plans for the usage of the biocomposite.

Moisture can cause both physical and chemical degradation of biocomposites. Physical changes were introduced by previous studies [129, 213, 214, 234, 293] as a key factor in biocomposites durability reduction. The source of physical changes is the swelling of the hydrophilic fibres which cause micro-cracks in the biocomposite [213, 215]. Then, capillary action transports water along the biocomposite layers [213, 215].


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Consequently, fibre and matrix debonding causes a decline in the mechanical properties [211, 294]. Chemical degradation reactions involve water molecules interacting with hydroxyl and carboxyl groups found in cellulose, hemicellulose and lignin which are the principal components of natural fibres [215]. These reactions cause reductions in the molar mass of the natural polymers and degradation of the bonding between fibre and matrix leading to further degradation of mechanical properties.

In this work, the sensitivity of the compression moulded flax fibre (FF)/PLA biocomposite, is examined in water saturated (WS), humid saturated (HS) and F/T environments, and the tensile and flexural properties of the biocomposite are reported, resulting in a comprehensive set of experimental data and the related kinetic data. The findings are also compared with those of previous works which have been produced for various applications. As characteristics of water saturated and dried (WSD), F/T, WSF/T biocomposites are rarely discussed in the literature, the discussion of this study is valuable for practitioners who are considering using FF/bio-matrix products.
Table 6-1 Previous studies on mechanical properties degradation of NFRP biocomposites using various materials, manufacturing processes and various environments.

<table>
<thead>
<tr>
<th>Material Fibre/Matrix</th>
<th>Manufacturing detail</th>
<th>Condition</th>
<th>Max. moisture content / Days</th>
<th>Degradation</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| Hemp/ unsaturated polyester | • Non-woven hemp  
• Method= Hand lay-up compression moulding  
• 21% fibre volume | WS | 11% / 6 | ≈38% decline in tensile strength and ≈97% in tensile modulus | [214] |
| Jute/ Bio-epoxy | • Plain weave jute  
• Method= low-pressure injection moulding  
• 40% fibre volume | WS | 26% / 14 | High rate of swelling  
Reduction in density of samples | [213] |
| Flax/ polypropylene | • non-woven needled flax  
• Method= blending in a twin-screw extruder  
• 38% fibre volume | WS | 18% / 60 | ≈25% decline in tensile  
≈40% decline in stiffness | [293] |
| Jute/ phenolic resin | jute hessian cloth | WS | 48% weight gained / 60 | ≈60% decline in tensile strength  
≈60% decline in flexural strength | [295] |
### Chapter 6: Evaluating Mechanical Properties in Moisture Related Environments

<table>
<thead>
<tr>
<th>Material Combination</th>
<th>Description</th>
<th>Processing Conditions</th>
<th>Property Change</th>
<th>References</th>
</tr>
</thead>
</table>
| Jute/PLA                              | • Short jute  
  Method= film stacking hot press  
  40% fibre volume               | HS at 70 °C             | 16% / 7  
  ≈75% decline in tensile strength       | [234]       |
| Jute/phenolic resin                    | jute hessian cloth                                                        | HS at 50 °C           | 10% weight gained / 60  
  ≈70% decline in tensile strength  
  ≈58% decline in flexural strength   | [295]       |
| Wood Flour/polyvinyl chloride         | • 16-mesh beech wood  
  Method= compression moulding  
  70% weight fraction               | F/T 3 cycles at 18°C | ---  
  30–40% decline in mechanical properties (tensile strength and modulus, and flexural strength and modulus) | [296]       |
6.2 EXPERIMENTAL PROCEDURE

6.2.1 Materials
Unidirectional (UD) flaxply fabric (180 g/m² flax) manufactured by the Lineo Company (France) was used in this study. PLA film (25 microns thick) was supplied by Magical Film Enterprises Co. Ltd. (Taiwan). Thermal transition temperatures of the PLA were measured for four samples using differential scanning calorimetry (DSC). The average glass transition temperature ($T_g$) was 61.9 °C and the crystalline melting temperature ($T_m$) was 146.2 °C.

6.2.2 Composites samples preparation
Flat aluminium plates (3 mm thick) were treated with a high-temperature release agent (Aliphatic Hydrocarbones, Marbocote Ltd, UK), and used as the lower and upper moulding surface. Two layers of PLA film were placed directly on the bottom mould surface followed by a single layer of fibre and two further layers of PLA. This pattern was repeated for ten fabric layers. There are totally 10 layers of FF between each reinforcement layer. The as-manufactured (AM) unidirectional (UD) biocomposite plate was moulded with a total thickness of approximately 2.5 mm, with a planar area of approximately $300 \times 300$ mm to a nominal fibre volume fraction of 48%.

The compression moulding machine (Carver Inc, Wabash, USA) was set to a temperature of 170 °C which is above the melting temperature of the PLA. The composite was compressed to a pressure of 300 kPa and held at the set temperature for 15 minutes consolidation time. The pressure was maintained while the top and bottom platens were cooled. The cooling process was manually controlled by a supply of cold water to the platens. To accurately repeat the cooling process, the temperatures of the upper and lower platens were recorded during the entire process using a data logger (USB TC-08, Pico Tech, UK) sampling at a rate of 1 Hz. The samples were cut by means of a laser cutter to the dimensions required for mechanical tests (tensile and flexural) and their edges were carefully coated with adhesive tape to prevent extra water contact through edges. A total five samples were tested for each condition.

For manufacturing of neat PLA, a sealed mould and a vacuum bag setup were used. The sealant (Airtech AT200Y high temperature tacky tape) was utilised for its ability to withstand temperatures up to 200°C. The mechanical properties were measured for three
samples and tests were performed at temperature of 170°C for 15 minutes consolidation time.

### 6.2.3 Water immersion tests

To test samples, they were immersed in distilled water at room temperature. The samples were weighed periodically using an analytical scale accurate to 100 µg and the time of each weight measurement was controlled with a stop watch. Before the weight measurements, the specimens were withdrawn from the water and wiped dry to remove the surface moisture. Then, the specimen weight and immersion time data were collected. The relative water absorption (WA) was calculated using Eq.(1):

\[
M_r(t) = \frac{[W(t) - W_0]}{W_0} \times 100
\]

Where \( M_r(t) \) = relative WA of the specimen at each time (t), \( W(t) \) = specimen weight at each time, \( W_0 \) = initial specimen weight. The tests were stopped after 60 days.

One set of the WS samples were completely dried (WSD) to evaluate the residual properties of samples that have been fully saturated but then dried. The drying process was carried out in a dehydrating oven at 40 °C for three days (until no changes in the samples weight were observed). This drying cycle (low temperature-long time) was chosen to avoid possible damage to the mechanical properties of the biocomposite at higher temperatures.

### 6.2.4 Warm Humid tests

To perform the warm humid test, specimens from each batch of tensile and flexural samples were put into an environmental test chamber with a relative humidity (RH) of 75% at 45 °C. During the ageing experiment, and at certain periods of time, specimens were periodically taken out of the chamber to assess the weight change. The weighing of the specimens was stopped after 60 days, when the weight reached saturation point, that is to say when the weight gain was nearly constant.
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6.2.5 Freeze/Thaw tests
Two types of F/T tests were designed: For first type, F/T cycling, at 1, 5 and 10 cycles, were performed on AM specimens following the ASTM D7031-04 standard recommendations. Each cycle consisted of placing the specimens in a freezer for a 24 h freezing period at -18 °C and removing them from the freezer to allow thawing at room temperature for another 24 hours. For second type, the WS samples were subjected to 1, 5 and 10 cycles of F/T; for a 24 h thawing period, the samples were kept in the water to ensure the water content remained at the saturation level. This type of test shows the mechanical performance of the materials under freezing process at the most favorable condition (AM samples) and the most unfavorable condition (maximum moisture content (MC) in the microstructure).

6.2.6 Mechanical properties evaluation
Test specimens were laser cut before exposure from the composite plates (parallel to the fibre direction). The test specimen dimensions were 250 mm × 15 mm and 80 mm x 12.7 mm for the tensile and flexural tests, respectively. Four samples were tested for each condition. Tensile testing was carried out using an Instron 3367 testing machine with an Instron 30 kN load cell (serial no. 68296). Gripping end tabs were used during the tensile testing as recommended by ASTM D3039/D3039 M. Crosshead displacement rate was 2 mm/min. The tensile strain in the specimens was measured with a 50 mm Instron extensometer attached to the in-plane surface of the sample. The tensile modulus was calculated over the axial strain range of 1000-3000 micro strain.

Three-point bending tests were performed with the same testing machine, a test span of 60 mm and a crosshead displacement rate of 2.4 mm/min. Load-displacement curves were obtained from these tests and flexural modulus and strength values were determined from these curves, according to the ASTM D790-03 standard.

6.3 RESULTS AND INTERPRETATION
6.3.1 Moisture absorption and physical changes

When a solid material is immersed in water, or exposed to a very humid environment a diffusion process takes place due to the water concentration gradient between the solid and the surroundings. If the water transport from one part of the system to another is carried out by means of random molecular motion driven by this concentration gradient, then Fick’s first law (Eq. (2)) is applicable:

\[ F = -D \frac{\partial C}{\partial x} \]  

(2)

where \( F \) is the rate of transfer in the \( x \) direction per unit area of a section, \( C \) is the concentration of the diffusion substance, \( x \) is the space coordinate measured normal to the section, and \( D \) is the diffusion coefficient of the solid.

In the case of composite materials and specially in vegetable fibre composites, there are some additional water transport mechanisms apart from the diffusive ones, such as: movement of water molecules into voids and defects at the fibre/matrix interface as a result of capillary action [214, 215], and capillary flow into micro-cracks in the matrix after swelling of natural fibres [213]. Therefore, Fick’s law assumptions are not accomplished in these materials. Several models have been developed to calculate the diffusion of molecules within a composite, however Fick’s second law (Eq. (3)) has still been widely used to estimate a one-dimensional time dependent WA process [297].

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  

(3)

In this case, if the diffusion coefficient is considered to be constant, the concentration gradient is only along the \( x \)-axis and diffusion is one-dimensional, then the fundamental differential equation of diffusion in an isotropic medium (and again, the composite is considered to be isotropic) is derived by considering a rectangle whose sides are parallel to the coordinate axes [297]. Thus, for a plane sheet with uniform initial distribution and a constant surface concentration, the moisture uptake with respect to exposure time can be calculated using Eq. (4)[297]:

\[ \frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[ -\frac{D(2n+1)^2 \pi^2 t}{4l^2} \right] \]  

(4)
where $M_t$ is the total mass of diffusion substance entering the sheet at time $t$, $M_\infty$ is the corresponding quantity after infinite time, and $l$ is the half thickness of the specimen.

Eq. (4) demonstrates that $M_t$ equals $M_\infty$ at infinite time, and infinite time is typically considered when MC is at the maximum level. The plateau section at the last stage of WA in Figure 6-1 shows the maximum level of MC or $M_\infty$. Furthermore, MC at the initial stage rises linearly with $t^{0.5}$ and can be simplified as Eq. (4) to Eq. (5) [297]:

$$M_t = \frac{2M_\infty \sqrt{D}}{\sqrt{\pi}} \frac{\sqrt{t}}{l}$$

Therefore, $D_{\text{average}}$, or average of diffusion coefficient, can be estimated by using Eq. (6) [297]:

$$D_{\text{average}} = \frac{\pi}{4} M_\infty^{-2} l^2 \Theta^2$$

where $\Theta$ is the slope of $M_t$ against $t^{0.5}$ plot.

However, these assumptions are again not realistic since the composite material is not isotropic, and the diffusion coefficient is unlikely to remain constant as the different transport mechanisms previously mentioned activate or arrest as the water absorption process takes place. The development of a realistic model accounting for all the phenomena occurring during water diffusion through vegetable fibre reinforced composites is beyond this work objective. Therefore, in order to obtain numerical values giving a tangible comparison of the diffusion characteristics of the biocomposites used in this study exposed to the different environments, Fick’s law was still used, and diffusion was evaluated by MC% measurements, and by considering the slope of the first part of MC against $t^{0.5}$. The calculated diffusion coefficient was then called “effective” diffusion coefficient, since it involves not only diffusive mechanisms for water transport through the material, but the others previously mentioned.
Figure 6-1 a) Moisture content (MC) and b) $M_t/M_\infty$ rates of water immersion of PLA and Flax/PLA biocomposites, warm humid and freeze/thaw (F/T) environments.

Figure 6-1a represents MC percentage as a function of time (NB: days on the time axis) for PLA and the FF/PLA biocomposite in the different environments, including WS, HS and F/T. Following Fick’s diffusion theory, the relative MC in the immersion process should display three stages, a linear rise against $t^{0.5}$ at the beginning, then the absorption rate decreases, and finally a (quasi-)steady saturated stage is reached. This behaviour was only observed for the water immersed biocomposites samples, although the behaviour is not perfectly Fickian. As can be seen in Figure 6-1a, MC at HS environment is significantly lower than WS environment. While MC is very low, it has three clear stages each separated by a step. This stepped process can be attributed to swelling stresses that arise as the fibres confined inside the matrix absorb water and
swell, and was previously observed and reported by Stamboulis et al. [129]. This mechanism slows down the approach to the final equilibrium moisture and a first apparent equilibrium occurs. After the initial absorption process, these stresses relax [298], and the equilibrium moisture condition changes as the diffusion proceeds. A new equilibrium is reached and the process can continue or stop, if the saturation moisture content in the material is attained. The biocomposites showed three equilibriums, the last one being reached after 20 days and showing a ≈2.5% MC. No further equilibriums were observed from that point up to the tests final, 40 days after, thus it can be certainly stated that ≈2.5% was the saturation moisture content in these materials under the HS condition.

Although it was anticipated that there would not be MC in the biocomposite after the F/T process, some weight increase was registered, meaning that WA did occur. The WA occurs probably because of the swelling/shrinkage tensions encountered by the biocomposite during the F/T process. Moreover, when the biocomposite is transformed from the freeze phase to the thaw phase, the moisture from the environment condenses on the cold composite surface. This condition simulates dew and rainfall, and results in both cyclic washing away of the specimen surface and water absorption through the material. MC of water saturated and freeze/thaw (WSF/T) at 1, 5 and 10 cycles were approximately 22%, showing that the MC does not change after the WSF/T condition.

MC of neat PLA in WS gradually increases and levels off at 0.99% after 42 days, which is in agreement with MC≈1% as reported by Wang et al. [299]. However, in the case of HDPE, it is reported that no moisture was gained after one year [297]. The very low MC in the matrix suggests that water penetrates through the fibres in the composite, which function like water channels [300].

Figure 6-1b shows the same data as Figure 6-1a except that the vertical axis has been normalized to the saturation moisture uptake, $M_\infty$. Table 6-2 shows the effective diffusion coefficients obtained by fitting Eq. (5) to the initial slope data against $t^{0.5}$ from each of the experiments. Eqs. (4) and (5) are plotted on Figure 6-1b for the cases of immersion and humid environments. Modelling of immersion and humidity tests show that the WA follows the initial stage of Fick’s law up to $M/M_\infty =0.6$. Data beyond this point were not used to estimate the initial slope for the effective diffusion coefficient. Therefore, it should be noted that only the first linear part of the HS specimens curve
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was used, and the effective diffusion coefficient represents the initial diffusion characteristics of the biocomposites.

Table 6-2 Kinetic data of water saturated (WS) PLA and Flax/PLA biocomposites at WS, humid saturated (HS) and freeze/thaw (F/T) environments.

<table>
<thead>
<tr>
<th>FF/PLA composites exposing conditions</th>
<th>Saturation moisture uptake $M_e$ (%)</th>
<th>Initial slope of plot $(\Theta) (M_t)$ versus $t^{0.5}$ $(s^{0.5} \times 10^{-3})$</th>
<th>Effective diffusion coefficient, $D$, $\times 10^{-12}$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PLA</td>
<td>0.99</td>
<td>0.4</td>
<td>10</td>
</tr>
<tr>
<td>WS</td>
<td>22</td>
<td>28</td>
<td>189</td>
</tr>
<tr>
<td>HS</td>
<td>2.60</td>
<td>2.8</td>
<td>136</td>
</tr>
</tbody>
</table>

To evaluate the physical changes of the biocomposite in different environments, the thickness of swollen material was calculated using Eq. (7):

$$f_{swelling(t)} = 100 \times \frac{T_{f,t} - T_{f,0}}{T_{f,0}}$$  \hspace{1cm} (7)

where $f_{swelling(t)}$ is the thickness swelling ratio, $T_{f,t}$ is the bio-composite thickness exposed to the environment, and $T_{f,0}$ is the AM biocomposite thickness.

Figure 6-2 represents the physical changes of the biocomposite in different environments over time. The swelling of the WS biocomposite is significantly higher than the swelling in other environments, displaying the same trend as the MC. As mentioned before, the chemical composition of FF is responsible for the composite physical changes and this phenomenon can clearly be shown by the value of $f_{swelling-PLA}$ in Figure 6-2, which is only 0.13% in comparison with 19.5% for the biocomposite. Moreover, the HS environment does not impact on the physical changes of the biocomposite in a significant way. The negligible swelling changes can be of interest to practitioners who want to use the biocomposite in a HS environment. In addition to that, F/T leads to limited swelling in the thickness of biocomposite over the entire cycling period. Furthermore, $f_{swelling}$ values of WSF/T at 1, 5 and 10 cycles were approximately 20%, 24% and 29%, showing significant F/T effects on the swelling of WS.
biocomposites after F/T cycling. As expected, these swelling values significantly affected the mechanical properties (explained in the following sections).

![Swelling rate of water saturated (WS) PLA and Flax/PLA biocomposites at WS, humid saturated (HS) and freeze/thaw (F/T) environments; b) magnified swelling rate of WS PLA, biocomposites at HS and F/T environments.](image)

Physical and chemical reactions, which cause the degradation process, occur in biocomposites. With the use of microscopes, initial defects have been seen to appear in the form of pores, micro-cracks and delamination [234]. These defects assist water permeating into the biocomposites by means of capillary transport, resulting in volumetric changes or swelling. Furthermore, hydrolytic reaction and the existence of H$_2$O, causes chemical chain reactions in –CHCH$_3$COO- groups of PLA molecules,
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which eventuate in the chain scission process and a decline in the molar mass and mechanical properties of the biocomposites [234]. All these reactions lead to interfacial and internal (centralized) degradations in the biocomposites. The following sections support this explanation.

6.3.2 Tensile properties

The typical stress-strain curves for the FF/PLA composite at the different environments are shown in Figure 6-3. For the immersion case and humid environment case, the examples shown in Figure 6-3 correspond to 60 days of exposure to moisture-related environments. The biocomposite shows strain to failures of 2.3 to 3.4% for the WSD, F/T and HS samples, while WS and WSF/T samples show 3.8 to 4.3%. Generally, aging processes cause declines in stress and increases in strain, especially in the wet environments, in contrast to AM samples.

![Stress-strain curve diagram](image)

Figure 6-3 Typical Flax/PLA biocomposites stress-strain curves at as-manufactured (AM), water saturated (WS), water saturated and completely dried (WSD), humid saturated (HS), freeze/thaw (F/T) and water saturated and freeze/thaw (WSF/T) environments.

Figure 6-4a-c shows the tensile properties (modulus, strength and strain at break) of the biocomposite exposed to various environments. Consistent with Figure 6-3, exposure to moisture causes a decrease in tensile strength and an increase in failure strain. The
elastic modulus determined by the initial slope of the stress/strain curves in Figure 6-3 is most significantly affected by the immersion tests.

The tensile properties (modulus and strength) of the biocomposites show significant reductions after WS environment. These properties (unexpectedly) are restored after a complete drying process (compare WS and WSD in Figure 6-3 and in Figure 6-4). This finding highlights the importance of the drying process for regaining the properties, and shows the opportunity of using the biocomposites after simply drying them. This would be of interest to the prospective biocomposite customers.

The HS environment also causes decreases (25%) in the tensile strength, but not as significantly as in the wet environment. One to ten cycles of F/T have a small negative impact on the tensile modulus. The mean tensile strengths are fairly consistent. However, 10 F/T cycling shows 29 and 23% decline in tensile modulus and strength, respectively, possibly due to the residual 1.5% MC of the sample. The tensile modulus and strength of the WSF/T biocomposite are as low as WS samples or even have some further degradation. This agrees with the fact that wet environment is the most deteriorating environment for biocomposites, even more than F/T environment.

The fracture strain almost doubles after WS. This can be explained by the WA plasticizing the NFRP biocomposites, as reported by Stamboulis et al. [129], thus leading to increases in the maximum strain of the biocomposites. The strain-to-failure of the biocomposites after F/T-1 cycle is fairly similar to AM samples, and positively and gradually increases over the periods of F/T and WSF/T.
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Figure 6-4 Tensile properties of the Flax/PLA biocomposite at as-manufactured (AM), water saturated (WS), water saturated and completely dried (WSD), humid saturated (HS), freeze/thaw (F/T) and water saturated and freeze/thaw (WSF/T) environments: (a) Modulus; (b) Tensile strength; and (c) Failure strain.

6.3.3 Flexural properties

The Flexural properties of FF/PLA biocomposites are shown in Figure 6-5a-b. Flexural modulus and strength values of WS samples drop by 69% and 76% and the values are restored to only fall by 20% and 22% respectively, after the drying process. The HS environment also negatively affects flexural modulus and strength values by 39% and 24%, respectively. Flexural properties are not significantly influenced by the F/T
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process. However, the properties of WSF/T samples show similar behaviours to those of WS.

The reduction in flexural property after WA can be attributed to the weak FF/PLA interface in which moisture travels after WA. The micro-cracks on the surface of the biocomposite, which result from exposure to the environments, constrained the efficiency of stress transfer from PLA (matrix) to FF, leading to poor flexural properties [301].

Figure 6-5 Flexural properties of the Flax/PLA biocomposite at as-manufactured (AM), water saturated (WS), water saturated and completely dried (WSD), humid saturated (HS), freeze/thaw (F/T) and water saturated and freeze/thaw (WSF/T) environments: (a) Modulus; (b) Tensile strength.
By comparing Figure 6-4 and Figure 6-5, it can be concluded that the trends of degradations in tensile and flexural properties are quite similar after exposure to the environments.

6.3.4 Effect of exposure time and moisture concentration on degradation

Figure 6-6 shows the deterioration of mechanical properties of the biocomposites which have similar deterioration trends over the process of WA, as the MC increased from initial point (AM specimens) to the saturation point (WS specimens).
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Figure 6-6 The correlation between moisture content (MC) and mechanical properties of Flax/PLA biocomposites: (a) tensile properties, (b) flexural properties.

Therefore, all above mentioned factors have constrained the NFRP biocomposite application for underwater usages. However, indoor applications or short outdoor applications can be considered for this kind of sustainable composites.

6.3.5 Visual observation of failures

Figure 6-7 shows the fracture images from the edge of the biocomposites after exposure to different environments. Generally, cracks, fibre fracture, matrix cracking, fibre pull-out and fibre debonding occur after an aging process, resulting in the sensitivity of biocomposites to different environments [126, 214, 302]. Figure 6-7b-f show the moisture-exposed biocomposite layers have split after tensile failure. This phenomenon shows how interfacial surfaces between flax mat and PLA film layers are degraded over the aging processes, which are attributed to FF and PLA degradations during WA processes [49, 303]. This degradation can be easily identified from the colour changes of the WS, WSD and WSF/T samples. The HS samples have an insignificant WA, but do show these splitting layers as well as fibre breakage. It can also be argued that debonding of cells, monomers and the chain scission process of FF and PLA trigger this kind of degradation at 45 °C temperature [49, 202, 241, 273, 304].

In addition, physical changes play an important role in the composite failures after environmental exposure. Newman et al. [208, 210] stated that the swelling of fibres causes stress in the surrounding matrix, as schematised in Figure 6-8a (highlighted in hatched section). Some stresses are relieved in the matrix after relaxation (Figure 6-8b). After the composite has dried, the matrix will not contract to the previous size due to distortion by molecular relaxation; although fibres do shrink on drying (Figure 6-8c). This gap may be present in single fibre cells or in a bundle of cells (technical fibres) [208]. Gassan et al.[209] also reported the same problem using optical microscopy for plain-weave jute fibre reinforced epoxy composites. Newman et al.[210] and Homkhiew et al.[301] have also stated that cracks within a technical fibre may have appeared due to other damage mechanisms like cell–cell debonding. Thus, the effects of physical changes on the failure of biocomposites are undeniable.
As the swelling of PLA shows low sensitivity to WA, biocomposite swelling is significantly caused by fibre swelling. PLA exposed to HS and F/T environment shows the physical deterioration because of changes occurring at +45°C or -18°C temperatures. Random shattering of PLA at high or negative temperature has been suggested by Karlsson and Ndazi [305] to be the reason of deterioration; this effect can be seen in Figure 6-7e-f.

<table>
<thead>
<tr>
<th>Side view of biocomposites after tensile tests</th>
<th>Tensile fracture mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Fibre breakage or fibre fracture and fibre pull out</td>
</tr>
<tr>
<td>b</td>
<td>Matrix cracking and fibre and matrix debonding</td>
</tr>
<tr>
<td>c</td>
<td>Fibre breakage, fibre pull out, and fiber and matrix debonding</td>
</tr>
<tr>
<td>d</td>
<td>Fibre breakage, and fibre and matrix debonding</td>
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<td>e</td>
<td>Fibre breakage, matrix cracking, and fibre and</td>
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<table>
<thead>
<tr>
<th>f</th>
<th>matrix debonding</th>
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</thead>
<tbody>
<tr>
<td>f</td>
<td>Fibre breakage, matrix cracking, fibre pull out, and fibre and matrix debonding</td>
</tr>
</tbody>
</table>

Figure 6-7 The fracture images from the side of the biocomposite after exposure to: a) as-manufactured (AM); b) water saturated (WS); c) water saturated and completely dried (WSD); d) humid saturated (HS); e) freeze/thaw (F/T) 10 cycles; and f) water saturated and freeze/thaw (WSF/T) 10 cycles and their fracture modes.

Figure 6-8 Mechanism for water damage: (a) expansion of a wet fibre, (b) wet composite after molecular relaxation processes, and (c) contraction of the fibre during drying (concept reproduced from [208]).

6.4 Discussion

This study lead to several key points on the moisture-related environmental behaviours of biocomposites, this section focuses on the effect of moisture, redrying and freeze and thaw.

6.4.1 Degradation due to the presence of moisture

Several publications report the effect of moisture on mechanical properties of green composites and the findings here agree [213, 215, 231, 303]. In particular, compared with other environments, wet environments show the most severe deterioration of mechanical properties of biocomposites (for both tensile and flexural properties) [214].
To understand the mechanisms involved in the degradation of the properties of green composites, much consideration has been given to how water interacts with the composite [31-33].

Two types of water are defined to exist in the WS biocomposites [7, 211]. First, free water is defined as water molecules which are relatively free to travel through the free volume, micro voids and pores, while bound water is defined as that dispersed within the polymer matrix or attached to the polar groups of the polymer [7, 211, 212]. Both free water and bound water may exist in moisture absorbed by NFRP biocomposites. It would be interesting, but outside the scope of this study, to use nuclear magnetic resonance spectroscopy and (micro-)computed tomography (magnetic resonance imaging (MRI)) to follow the interactions of the two forms of water during diffusion [306].

Moisture diffusion, and the consequent WA, in polymer composites is directed and controlled by various mechanisms:

i. diffusion of water molecules into the free volume between the polymer molecular chains [214] and consequent plasticisation of the matrix,

ii. diffusion of water molecules into the structure of fibres (resulting in hydrogen bonding with hydroxyl group of cellulose molecules) [215],

iii. movement of water molecules into voids and defects at the fibre/matrix interface as a result of capillary action [214, 215], and

iv. capillary flow into micro-cracks in the matrix after swelling of fibres [213].

The hydrophilic nature of FF in which many hydroxyl groups (-OH) form numerous hydrogen bonds between the macromolecules of the cellulose and polymer, cause poor interfacial bonding between FF and PLA, leading to mechanical properties deterioration [129, 303]. MC of the biocomposite, which increases by means of capillary transport of water in the FF, can negatively impact the FF/PLA interface and lead to delamination of the composites (see Figure 6-7). These effects can be identified after the tensile fracture of the biocomposite (see Figure 6-6).

To explain the role of fibres’ structure, amorphous hemicelluloses (plant cell wall material associated with cellulose) and lignin are largely responsible for WA in plant fibres [7, 60] because they have higher free volume than the crystalline cellulose and
hence facilitate easier water transport and access to hydrophilic groups. Since hemicelluloses constitute 16.7% of FF [15], this can result in greater WA and then swift bio-degradation in plant fibres [7, 60, 217].

The changes to the material due to moisture directly correspond to a decline in mechanical properties. Based on Figure 6-4 and Figure 6-5, tensile properties are less sensitive to HS condition than flexural properties. Compared with full immersion all degradation mechanisms that occur in wet environments also take place in HS samples but with lower intensity. This can be observed by comparing the cases of AM, WS and HS in Figure 6-4 and Figure 6-5. Mechanical properties of biocomposites are sensitive to a high temperature and it can accelerate the degradation process of biocomposites [273]. Dhakal et al. [214] examined the mechanical properties of hemp/unsaturated polyester composites in water at various temperatures. They concluded that MC at 100°C reaches to equilibrium very fast compared to the samples immersed at lower temperatures; and consequently the composites significantly degraded due to crack development in the composites and loss of matrix at high accelerated aging process. Hu et al. [234] also reported that the tensile strength of jute/PLA appeared to decrease (≈75%) after five days exposure at a hygrothermal environment, at 70°C.

The presence of moisture also leads to chemical degradation of the matrix and fibre of the biocomposite. Although the hydrolysis process is very slow at 45 °C for PLA, it can produce PLA degradation by breaking PLA molecular chains. The hydrolytic reaction (Eq. (8)) also occurs when \(-\text{CHCH}_3\text{COO}^\text{-}\) groups on PLA molecules react with \(\text{H}_2\text{O}\) and form low molecular weight biocomposites [168, 234]:

\[
-\text{CHCH}_3\text{COO}^\text{-} + \text{H}_2\text{O} \rightarrow -\text{CHCH}_3\text{OH} + \text{HOOC}^\text{-}
\]  

(8)

Based on Figure 6-4 and Figure 6-5, 25% and 24% reduction in tensile strength and flexural strength, respectively, occur after 60 days. These levels may be acceptable for users who are planning to use cheap and green composites for very short term applications in humid environments.
6.4.2 Redrying of wet biocomposites

It has been reported by Baley et al. [126] that drying of natural fibres prior to composite manufacturing is not beneficial to tensile properties of biocomposites since it causes fibre shear and fibre peeling damages. However, the circumstances are different here in that the composite has already been manufactured and the level of water saturation is high.

As shown by comparing WS and WSD environments in Figure 6-3, mechanical properties which are significantly influenced by an extremely wet environment, can be greatly restored by using an additional drying process. The practical implication is that if a biocomposite for short-term outdoor applications becomes wet, then simply allowing it to dry before reuse is a good strategy, especially when tensile properties/functions of the biocomposite are important.

6.4.3 Degradation mechanism in F/T environment

In the literature, the effect of F/T environment has been only studied regarding the unsustainable composites, carbon fibre (CF) or glass fibre (GF) reinforced polymer composites (e.g.[27, 307-309]). Belarbi et al. [307] reported insignificant effects of F/T condition on shear, axial and flexural properties of CF or GF reinforced polymer composites. However, the unsustainable composites become more brittle and fail catastrophically after the F/T cycling process [27, 308]. Cormier et al. [309] also provided a literature review on CF/epoxy and GF/epoxy composites with various constituents and processes used to manufacture composites, and concluded that F/T condition has a small negative effect on these composites.

In this study, the findings identified that F/T cycling has small negative impacts on mechanical properties of biocomposites. Tensile strength and flexural strength shows degradation as F/T cycling numbers increase, as samples are inclined to absorb moisture by which degradation happens. Biocomposite F/T cycling may produce internal stresses which cause micro-cracks, resulting in loss of tensile and flexural properties. In other words, moisture present in the fabrics prior to the manufacturing process, plus the moisture that was absorbed after every F/T cycle, suffered cycles of ice/water transformations, generating volume changes inside the materials microstructure, and thus internal stresses.
Biocomposites deteriorate significantly after WSF/T cycling. In this case, biocomposites contain substantial water in their microstructure which solidifies and melts in every F/T cycle. Therefore, these degradation mechanisms happen simultaneously with the ones caused by water immersion, leading to significant physical and chemical degradation, which are identifiable in both quantitative findings and image observations. In addition to similar damages from WS condition, WSF/T samples show significant physical and chemical degradation, which are identifiable in the results (cf. Figure 6-4 and Figure 6-5).

6.5 Conclusion

The sensitivity of properties of FF/PLA biocomposites to different environments was studied. Composites were exposed to the following conditions: water immersion, warm humid and F/T cycling environments. The mechanical performance (tensile and flexural properties), MC and physical changes (dimensional stability) of the composites during the exposure to the different environments were analyzed.

When FF/PLA composites are immersed in water, WA followed Fick’s law. Tensile and flexural modulus and strength decreased significantly due to the quantity of water absorbed by the composites, which led to the development of different degradation mechanisms, such as the weakening of the FF/PLA interface and plasticisation. However, the tensile strain value found for the saturated specimens almost doubled that of “as manufactured” specimens due to the plasticizing effect of water in FF/PLA biocomposites. Physical changes are relatively large, as the thickness of the samples increased considerably during the test.

After the saturation MC was reached in the immersion tests, some samples were completely dried to analyse the residual properties of the composites. The drying process proved to be effective in partially restoring the mechanical properties. However, the “as manufactured” properties were not reached, inferring that some permanent damage was caused after the immersion tests, which is most likely to be at the fibre-matrix interface. Nevertheless, it is advantageous to completely dry biocomposite prior to their structural application if they have high water content.
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When exposed to a warm humid environment, both WA and physical changes were much lower than for water immersion, leading to lesser reductions in mechanical properties. In addition, hydrolysis process can be involved in the PLA degradation, decreasing the properties of the matrix and degrading the interfacial bonding between FF and PLA by molar mass degradation.

Freeze and thaw cycling has small negative impacts on tensile and flexural properties owing to small WA and physical changes, causing internal stresses.

Freeze and thaw cycling of WS specimens shows further deterioration of properties in comparison with the WS only specimens. WSF/T cycling damages the material because of the negative synergy caused by water trapped in the microstructure and freeze/thaw cycles, which leads to the development of internal stresses.

Altogether, based on the measurements and analyses, direct contact with liquid water is the most deteriorating environment for biocomposites and therefore underwater applications of these materials are strongly discouraged. In such cases, a drying process can restore partially the mechanical performance of these materials. On the other hand, biocomposites can endure reliably in warm humid environments and in those that could create F/T cycles for short-term outdoor applications.
This final chapter presents a summary of the key outcomes of this research. The contributions and limitations of the research are detailed along with recommendations for future research directions. Section 7.1 restates the research objectives. Section 7.2 identifies the theoretical and practical contributions made by this study. The limitations of the research, and suggestions for future study in NFRP biocomposite degradation are presented in Section 7.3. Section 7.4 concludes the chapter and thesis discourse.

7.1 Research Objectives and Outcomes
The principle objective of this research was to understand the various characteristics in the degradation of flax natural fibre. PLA biopolymer and their composites due to the temperatures of the manufacturing process. More specifically, the study aimed to establish a good understanding of the chain-scission degradation model of the popular biopolymer PLA, considering the subsequent degradation and the changes in molar mass of the system; this understanding then led to a secondary objective to revise and the model to reduce mathematical complexity and time concerns. Next, the effect of transient temperature variations on the degradation process during the manufacturing process was studied and simulated. Moreover, a method was established to correlate the tensile strengths of flax/PLA biocomposites with degree of polymerization after exposure to high temperatures. Finally, the mechanical property performance of the flax/PLA biocomposites was investigated when exposed to moisture-related environments. To achieve the specified objectives, a number of research activities were carried out. A summary of these research activities and their associated outcomes are presented in Figure 1-1 and also summarized below.
7.1.1 Knowledge acquisition
To establish a robust framework for the research, existing literature including research publications, academic and industry reports were critically reviewed as presented in Chapter 2 and the introductory sections of Chapters 3 through to 6. The review focused predominantly on degradation of flax fibres and PLA biocomposites during and after manufacturing. Based on the identified limitations in using flax fibres and PLA at high temperatures, and using flax/PLA biocomposites in moisture-related environments, there was a need to carefully study the degradation mechanisms at each stage. The establishment of wider research objectives allowed for the formation of paper-specific objectives and research questions to address some of the gaps identified in this phase of the research. Four distinct phases emerged being, (i) constructing an optimum processing window for a biocomposite, (ii) simplifying and revising a complex model, (iii) estimating mechanical property degradation, and (iv) evaluating mechanical properties in moisture-related environments.

7.1.2 Constructing an optimum processing window for a biocomposite
Phase 2 of the research involved the collection of the necessary kinetic data and proposing new assumptions to define flax/PLA biocomposites degradation at various times and temperatures. In other words, a window of suitable temperatures and consolidation times for compression moulding of a flax/PLA biocomposite was mapped out using kinetic data and available models from the literature for thermal penetration, melt-fibre impregnation, pyrolysis and thermo-chemical degradation processes of both fibre and matrix. The processes were expressed using dimensionless progress variables, and then a convenient temperature/time map was constructed enabling manufacturers to have an overview of degradation processes during the manufacturing process. This made it possible to optimize the manufacturing time, ensuring that degradation in properties of the biocomposite is minimized.

The map derived for flax/PLA composite suggests that the most important processes are penetration of the melt into the yarn which defines a minimum consolidation time and thermo-chemical degradation of the natural fibres which defines a maximum consolidation time allowed to avoid major degradation of the biocomposite mechanical
strength. Consistent with the model, experimental data showed a considerable reduction in tensile strength for the composite for consolidation times greater than 45 min.

7.1.3 Simplifying and revising a complex model
Phase 3 primarily involved simplifying and revising a complex model of biopolymer degradation. In this phase, the model for thermo-chemical degradation of PLA proposed by previous scholars was significantly simplified by assuming that the total number of monomer units is invariant as reactions progress. To validate the simplified and revised model, the model was used to accurately simulate the experimental data of other studies and was successfully implemented without the need to recalculate the original activation energies or pre-exponentials.

Phase 3 also involved evaluating the effect of time dependent process temperature variation during manufacture of NFRP biocomposites. An empirical map was presented to identify the effect of temperature history on the degradation progress and effects on tensile strength. This phase followed by evaluating the effect of the heating and cooling rate on the degradation of NFRP biocomposites at three rates (slow, average and fast). Then, the progress variable (κ) changes of PLA and flax fibre, which result from the simulated heating and cooling rate, based on a processing temperature of 170 ºC, are also presented. PLA shows insignificant reactions to the rate changes while flax fibre shows notable additional degradation during the heat-up period for slow heating. In the case of PLA, two processes (degradation and recombination) are responsible for the degradation progress at high temperature during the thermal processing. For PLA, the final state of degradation (>150 min) is almost identical even though the slower heating/cooling case shows slightly lower values for κ during consolidation. Thus this research has demonstrated that the proposed model is a useful tool for predicting the degradation effect of any temperature history to which the composite is subjected during manufacture.
7.1.4 Estimating mechanical property degradation
The goal of this phase was introducing a link between the chemical degradation of NFRP biocomposite during thermal processing and their mechanical properties. The following processes were taken into account: (i) mechanical properties of the biocomposite can be calculated by estimating their relationship with the changes of degree of polymerization (DP) over the temperature and time. This relationship has separately been proposed for both matrix and fibre, (ii) the modulus of elasticity for both the flax fibre and for PLA may be assumed to be independent of the thermal processing, (iii) a linear relationship between strength and 1/DP, as proposed in the literature, was used to calculate the tensile strength of matrix and fibre, and for the first time used to predict the mechanical properties of NFRP biocomposites, (iv) to predict the tensile strength of NFRP biocomposite, the linear model was neither reliable nor practical for extended periods of time; subsequently a new exponential model was proposed which is realistic with just 10% uncertainty. Thus, the tensile strength of PLA and flax can be predicted as a function of their temperature history during processing using the proposed equations.

7.1.5 Evaluating mechanical property – environment relationships in moisture-related environments
In this phase, the sensitivity of properties of flax/PLA biocomposites to different moisture-related environments was studied. Composites were exposed to the following conditions: water immersion, warm humid, and ‘freeze and thaw’ cycling environments. The mechanical performance (tensile and flexural properties), Moisture content and physical changes (dimensional stability) of the composites during the exposure to the different environments were analyzed.

When the flax/PLA composites were immersed in water, water absorption sensibly followed Fick’s law. Tensile and flexural modulus and strength decreased significantly due to the quantity of water absorbed by the composites, which led to the development of different degradation mechanisms, such as the weakening of the flax/PLA interface and plasticisation. However, the tensile strain value of the saturated specimens was almost double that of “as manufactured” specimens due to the plasticizing effect of
water in flax/PLA biocomposites. Physical changes are relatively large, as the thickness of the samples increased considerably during the test.

After the saturation moisture content was reached in the immersion tests, some samples were completely dried to analyse the residual properties of the composites. The drying process proved to be effective in partially restoring the mechanical properties. However, the “as manufactured” properties were not reached, inferring that some permanent damage was caused after the immersion tests, which was attributed to degradation of the fibre-matrix interface. Nevertheless, the results suggest that it is advantageous to completely dry biocomposite prior to use in structural applications if the fibres have high (saturated) water content.

When exposed to a warm humid environment, both water absorption and physical changes were much lower than for water immersion, leading to less significant reductions in mechanical properties. In addition, hydrolysis is involved in the PLA degradation, decreasing the properties of the matrix and degrading the interfacial bonding between flax and PLA by molar mass degradation.

Freeze-and-thaw cycling has small negative impacts on tensile and flexural properties owing to low water absorption and small physical changes, causing internal stresses.

Freeze and thaw cycling of water-saturated specimens shows further deterioration of properties in comparison with the water saturated only specimens. Water saturated and freeze/thaw cycling damages the material because of the detrimental synergy caused by water trapped in the microstructure and freeze/thaw cycles, which leads to the development of internal stresses.

Altogether, based on the measurements and analysis, direct contact with liquid water is the most deteriorating environment for biocomposites and therefore underwater applications of these materials are strongly discouraged. In such cases, a drying process can restore partially the mechanical performance of these materials. On the other hand, biocomposites can survive reliably in warm humid environments and in those that could create freeze-and-thaw cycles for short-term outdoor applications.
7.2 Study contributions

Over the last decade, significant outcomes achieved from intensive studies have allowed sustainable flax/PLA biocomposites to occupy a partial place in the automotive, sport and furniture markets. Low cost, along with relatively acceptable mechanical performance, can be important benefits of flax/PLA biocomposites. However, there are still some constraints in exposing flax/PLA biocomposites to high temperatures, and in their extended application in outdoor environments. Despite numerous efforts, no research has thoroughly focused on the mechanism of the degradation problem and yet more studies are required to advance the existing body of knowledge and generate practical research outcomes that benefit the manufacture of flax/PLA biocomposites or their potential applications. With this demand in mind, this research study was conducted with the view to provide fundamental and necessary information regarding the degradation of flax/PLA biocomposites during and after the manufacturing process. This information can be used for the development of NFRP biocomposites manufacture and their potential future longevity in environments. Contributions to the existing body of knowledge for the science of NFRP biocomposites are outlined in the following paragraphs.

Previous research in the field of biocomposite performance has provided a great deal of background knowledge which can be used in research study into degradation of flax/PLA biocomposites during and after manufacturing. However, prior to this thesis, several specific knowledge gaps existed in this field, as follows:

- in regard to the degradation rate during a compression moulding process, no methodology existed to construct a map or window for setting practical upper and lower limits to consolidation temperature and processing time;
- models to determine the chain-scission degradation of PLA biopolymer are very complex and difficult to use;
- no attempt to calculate the effect of transient temperature on the degradation of NFRP biocomposites was identified;
- no particular article existed explaining or describing the degradation rate of NFRP biocomposites at high temperatures in association with molar mass changes or degree of polymerisation;
Chapter 7: Conclusion and Contributions

- no complete study or discussion existed on the performance of flax/PLA biocomposites in moisture-related environments such as wet, freezing and humid conditions.

To fill and respond to these gaps, the study has been performed in four key steps, outlined below, which have made a significant contribution to the discipline of NFRP biocomposites.

- The key considerations were highlighted and a quantitative guide was proposed for moulding time limits based on the available literature, along with a practical study of a representative flax/PLA biocomposite (Chapter 3).
- A well-established model for simulation of the chain-scission process of polylactic acid (PLA) during thermal processing was simplified and revised. The revised model is in excellent agreement with the more complex model and experimental results for PLA degradation reported in the literature. This simplified model has the potential to be applied to other thermoplastics (Chapter 4).
- In addition, it has been demonstrated that the model in Chapter 4 is a useful tool for predicting the degradation effect of any temperature history experienced by the composite during manufacture. Moreover, kinetic data were used to calculate degradation progress parameters, defining experiment process maps for identifying the effect of the temperature history on the degradation progress, and effects on the tensile strength. The proposed model can also express the tensile strength changes in comparison with other degradation parameters (Chapter 4).
- Molar mass degradation or reduction in degree of polymerisation was taken into account as a critical indicator of the extent of thermo-chemical degradation making it possible to determine the rate of deterioration of mechanical properties for both matrix and fibre. Data produced from the proposed models can be used to predict or optimise the mechanical properties of biocomposites. For the first time, this study has brought the thermochemical degradation concepts together with the models which have been used for composites, to predict the tensile strength of NFRP biocomposites after thermal processing (Chapter 5).
Chapter 7: Conclusion and Contributions

- The sensitivity of the compression moulded flax/PLA biocomposite, was examined in moisture-related environments such as wet, humid, and freeze and thaw. Then, the tensile and flexural properties of the biocomposite were examined, resulting in a comprehensive set of experimental data and the related kinetic data. The findings were also compared with those of previous works which had been produced for various applications. Then, characteristics of water-saturated and dried samples, freeze/thaw samples, water-saturated and freeze/thaw samples of flax/PLA biocomposites were carefully discussed noting that they are rarely discussed in the literature. Finally, a valuable discussion was provided for practitioners who are considering using natural fibre reinforced bio-based matrix products (Chapter 6).

7.3 Study Limitations and Future Research Directions
The present study used a variety of kinetic data to analyse the complex degradation rate of flax/PLA biocomposites, which are in good agreement with practical results that can be applied to the field of NFRP biocomposites. Of course, like any research activity, there exist some limitations which are summarised as follows:

- the applied values were used to identify the pyrolysis degradation rate of the existing categories presented in Chapter 3 which was achieved through the available literature (because TGA was not available in our university). However, for more accurate identification of kinetic data, further researchers may collect their own kinetic data;

- the simplified and revised model was validated using the experimental data of two articles which evaluated the degradation rate of PLA biopolymer; the simplified and revised model can be used to evaluate the degradation rate of other biopolymers, especially poly(caprolactone) and the poly(hydroxyalkanoates);

- the simplified and revised model was validated for lignocellulosic fibres…, and might be extended to other bast fibres, e.g. hemp and jute.
Chapter 7: Conclusion and Contributions

- to improve the degradation models, future chemistry discipline research can be of great assistance by determining the changes in the value of functional groups (e.g., –ester- bonding), in order to determine whether the degradation rate would be close to the present models or not. A statistical model may be useful to estimate the extent of complex separation of -ester- bonding;

- to develop the knowledge of the degradation of NFRP biocomposites, constructing a degradation window or map, which shows the effect of all the important factors on the degradation of NFRP biocomposites in moisture-related environments is needed. This, along with the use of available models can be beneficial for the illustration of the significance of each factor on the degradation process;

- to develop the existing knowledge in this field, a link between mechanical properties changes and molar mass changes (with the use of size exclusion chromatography) can be valuable for those who want to study the factors affecting the durability of NFRP biocomposites or for those who want to undertake “life cycle assessment” procedures, which will eventually help to increase the effectiveness and life time of NFRP biocomposites;

- to estimate the mechanical properties of NFRP biocomposites, the calculation of the effect of transient factors on the durability of NFRP biocomposites in moisture related environments can be useful for highlighting the significance of the unknown factors on the degradation mechanism of NFRP biocomposites;

- mixing PLA with the other less biocompatible materials (e.g., PVA) may limit the sensitivity of NFRP biocomposites to degradation mechanisms and might be more practical and may increase the potential outdoor applications of NF reinforced polymer composites, while the composites somehow still maintain some sustainable or biodegradable characteristics;

- since direct contact of water is a significant factor for the degradation of NFRP biocomposites in moisture-related environments, the use of contact angle studies can give additional information to unlock or reduce the problem of the fast
Chapter 7: Conclusion and Contributions

degradation rate of NFRP biocomposites. A new frame of research can be defined by focusing on this subject;

- the most important factor, however, is that the research on the degradation of NFRP biocomposites needs to be broadened. “Everyone in the composites industry needs to get in the game,” for the improvement of the quality of the manufactured NFRP biocomposites, as much as they can. The use of sustainable or green composites is significant for the public and it is not emotional anymore. Scholars should focus on more fundamental research approaches for NFRP biocomposites to compete with traditional/unsustainable materials. Eventually, our industry needs to show the benefits of using green composites with the help of researchers.

7.4 Closure

A comprehensive study on the degradation of flax/PLA biocomposites was carried out to develop and improve knowledge in the field of sustainable NFRP biocomposites. More specifically, the study initially constructed a process window for degradation of a flax/PLA biocomposite, during manufacture and service, with the available kinetic data on thermal penetration, melt infusion, thermal degradation, and chemical degradation models. The work then recognised a need to simplify and revise the existing complex model of biopolymer degradation. After succeeding at this stage, the effects of transient temperatures on the degradation of a biocomposite were evaluated. By recognising that the degree of polymerization is correspondent to degradation and (re) combination of both fibre and matrix, a methodology along with a new model was proposed and validated in order to estimate the tensile strength of a biocomposite. The study was completed with a valuable discussion on the degradation of NFRP biocomposites in moisture related environments, for which several sets of experimental tests were performed.

In the first two chapters of the thesis, an introduction and principal literature review were presented. These chapters highlighted the content and necessity of the research. Then, the main part of the thesis was presented, being predominantly composed of peer-reviewed papers related to the key research objectives contained within the four distinct
phases of the project namely, constructing an optimum processing window for a biocomposite, simplifying and revising a complex model, estimating mechanical property degradation, evaluating mechanical properties in moisture-related environments. Chapters 3 to 6 are the reformatted published journal manuscripts that include their own background, literature review, research method, data analysis, results and discussion. Finally, this thesis concluded with a summary of the research conclusion and contributions as well as proposed recommendations for future research in the field of NFRP biocomposites.
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Reference


Appendix A

The below statistical model is used to calculate the concentration of a polymer of length \( n \), which is based both degradation and recombination reactions which occur during the thermal processing. The final result is the same as that derived by Wachsen et al (1997). The following steps show the deriving approach:

The degradation process is:

\[
\begin{align*}
\text{P}_2 & \rightarrow \text{P}_1 + \text{P}_1 & \frac{d[\text{P}_1]}{dt} & = 2k_d[\text{P}_2] - k_d[\text{P}_2] - k_d[\text{P}_3] - k_d[\text{P}_4] - k_d[\text{P}_5] \\
\text{P}_3 & \rightarrow \text{P}_1 + \text{P}_2 & \frac{d[\text{P}_2]}{dt} & = k_d[\text{P}_3] - k_d[\text{P}_3] - k_d[\text{P}_4] - k_d[\text{P}_5] \\
\text{P}_3 & \rightarrow \text{P}_2 + \text{P}_1 & \frac{d[\text{P}_3]}{dt} & = k_d[\text{P}_3] - k_d[\text{P}_3] - k_d[\text{P}_4] - k_d[\text{P}_5] \\
\text{P}_4 & \rightarrow \text{P}_3 + \text{P}_1 & \frac{d[\text{P}_4]}{dt} & = k_d[\text{P}_4] - k_d[\text{P}_4] - k_d[\text{P}_5] \\
\text{P}_4 & \rightarrow \text{P}_2 + \text{P}_3 & \frac{d[\text{P}_5]}{dt} & = k_d[\text{P}_4] - k_d[\text{P}_4] - k_d[\text{P}_5] \\
\text{P}_5 & \rightarrow \text{P}_1 + \text{P}_4 & \frac{d[\text{P}_1]}{dt} & = k_d[\text{P}_5] - k_d[\text{P}_5] \\
\text{P}_5 & \rightarrow \text{P}_3 + \text{P}_2 & \frac{d[\text{P}_2]}{dt} & = k_d[\text{P}_5] - k_d[\text{P}_5] \\
\text{P}_5 & \rightarrow \text{P}_2 + \text{P}_3 & \frac{d[\text{P}_3]}{dt} & = k_d[\text{P}_5] - k_d[\text{P}_5]
\end{align*}
\]

Then, the following equations in order to find the degradation rate can be:

\[
\begin{align*}
\frac{d[\text{P}_1]}{dt} & = 2k_d[\text{P}_2] + 2k_d[\text{P}_3] + 2k_d[\text{P}_4] + \ldots \\
\frac{d[\text{P}_2]}{dt} & = -k_d[\text{P}_2] + 2k_d[\text{P}_3] + 2k_d[\text{P}_4] + 2k_d[\text{P}_5] + \ldots \\
\frac{d[\text{P}_3]}{dt} & = -2k_d[\text{P}_3] + 2k_d[\text{P}_4] + 2k_d[\text{P}_5] + \ldots \\
\frac{d[\text{P}_4]}{dt} & = -3k_d[\text{P}_4] + 2k_d[\text{P}_5] + \ldots
\end{align*}
\]

Next, generally the degradation rate is:
\[
\frac{d[P_i]}{dt} = -(n-1)k_d[P_n] + 2k_d \sum_{i=n+1}^{\infty} [P_i]
\]

And, the recombination process is:

<table>
<thead>
<tr>
<th>(P_i + P_j)</th>
<th>(\longrightarrow)</th>
<th>(P_k)</th>
<th>(\frac{d[P_i]}{dt})</th>
<th>(\frac{d[P_j]}{dt})</th>
<th>(\frac{d[P_k]}{dt})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_1 + P_1)</td>
<td>(\longrightarrow)</td>
<td>(P_2)</td>
<td>(-2k_c[P_1]^2)</td>
<td>(k_c[P_1]^2)</td>
<td>(-)</td>
</tr>
<tr>
<td>(P_1 + P_2)</td>
<td>(\longrightarrow)</td>
<td>(P_3)</td>
<td>(-k_c[P_1][P_2])</td>
<td>(-k_c[P_1][P_2])</td>
<td>(k_c[P_1][P_2])</td>
</tr>
<tr>
<td>(P_1 + P_3)</td>
<td>(\longrightarrow)</td>
<td>(P_4)</td>
<td>(-k_c[P_1][P_3])</td>
<td>(-)</td>
<td>(-k_c[P_1][P_3])</td>
</tr>
<tr>
<td>(P_2 + P_2)</td>
<td>(\longrightarrow)</td>
<td>(P_4)</td>
<td>(-)</td>
<td>(-2k_c[P_2]^2)</td>
<td>(-)</td>
</tr>
<tr>
<td>(P_1 + P_4)</td>
<td>(\longrightarrow)</td>
<td>(P_5)</td>
<td>(-k_c[P_1][P_4])</td>
<td>(-)</td>
<td>(-)</td>
</tr>
<tr>
<td>(P_2 + P_3)</td>
<td>(\longrightarrow)</td>
<td>(P_3)</td>
<td>(-)</td>
<td>(-k_c[P_2][P_3])</td>
<td>(-k_c[P_2][P_2])</td>
</tr>
</tbody>
</table>

Then, the following equations in order to find the recombination rate can be:

\[
\frac{d[P_1]}{dt} = -2k_c[P_1]^2 - k_c[P_1][P_2] - k_c[P_1][P_3] - .......
\]

\[
\frac{d[P_2]}{dt} = k_c[P_1][P_2] - k_c[P_2][P_1] - 2k_c[P_2][P_2] - k_c[P_2][P_3] - .......
\]

\[
\frac{d[P_3]}{dt} = k_c[P_1][P_3] - k_c[P_2][P_2] - k_c[P_3][P_1] - 2k_c[P_3][P_3] - .......
\]

\[
\frac{d[P_4]}{dt} = k_c[P_1][P_4] - k_c[P_2][P_3] - k_c[P_4][P_1] - 2k_c[P_4][P_2] - .......
\]

Then, generally the recombination rate is:

\[
\frac{d[P_n]}{dt} = \frac{1}{2} k_c \sum_{i=n+1}^{\infty} [P_i] - k_c[P_n] \sum_{i=n+1}^{\infty} [P_i]
\]

Therefore, the total degradation rate is the sum of degradation and recombination rate as:

\[
\frac{d[P_n]}{dt} = -(n-1)k_d[P_n] + 2k_d \sum_{i=n+1}^{\infty} [P_i] + \frac{1}{2} k_c \sum_{i=n+1}^{\infty} [P_i] - k_c[P_n] \sum_{i=n+1}^{\infty} [P_i]
\]
which was first presented by Wachsen et al (1997) for PLA degradation.

Appendix A-2

As explained in the chapter 3, the differential equations can be solved using Runge Kutta fourth order as the following steps.

The fourth-order Runge Kutta approach to solve the problem is introducing parameters as:

$$\frac{dy}{dt} = f(t, y) \quad \text{Initial conditions: } y_0 \text{ given (} t=0 \text{)}$$

let say that:

$\Delta t = \text{numerical time step}$

$y_j = \text{value of } y \text{ at time step number } j$

$t_j = \text{value of time at time step number}$

Then,

$$A_j = \Delta t \times f(t_j, y_j)$$

$$B_j = \Delta t \times f(t_j + \frac{1}{2} \Delta t, y_j + \frac{1}{2} A_j)$$

$$C_j = \Delta t \times f(t_j + \frac{1}{2} \Delta t, y_j + \frac{1}{2} B_j)$$

$$D_j = \Delta t \times f(t_j + \Delta t, y_j + C_j)$$

$$D_j = \Delta t \times f(t_j + \Delta t, y_j + C_j)$$

$$y_{j+1} = y_j + \frac{1}{6}(A_j + 2B_j + 2C_j + D_j)$$
For our problem, start with an initial distribution (e.g. \([P_1]_0=0\), \([P_2]_0=0\), \([P_3]_0=0\), \ldots, \([P_{n-\text{start}}]_0=1\), \([P_{n-\text{start}+1}]_0=0\), \([P_N]=0\)).

From Eq. \(A_j = \Delta t \times f(t_j, y_j)\):

\[
\frac{d[P_n]}{dt} = f_n(t, [P_1], [P_2], [P_3], \ldots, [P_n], \ldots, [P_N])
\]

After dropping brackets for convenience:

\[
A_{j,n} = \Delta t \times f_n(t, P_1, P_2, P_3, \ldots, P_n, \ldots, P_N)(n = 1, N)
\]

\[
A_{j+n} = \Delta t \times f_n(t + \frac{\Delta t}{2}, P_1 + \frac{A_{j,1}}{2}, P_2 + \frac{B_{j,1}}{2}, \ldots, P_n + \frac{A_{j,n}}{2}, \ldots, P_N + \frac{A_{j,N}}{2})
\]

\[
B_{j+n} = \Delta t \times f_n(t + \frac{\Delta t}{2}, P_1 + \frac{A_{j,1}}{2}, P_2 + \frac{A_{j,1}}{2}, \ldots, P_n + \frac{A_{j,n}}{2}, \ldots, P_N + \frac{A_{j,N}}{2})
\]

\[
C_{j+n} = \Delta t \times f_n(t + \frac{\Delta t}{2}, P_1 + \frac{B_{j,1}}{2}, P_2 + \frac{B_{j,1}}{2}, \ldots, P_n + \frac{B_{j,n}}{2}, \ldots, P_N + \frac{B_{j,N}}{2})
\]

\[
D_{j+n} = \Delta t \times f_n(t + \Delta t, P_1 + C_{j,1}, P_2 + C_{j,2}, \ldots, P_n + C_{j,n}, \ldots, P_N + C_{j,N})
\]

\[
[P_n]_{j+1} = [P_n]_j + \frac{1}{6_n} \left( A_{j,n} + 2B_{j,n} + 2C_{j,n} + D_{j,n} \right)
\]
Appendix B

Experimental Data of the 16 tested samples for flax/PLA biocomposite used in Chapter 3 using flax fibre set #1.

Tensile modulus (GPa) (ranked ascending):

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>15 min</th>
<th>30 min</th>
<th>45 min</th>
<th>60 min</th>
<th>120 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.8</td>
<td>20.2</td>
<td>15.0</td>
<td>19.1</td>
<td>15.1</td>
</tr>
<tr>
<td>2</td>
<td>19.0</td>
<td>21.4</td>
<td>23.1</td>
<td>20.0</td>
<td>15.6</td>
</tr>
<tr>
<td>3</td>
<td>19.1</td>
<td>21.4</td>
<td>25.3</td>
<td>20.2</td>
<td>16.2</td>
</tr>
<tr>
<td>4</td>
<td>19.1</td>
<td>21.6</td>
<td>25.5</td>
<td>20.3</td>
<td>17.4</td>
</tr>
<tr>
<td>5</td>
<td>19.3</td>
<td>21.9</td>
<td>25.8</td>
<td>20.3</td>
<td>18.8</td>
</tr>
<tr>
<td>6</td>
<td>19.7</td>
<td>22.4</td>
<td>27.4</td>
<td>20.9</td>
<td>19.3</td>
</tr>
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<td>7</td>
<td>20.0</td>
<td>22.6</td>
<td>27.7</td>
<td>22.0</td>
<td>19.3</td>
</tr>
<tr>
<td>8</td>
<td>20.6</td>
<td>22.7</td>
<td>27.7</td>
<td>22.3</td>
<td>19.4</td>
</tr>
<tr>
<td>9</td>
<td>21.0</td>
<td>22.8</td>
<td>28.0</td>
<td>22.4</td>
<td>20.7</td>
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<tr>
<td>10</td>
<td>21.2</td>
<td>23.2</td>
<td>28.1</td>
<td>22.6</td>
<td>20.9</td>
</tr>
<tr>
<td>11</td>
<td>21.3</td>
<td>23.3</td>
<td>28.2</td>
<td>22.2</td>
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</tr>
<tr>
<td>12</td>
<td>21.4</td>
<td>23.2</td>
<td>28.3</td>
<td>23.2</td>
<td>22.5</td>
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<td>24.5</td>
<td>29.3</td>
<td>23.2</td>
<td>22.5</td>
</tr>
<tr>
<td>15</td>
<td>22.8</td>
<td>25.6</td>
<td>30.1</td>
<td>23.8</td>
<td>23.8</td>
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Appendix

Tensile Strength (MPa) (ranked ascending):

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### Appendix

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Appendix C

The following steps were taken to derive the equation 11 presented in chapter 4:

\[
\frac{d\lambda_0}{dt} = k_d (\lambda_1 - \lambda_0) - \frac{k_c \lambda_0^2}{2}
\]

\[
\lambda_{0-initial} = \rho / M_{n-start}
\]

\[
k_d = A_d \exp(-E_{ad} / RT)
\]

\[
k_c = A_c \exp(-E_{ac} / RT)
\]

For the isothermal case, \( T \) does not change with \( t \) and therefore \( k_d \) and \( k_c \) are constants. Hence it is possible to separate the variables:

\[
\int \frac{d\lambda_0}{k_d \lambda_1 - k_d \lambda_0 - \frac{k_c \lambda_0^2}{2}} = \int dt
\]

Then, considering the following form of parameters as:

\[
a = -k_c / 2, \quad b = -k_d, \quad \text{and} \quad c = k_d \lambda_1
\]

\[
\int \frac{1}{ax^2 + bx + c} dx = \frac{2}{\sqrt{4ac - b^2}} \tan^{-1} \left( \frac{2ax + b}{\sqrt{4ac - b^2}} \right)
\]

results in:

\[
\frac{2}{\sqrt{4 \times \frac{-k_c}{2} \times k_d \lambda_1 - k_d^2}} \tan^{-1} \left( \frac{2 \times \frac{-k_c}{2} \times \lambda_0 - k_d}{\sqrt{4 \times \frac{-k_c}{2} \times k_d \lambda_1 - k_d^2}} \right) = t + C
\]
\[
\frac{2}{\sqrt{-2k_c k_d \lambda_1 - k_d^2}} \tan^{-1} \left( \frac{-k_c \lambda_0 - k_d}{\sqrt{-2k_c k_d \lambda_1 - k_d^2}} \right) = t + C
\]

\[
- k_c \lambda_0 - k_d = \frac{\sqrt{-2k_c k_d \lambda_1 - k_d^2}}{k_c} \tan \left( (t + C) \frac{\sqrt{-2k_c k_d \lambda_1 - k_d^2}}{2} \right)
\]

\[
\lambda_0 = -\frac{k_d}{k_c} \frac{\sqrt{-2k_c k_d \lambda_1 - k_d^2}}{k_c} \tan \left( (t + C) \frac{\sqrt{-2k_c k_d \lambda_1 - k_d^2}}{2} \right)
\]

\[
\lambda_0 = -\frac{k_d}{k_c} + i \frac{\sqrt{2k_c k_d \lambda_1 + k_d^2}}{k_c} \tan \left( i (t + C) \frac{\sqrt{2k_c k_d \lambda_1 + k_d^2}}{2} \right)
\]

\[
\lambda_0 = -\frac{k_d}{k_c} + \frac{\sqrt{2k_c k_d \lambda_1 + k_d^2}}{k_c} \tanh \left( (t + C) \frac{\sqrt{2k_c k_d \lambda_1 + k_d^2}}{2} \right)
\]

When \( t = 0 \) and \( \lambda_0 = \lambda_{\text{start}} \)

\[
\lambda_{\text{start}} = -\frac{k_d}{k_c} + \frac{\sqrt{2k_c k_d \lambda_1 + k_d^2}}{k_c} \tanh \left( C \frac{\sqrt{2k_c k_d \lambda_1 + k_d^2}}{2} \right)
\]

\[
(\lambda_{\text{start}} + \frac{k_d}{k_c}) \times \frac{k_c}{\sqrt{2k_c k_d \lambda_1 + k_d^2}} = \tanh \left( C \frac{\sqrt{2k_c k_d \lambda_1 + k_d^2}}{2} \right)
\]

\[
C = \frac{2}{\sqrt{2k_c k_d \lambda_1 + k_d^2}} \tanh^{-1} \left( \left( \lambda_{\text{initial}} + \frac{k_d}{k_c} \right) \frac{k_c}{\sqrt{2k_c k_d \lambda_1 + k_d^2}} \right)
\]
Experimental Data of the 16 tested samples for flax/PLA biocomposite used in Chapter 5 3 using flax fibre set #2.

Tensile modulus (GPa) (ranked ascending):

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## Appendix

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Appendix E

Experimental Data of the 5 tested samples for flax/PLA biocomposite used in Chapter 6.

Tensile modulus (GPa) (ranked ascending):

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Experimental steps design: 1) fabric and PLA cutting, 2) stacking sequence, 3) compression moulding, 4) fabricated bio-composite plate, 5) cutting sample using a laser cutter, 6) Tensile test, 7) failure mode imaging, 8) data analysis and discussion.

Fig. F. 1. The experimental procedure of flax/PLA biocomposite manufacturing
I, John Summerscales CEng, CEnv, CSci, Professor of Composites Engineering at the University of Plymouth in the United Kingdom hereby confirm, in lieu of signatures on the appropriate pages of the Hossein Mohammad Khanlou doctoral thesis entitled Degradation of flax PLA biocomposites during and after manufacture, that the various Statement(s) of contribution to co-authored published paper(s) are a true and correct record.

Signed on 12 January 2018 by

John Summerscales CEng, CEnv, CSci,
Professor of Composites Engineering,
School of Engineering,
Faculty of Science and Engineering,
University of Plymouth, Plymouth PL4 8AA, United Kingdom.