PREPARATION AND CHARACTERISATION OF POLYMERIC BIOCOMPOSITES USING PLANT-BASED MATERIALS

WONG PING KEONG

MASTER OF SCIENCE

FACULTY OF SCIENCE
UNIVERSITI TUNKU ABDUL RAHMAN
SEPTEMBER 2011

PREPARATION AND CHARACTERISATION OF POLYMERIC BIOCOMPOSITES USING PLANT-BASED MATERIALS

By

WONG PING KEONG

A thesis submitted to the Department of Chemical Science,
Faculty of Science,
University Tunku Abdul Rahman,
in partial fulfillment of the requirements for the degree of
Master of Science
September 2011

ABSTRACT

PREPARATION AND CHARACTERISATION OF POLYMERIC BIOCOMPOSITES USING PLANT-BASED MATERIALS

WONG PING KEONG

Hybrid polymer (HP) was synthesised by graft copolymerisation of acrylamide and butyl acrylate onto sodium alginate using redox initiator system of potassium persulfate and sodium formaldehyde sulfoxylate in the presence of *N*,*N*-methylenebisacrylamide crosslinking agent. The incorporation of bamboo leaves fibre as fibrous filler into HP formed hybrid polymer-fibre composite (HPFC). Hybrid polymer-$CaCO_3$ composite (HPCC) was prepared with $CaCO_3$ as crosslinking agent and particulate filler.

The effect of various grafting conditions such as monomer-sodium alginate ratio, reaction time, reaction temperature, drying temperature, stirring speed, and type and amount of crosslinker on mechanical properties of HP and its composites such as tensile strength, Young's modulus and elongation at break were investigated. Other variables such as different addition sequence of water (solvent) and sodium alginate, amount, size and sequence of fibre incorporation, pH and amount of Ca^{2+} and glycerol were also studied. HPFC has lower tensile strength, Young's modulus and elongation at break than HP and HPCC. The optimum preparation conditions for maximum tensile strength of HPCC (38 MPa) were obtained with the following: monomer to sodium alginate ratio of 1: 0.24, addition of sodium alginate into water during gelatinisation process, 5 wt% of calcium carbonate, pH 8, reaction and drying temperature of 50 ^{o}C and stirring speed of polymerisation process of 1000 rpm.

The solubility of HP and HPCC in various solvents, namely water, acetonitrile, dimethylformamide, chloroform and toluene was analysed. Both HP and HPCC disintegrated in water but have very low swelling and solubility in other solvents. Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) were used to characterise HP and its composites. The FTIR spectra obtained indicate that monomers were grafted onto sodium alginate in the presence of crosslinker. According to the TGA results, HPCC showed better thermal stability compared to HP and HPFC.

ACKNOWLEDGEMENT

This thesis would not have been possible without the help and guidance of many whom in one way or another contributed their valuable assistance in the preparation and completion of this study. It is a pleasure to convey my gratitude to them all in my humble acknowledgment.

First of all, I would like to express my utmost gratitude to my supervisor, Dr. Chee Swee Yong for her advice, supervision and guidance from the very early stage of this research as well as giving me extraordinary experiences through out the work. Her patient and effort in explaining the concept of the research and correcting my writing is very much appreciated.

I gratefully acknowledge the Malaysian government for funding the research project through ScienceFund under the Ministry of Science, Technology and Innovation and UTAR for awarding me the Research Scholarship Scheme under the UTAR Research Fund that enable me to carry out my research smoothly.

I am indebted to many UTAR laboratory officers for giving me their technical assistance during my research work. Many thanks to Mr. Jason Chong Zhe Xin, Mr. Ooh Keng Fei from Faculty of Science and Puan Rosmawati binti Ariffin from Faculty of Engineering and Science for aiding me in running various equipment to analyse my samples. Besides that, I also want to acknowledge my fellow postgraduates especially Ms. Phang Ying Ning for sharing their valuable information with me regarding the project.

Lastly, I would like to extend my gratitude to my family for always supporting me and encouraging me with their best wishes. My girlfriend, Ms. Chan Sze Mun was always there cheering me up and stood by me through the good times and bad. I would also like to express my apology that I could not mention personally one by one.

FACULTY OF SCIENCE

UNIVERSITI TUNKU ABDUL RAHMAN

Date: _____________

SUBMISSION OF THESIS

It is hereby certified that Wong Ping Keong (ID No: 09UEM02132) has completed this thesis entitled **"PREPARATION AND CHARACTERISATION OF POLYMERIC BIOCOMPOSITES USING PLANT-BASED MATERIALS"** under supervision of Dr. Chee Swee Yong from the Department of Chemical Science, Faculty of Science.

I understand that the University will upload softcopy of my thesis in pdf format into UTAR Institutional Repository, which may be made accessible to UTAR community and public

Yours truly,

____

(WONG PING KEONG)

APPROVAL SHEET

This thesis entitled “**PREPARATION AND CHARACTERISATION OF POLYMERIC BIOCOMPOSITES USING PLANT-BASED MATERIALS”** was prepared by **WONG PING KEONG** and submitted as partial fulfilment of the requirements for the degree of Master of Science at Universiti Tunku Abdul Rahman.

Approved by:

Supervisor

Date:……………………

(Dr. Chee Swee Yong)
Assistant Professor
Department of Chemical Science
Faculty of Science
Universiti Tunku Abdul Rahman

DECLARATION

I WONG PING KEONG hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTAR or other institutions.

(WONG PING KEONG)

Date

TABLE OF CONTENTS

Page

CHAPTER

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
BR	Butadiene rubber
D	Dextrorotation
FTIR	Fourier transform infrared
G	Guluronic
HP	Hybrid polymer
HPCC	Hybrid polymer-$CaCO_3$ composite
HPFC	Hybrid polymer-fibre composite
ISO	International Organization for Standardization
kN	Kilo Newton
L	Levorotation
MAS	Magnesium aluminum silicate
M	Mannuronic
MPa	Megapascal
N-MBA	*N*,*N*-methylenebisacrylamide
PCL	Polycaprolactone
PE	Polyethylene
PET	Poly(ethylene terephthalate)
PGMA	Poly(glycidyl methacrylate)
PHB	Polyhydroxybutyrate
PLA	Polylactic acid
PP	Polypropylene

PVC	Polyvinyl chloride
SEM	Scanning electron microscopy
SFS	Sodium formaldehyde sulfoxylate
SPI	Soy protein isolate
TGA	Thermo gravimetric analysis
TPS	Thermoplastic starch
WVP	Water vapour permeability

CHAPTER 1

INTRODUCTION

1.1 Conventional Plastics

Plastics, with spectacular growth in both application and adaptation, are one of the most engineered (Agamuthu and Faizura, 2005) man made long chain polymeric materials (Shah et al., 2008). Polyethylene (PE), including low density, high density and linear low density, polypropylene (PP), polystyrene, poly(vinyl chloride) (PVC), polyurethane, poly(ethylene terephthalate) (PET), poly(butylene terephthalate) and nylons are the most widely used plastics for packaging purposes. Every year, approximately 140 million tons of various petroleum-based synthetic polymers are produced worldwide (Shah et al., 2008). Most resins made from petroleum are non-biodegradable and non-recyclable in the composite form (Huang and Netravali, 2009; Zhang et al., 2005) as plastic materials were designed to resist microbial attack that cause degradation (Mohee et al., 2008; Shah et al., 2008). Plastic waste is normally disposed off through recycling, land filling and incineration (Shah et al., 2008). Landfills are the dominant disposal sites for waste plastics (Kim, 2003) and most of plastics end up overburdening on landfill as their degradation requires a long time (Xu et al., 2005).

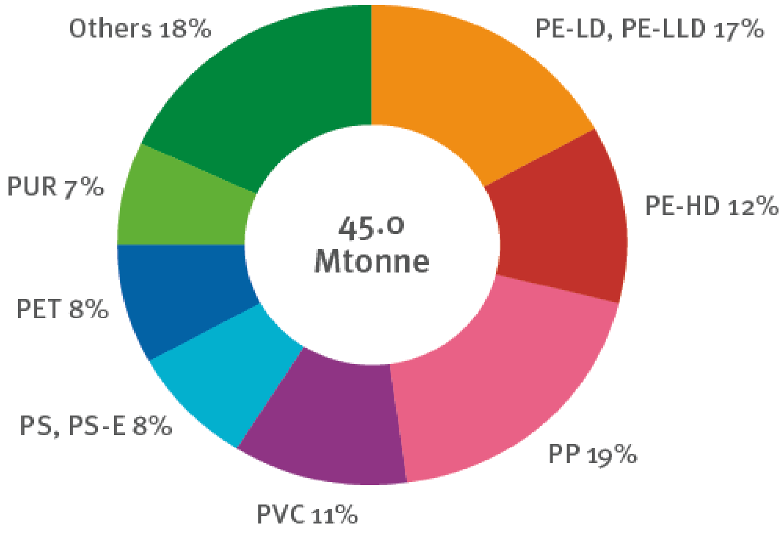


Figure 1.1: Europe Plastics Demand by Resin Types 2009 (The Plastics Portal, 2010)

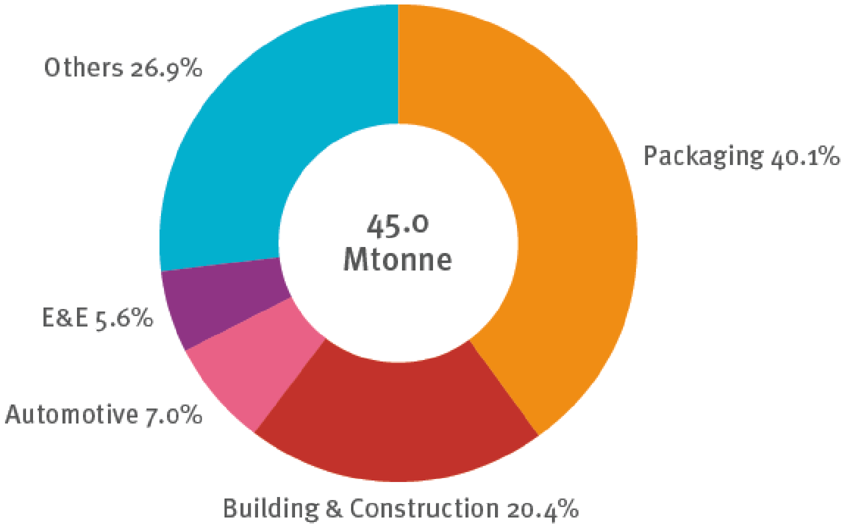


Figure 1.2: Europe Plastics Demand by Segments 2009 (The Plastics Portal, 2010)

The plastic component in Malaysian municipal solid waste from Kuala Lumpur averages 24% (by weight), whereas the national mean is about 15%. The 144 waste dumps in the country receive about 95% of the municipal solid waste, including plastic waste (Agamuthu and Faizura, 2005). Improperly disposed plastic materials could significantly pollute the environment and potentially harm life (Shah et al., 2008). The use of plastics and emissions during incineration caused pollution that is affecting food, water, air and threatening the right of human beings to live (John and Thomas, 2008). At the current rate of petroleum consumption, the fossil fuel is estimated only to last for another 50–60 years (Huang and Netravali, 2009). Besides, materials with combination of properties usually required by modern technologies are not found in conventional polymeric materials, such as lightweight and rigidity (Barbosa Jr. et al., 2010).

1.2 Research and Development on Biodegradable Plastics

Biodegradation is known as the process by which organic substances are broken down by living organisms. The term is often used in relation to waste management, environmental remediation, ecology and also to plastic materials, due to their long life span (Shah et al., 2008). As the demand for real biodegradable polymers that are compatible with the environment is getting higher (Mohee et al., 2008), there is a growing worldwide interest to increase the use of renewable resources in commodity plastic products, particularly in packaging applications (Sanchez-Garcia et al., 2008).

Polylactic acid, PLA is a thermoplastic biopolyester produced from L-lactid acid, which is usually obtained from the fermentation of corn starch. Currently, PLA is being commercialized as a food packaging polymer for short shelf-life products with common applications such as containers and lamination films. Polyhydroxybutyrate (PHB) is a naturally occurring β-hydroxyacid. PHB polymers are already being used in small disposable products and in packaging materials. Polycaprolactone (PCL) is thermoplastic biodegradable polyester synthesised by chemical conversion of crude oil. PCL with it's properties such as good solvent resistance and is easily processed using conventional melt blending technologies has been investigated for its use in pharmaceutical controlled release systems, biomedical utensils and in biodegradable packaging (Sanchez-Garcia et al., 2008). However, although these polymers are fully biodegradable, their high cost compared to petroleum-based commodity plastics prevents a larger commercial usage and thus limits their applications only in niche sectors (Avella et al., 2005).

1.3 The Application of Natural Polymer in Biodegradable Composite

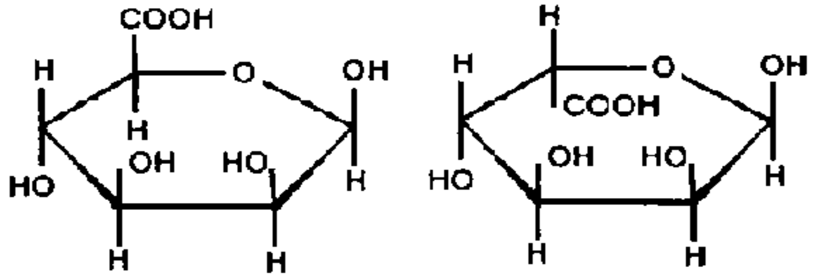
Natural polymers, which are easily available from renewable agriculture resources, are modified for production of new biomaterials with specific properties (Işıklan et al., 2010). Natural polymers such as polysaccharides are environmentally friendly as they could be degraded by microorganisms without further assistance. Other natural polymers or related carbohydrate groups, such as proteins, lignin and cyclodextrins, are used as constituents of polysaccharide-containing composites (Šimkovic, 2008). Protein, starch and cellulose have been used to prepare biodegradable resins or composites for various applications (Huang and Netravali, 2009).

Starch is a semi-crystalline polymer stored in granules as a reserve in most plants (Avella et al., 2005). In the food packaging sector, starch-based composite material received great attention due to its biodegradability, low cost and wide availability (Avella et al., 2005). Starch has been investigated widely for the potential manufacture of products such as flushable liners and bags, and medical delivery systems and devices (Ma et al., 2005).

Unfortunately, starch-based material presents some drawbacks, such as its strong hydrophilic behaviour (Avella et al., 2005; Ma et al., 2005) and brittleness (Xu et al., 2005). Compared to conventional non-biodegradable plastic films used in the food packaging industries, starch has poorer mechanical properties (Avella et al., 2005; Ma et al., 2005). Besides, the addition of starch to conventional plastic usually weakens the mechanical strength of films (Kim, 2003).

1.4 Alginate and Its Potential as Polymer Composite Film

Alginates are natural occurring polysaccharides abundant in nature as a structural component in marine brown algae (Phaeophyceae) and as capsular polysaccharides in soil bacteria (Laurienzo et al., 2005). Alginates exist in the form of insoluble gel of mixed calcium, magnesium, sodium and potassium salts (Avella et al., 2007). They are composed of guluronic (G) and mannuronic (M) acid units forming regions of M-blocks, G-blocks and blocks of alternating sequence (MG-blocks), where the relative proportions of these sequential organizations depends on the source (Chee et al., 2011; da Silva et al., 2009). Mannuronic acid forms (1–4) linkage and the M-block segments show linear and flexible conformation. Guluronic acid gives rise to (1–4) linkage and forms a steric hindrance around the carboxyl groups (Avella et al., 2007).



β - D - Mannuronic Acid α - L - Guluronic Acid

Figure 1.3: Monomeric units of alginate/alginic acid (McHugh, 1987)

Selective binding of multivalent cations, which is the basis for gel formation, is the most important feature of alginate's physical properties (Draget and Taylor, 2011). In the presence of divalent ions such as $Ca^{2+,}$ Ba^{2+}, or Sr^{2+}, they instantaneously form gel-spheres by ionotropic gelation (Avella et al., 2007; Laurienzo et al., 2005). Due to the strong interaction between the divalent cations and the COO^{-} groups of the base residual of guluronic acid (Avella et al., 2007), selective binding of certain alkaline earth metals ions increases with increasing content of α-L-guluronate residues in the chains (Draget and Taylor, 2011). Cations can be trapped in a stable, continuous and thermo-irreversible three-dimensional network, whose conformation is typical of an egg box (Avella et al., 2007; Draget and Taylor, 2011). Because of that, alginates are widely used as a gel-entrapment system for microencapsulation and immobilisation of cells (Laurienzo et al., 2005). Besides, they are also used in food applications, where the polysaccharide plays an important role as phytocolloid as well as an emulsifying agent (Avella et al., 2007).

Due to alginate’s unique colloidal properties, which include thickening, stabilising and film forming ability, it is seen as a potential biopolymer film or coating component. The potential to develop alginate as a source for biodegradable or edible films is high, considering its potential amount available as a natural resource and the reproducibility of alginic acid (Rhim, 2004). Edible films can serve as carriers of additives such as antimicrobials, antioxidants and colours, producing a modified atmosphere in food (Olivas and Barbosa-Canovas, 2008).

Since alginate films are hydrophilic films, they constitute poor moisture barriers. Their ability to form insoluble and strong gels with divalent cations can be used to improve the weakness (da Silva et al., 2009). Through incorporation of calcium, water vapour permeability (WVP) of these films can be reduced, making them water insoluble. Calcium has the ability to crosslink alginate by binding with guluronic (G) acid unit (Olivas and Barbosa-Canovas, 2008). The solvent is trapped in the interstices of a three dimensional network, linked by junction zones that involve cooperative association of extended segments of the polymer chains (da Silva et al., 2009).

1.5 Plasticiser and Its Impact on Polymer Composite Film

Commonly used plasticisers in edible carbohydrate based films are polyols, mainly glycerol and sorbitol. Plasticisers are required in cohesive films produced by the dehydration of carbohydrate's gelified structure. With the addition of plasticiser, intermolecular forces along polymer chains are decreased and the chain mobility is improved (da Silva et al., 2009). Plasticiser interspersed between polymer chains causes the chains to move apart and reduces the rigidity of structures, thus film flexibility is increased (Olivas and Barbosa-Canovas, 2008). Plasticisers also help to avoid film shrinking during handling and storage. As a result, it is easier for a plasticised film to be peeled off from the support during manufacturing (da Silva et al., 2009).

Several adverse effects of plasticisers such as increase in gas, solute and water vapour permeability and the decrease in cohesion in film were found to affect the mechanical properties of edible film (da Silva et al., 2009). An internal plasticiser that can chemically bond to polymer molecules, such as protein, via strong covalent bonds can prevent the glycerol from leaching out. However, as glycerol is bound to the protein molecules via weak hydrogen bonds and leaches out over time, the mechanical properties of the polymer are thus greatly affected (Lodha and Netravali, 2005b).

1.6 The Application of Filler as Reinforcement in Polymer Composite

There are two types of reinforcement in polymer composite in use: fibrous and particulate fillers. According to the compilation of American Society for Testing and Materials Standard Definitions, particulate filler or non-fibrous filler is described as solid compounding material usually in finely divided form which may be added in relatively high proportion to a polymer for technical and economic reason. Fibrous or fibre filler is described as particle with a length-to-diameter ratio greater than 10 to 1 (Katz, 1998). Improved stiffness, decreased thermal expansion, improved long-term mechanical performance and reduced costs are the advantages of filler-reinforced thermoplastic composites (Suresha et al., 2010).

1.6.1 Fibrous or Fibre Filler

Natural fibres are found in plants, animals or minerals. Plant fibres include bast fibres, wood, leaf or hard fibres, seed, fruit, cereal straw, and other grass fibres (John and Thomas, 2008). Natural fibres such as kenaf, bamboo and hemp are strong, light, inexpensive and most importantly, renewable (John and Thomas, 2008; Kinoshita et al., 2009). Natural fibres can be sourced from agricultural crops-residues. In North America alone each year, there are an estimated 500 million tones of agricultural residues available (Alemdar et al, 2008).

The overall properties of fibres are determined by the microfibrillar angle, defects, structure, cell dimensions and its chemical composition. Young's tensile strength and modulus of fibres increases with increasing cellulose content (John and Thomas, 2008). To develop short-fibre-reinforced composites' fully stressed condition in the polymer matrix, a critical length of the fibre is required (Ibrahim et al., 2010). Compatible fibre–matrix interaction can be achieved by using short fibres as shorter fibres tend to be more evenly distributed. Fibre attrition, holes and agglomeration on the fracture surface of composite with longer fibre length suggest poor interface region that lead to reduced strength (Thwe and Liao, 2003).

Natural fibre is a reinforcement that has attracted attention of researchers due to its advantages over other established materials (Ibrahim et al., 2010). Natural fibre's ability to be disposed through composting or incineration is facilitated by their renewable and biodegradable characteristics (Xie at al., 2010b). Despite the advantages, use of natural fibre reinforced composites has been restricted due to problems such as poor wettability, high moisture absorption tendency, low thermal stability during processing and poor adhesion with the synthetic counterparts (Nayak et al., 2009). Poor interfacial adhesion of the nonpolar and hydrophobic matrix material with polar and hydrophilic fibre results in poor mechanical properties in the final material. Many attempts have been made in modifying the interfacial bonding between the fibre and the polymer matrix to solve the problem (Nayak et al., 2009).

1.6.2 Non-fibrous or Particulate Filler

Glass fillers, glass beads, carbon black, and wood flour, are currently used as fillers in thermoplastic composites (Suresha et al., 2010). Calcite particles constitute one of the common fillers in composite materials such as plastic and paper (Shui, 2003). Compared to metals, the mechanical properties of common polymers are not very good and this has prompted the attempt to cast particulate filled polymer composites. In the last 30 years, the tribological properties of polymer composites have been extensively studied. Some of the fillers that are effective in reducing wear and friction are MoS_2, CuO, CuS, and Al_2O_3. The use of graphite as a filler material is known to improve the mechanical and tribological properties of polymer matrix composites (Suresha et al., 2010).

Ideally, filler must be well dispersed in the matrix to avoid zones of weaker cohesion where flaws and other defects will be initiated upon stressing. Those fillers are usually chemically treated to enhance the filler and polymer interaction. In composites, filler and polymer are bound with secondary forces. Although chemical characteristic of the components, filler content and characteristics significantly influence the rheological and mechanical properties of polymer composites, these properties could also be affected by any changes in polymer/filler interaction. This effect depends both on the strength of the interaction and the size of the contacting surfaces. The nature and the intensity of the particle–particle or particle–matrix interactions are interdependent upon one another. As a result, it is critical in developing an understanding of the forces of interaction between filler and substrate (Shui, 2003). In addition, there has been little investigation on the properties of polymer composites by incorporating nano particles compared to conventional fillers. Therefore, the load carrying capacity of such composite systems compounded with nano and micro particulate fillers are worthwhile to be explored. A good understanding of the role of fillers, especially the addition of nano particles, in modifying the mechanical behaviour of polymer composites is essential (Suresha et al., 2010). However, only few reports appear in literature although a thorough investigation of the filler–modifier interface is much needed (Shui, 2003).

1.7 Bamboo Fibres as Fibrous Filler

Bamboos are perennial, arborescent, tall grasses belonging to the Bambusae, a tribe under Graminae. They are typical natural composite materials with its fibres distributed densely in the outer surface region and sparsely in the inner surface region (Rao and Rao, 2007). Bamboos are replenishable agricultural resource and abundantly available in some countries such as China, India and within the Southeast Asia region (Nayak et al., 2009). As the growth rate of the bamboo is very rapid, the supply of the bamboo fibres has been stabilised (Kinoshita et al., 2009). Bamboo can be harvested three or even four times a year (Huang and Netravali, 2009). Though the specific tensile strength and specific gravity of bamboo are considerably less than those of glass fibres, cost considerations still make bamboo an attractive fibre for reinforcement (Rao and Rao, 2007).

1.8 Calcium Carbonate as Particulate Filler and Crosslinker

Calcium carbonate is non-irritating, non-toxic, odourless and is white in colour. It is one of the lowest cost particulate fillers. There is an abundant supply of this mineral filler and it is commercially available in a wide range of particle size (Katz, 1998). Therefore, calcium carbonate based fillers have been used extensively. More than 80% of the fillers used in thermoplastics are based on calcium carbonate minerals (Sahebian et al., 2009). As its use reduces shrinkage during moulding and curing, it is usually used in low shrink polyester sheet moulding compounds. It provides relatively low stiffness to the composite even with high loadings (Katz, 1998).

There have been a lot of researches on the characterisation of calcium carbonate as filler to form composites. Different kinds of engineered calcium carbonate particulates are produced by chemical precipitation from calcium hydroxide. These particulates are often produced especially for its application as filler in polymers (Sahebian et al., 2009). The industrial importance of precipitated calcium carbonate as filler in composite materials such as textiles, plastics, rubbers, paints, pigments, and paper is well known (Lam et al., 2009). Besides, due to the ability of Ca^{2+} to form strong interaction with polyuronates such as alginate (da Silva et al., 2009), calcium carbonate was also used as crosslinking agent in alginate to form biocomposite (Xie et al., 2010a).

1.9 The Importance of Polymer Composites

Composite materials have a combination of different properties and design for applications that require multiple functionalities. Filler-reinforced thermoplastic composites can decrease thermal expansion, improve stiffness, reduce costs and improve long-term mechanical performance (Suresha et al., 2010). Many green composites which consist of biodegradable resin as a matrix material and natural fibres as reinforcements have been proposed (Kinoshita et al., 2009). Green composites are biocomposites derived from plant fibre (natural/biofibre) and crop/bioderived plastic (biopolymer/bioplastic) which is more eco-friendly (John and Thomas, 2008). It is believed that biodegradable plastics based on biomass feedstock and renewable agricultural by-products can form sustainable, eco-efficient products that would compete and capture markets which are currently dominated by petroleum-based products (Mohee et al., 2008).

Green composites have been used effectively in many applications such as products intended for one time or short time use before disposal or mass produced consumer products with short life cycles (John and Thomas, 2008). The development of composites based on constituents obtained from natural sources (biobased composites) is of great importance. Biobased composites reduce the dependence on materials obtained from non-renewable sources (fossil-based) and normally show good mechanical properties, leading to both environmental and economical benefits (Barbosa Jr. et al., 2010).

Conventional particulate polymer composites (or known as filled polymers) are of significant commercial importance as materials in industrial applications (Rai and Singh, 2003). It has been observed that incorporation of filler particles into the matrix of fibre reinforced composites has positive synergistic effects, achieved in the form of higher modulus and reduced material costs (Hartikainen et al., 2005).

It is known that hybrid reinforced composites form a complex system. There is still inadequate data available on property changes due to the addition of particulate fillers into fibre reinforced thermoplastic composites (Hartikainen et al., 2005).

The development of biodegradable composites becomes an important provider of opportunities to improve the standard of living of people around the world, besides being a great motivating factor for materials scientists. Since many of the renewable materials are based on agricultural products as a source of raw materials, particularly to plastic industries, a non-food source of economic development for farming and rural areas in developing countries could be generated. For example, generation of jobs by agro-based materials can be provided by the use of rice husk, which constitutes more than 10% of world rice production. It was reported that increasing use of renewable materials would create or secure employment in rural areas, especially in sectors such as forestry, and agriculture (Satyanarayana et al., 2009).

1.10 Scope of Study

This study focuses on the preparation of hybrid polymer and polymer composites that consist of sodium alginate, synthetic monomers and both fibrous and non-fibrous fillers. Hybrid polymer is defined as polymer or polymer network comprised of inorganic and organic components while hybrid polymer composite is hybrid polymer incorporated with fibrous or particulate filler. Synthetic monomers, namely acrylamide and butyl acrylate, are grafted onto sodium alginate using potassium persulfate and sodium formaldehyde sulfoxylate (SFS) as initiators and *N,N*-methylenebisacrylamide (*N*-MBA) as crosslinker to form hybrid polymer. The composite with fibrous fibre is formed by incorporation of bamboo leaves fibre, whereas composite with particulate filler is by the introduction of $CaCO_3$ into the polymer system.

Effects of reaction variables such as monomer to sodium alginate ratio, amount of crosslinker and fibre on the mechanical properties of the hybrid polymer and its composites will be investigated using microtester. Different grafting conditions such as reaction temperature, reaction time, drying temperature, stirring speed will be studied. Analysis on the solubility of hybrid polymer and its composites in various solvents will be carried out. Fourier transform infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy will be used for the characterisation of hybrid polymer and its composites.

The purpose of this research is to prepare hybrid polymer and polymer composites partly from natural resources and fillers by viable method in term of cost and compatibility. In this study, the film of the hybrid polymer and its composites with comparable mechanical properties, especially tensile strength, to commercial plastics would be prepared.

1.11 Research Objectives

The main objectives of this study are:

(a) To synthesise hybrid polymer (HP) derived from sodium alginate and synthetic monomers by graft polymerisation in the presence of *N*-MBA as crosslinking agent.

(b) To synthesise hybrid polymer-fibre composite (HPFC) by incorporating bamboo leaves fibre as fibrous filler into the hybrid polymer.

(c) To synthesise hybrid polymer-$CaCO_3$ composite (HPCC) derived from sodium alginate and synthetic monomers by graft polymerisation, in the presence of $CaCO_3$ as particulate filler.

The other objectives of this research are:

(a) To study the effects of the following variables on the mechanical properties such as tensile strength, Young's modulus and elongation at break of the hybrid polymer and its composites using a microtester:

  i. Different monomer to sodium alginate ratio

  - **ii.** Different addition sequence of materials
  - **iii.** Different reaction time
  - **iv.** Different reaction and drying temperature
  - **v.** Different agitation speed
  - **vi.** Different fibrous fibre amount, size and incorporation sequence
  - **vii.** Different crosslinking agent type and amount
  - **viii.** Different pH of reaction mixture
  - **ix.** Ca^{2+} and glycerol post-treatment

- **(b)** To determine the swelling and solubility percentage of the hybrid polymer and composites in different solvents
- **(c)** To determine the functional groups and chemical structure of the hybrid polymer and its composites with Fourier Transform Infrared Spectroscopy (FTIR).
- **(d)** To determine the thermal properties of the hybrid polymer and its composites by thermogravimetric analysis (TGA).
- **(e)** To determine the surface morphology of the hybrid polymer and its composites by scanning electron microscopy (SEM).

CHAPTER 2

LITERATURE REVIEW

2.1 Petroleum-based Plastics and Their Environmental Impacts

Petroleum-based plastics are widely used in different fields due to their low density and excellent mechanical and physical properties (Huang and Netravali, 2009). While the stability and durability of plastics have been improved continuously, this group of materials is resistant to many environmental influences (Shah et al., 2008). Most of these polymers are introduced in the ecosystem as industrial waste products (Shah et al., 2008). In the past 20 years, the production and the use of plastics in the world have increased enormously, which was from 1.5 million tonnes in 1950 to 230 million tonnes in 2009 (Figure 2.1). Thus, this trend is worsening the waste disposal problem (Avella et al., 2005), besides its negative effect in terms of both cost and ethics (Wang et al., 2010).

The disposal of petroleum-based plastics has become a critical issue as the usage of these materials grows in the past few years (Huang and Netravali, 2009). The need to develop polymers with controllable lifespan and environmentally acceptable manufacturing, application, recycling and disposal methods are accelerated by the problems of polluted marine waters, overflowing landfill (Lodha and Netravali, 2005b), and polluted air as persistent organic pollutants such as dioxins and furans were produced by the burning of poly(vinyl chloride) (Shah et al., 2008).

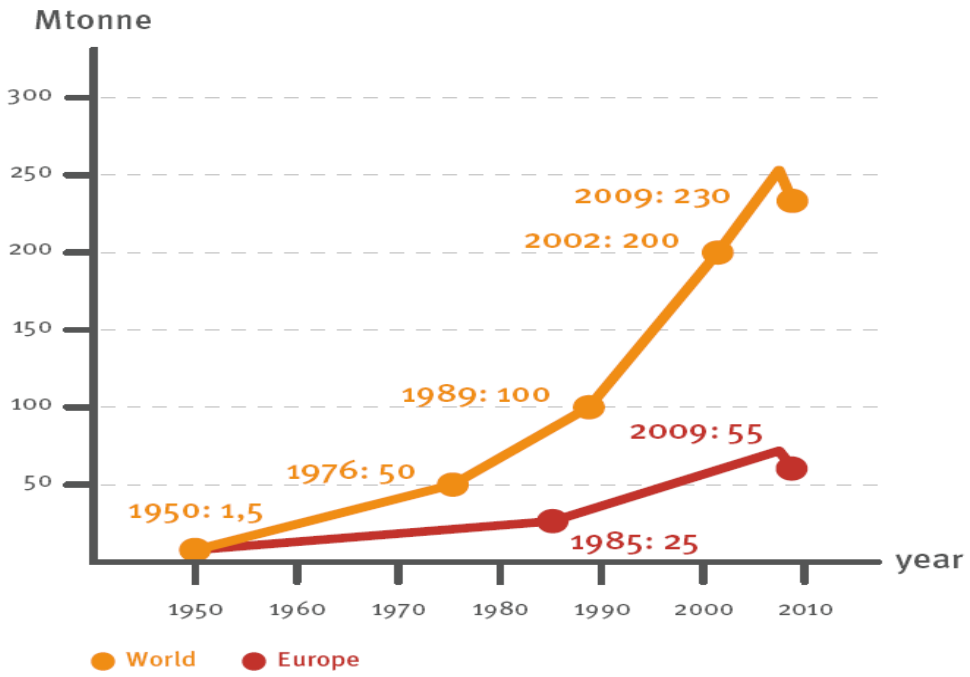


Figure 2.1: World Plastics Production 1950-2009 (The Plastics Portal, 2010)

Over the time, the raw materials used to manufacture plastic have changed from coal, milk, cellulose to petroleum and the latter is currently the main raw material (Agamuthu and Faizura, 2005). Previous studies related to the environmental impacts of petroleum-based and bio-plastics have focused on the impact categories of fossil fuel depletion and global warming. There were studies of biopolymer, poly(β-hydroxybutyric acid) (PHB) in comparison to conventional plastics such as polypropylene (PP), polyethylene (PE), polystyrene (PS) and poly(ethylene terephthalate) (PET) that focused on carbon dioxide emissions and energy requirements (Harding et al., 2007).

Harding et al. (2007) studied on cradle-to-gate life cycle assessment of PHB production taking into account net CO_2 generation and all major impact categories. Cradle-to-gate is the life cycle of a product or process from manufacture to end user, which is also known as environmental product declarations (Shiwanov, 2008). The findings was compared with similar studies of PP and PE and it was found that, in all of the life cycle categories, PHB is superior to PP. Energy requirements are slightly lower than previously observed and significantly lower than those for polyolefin production (Harding et al., 2007). The exhaustive use of petroleum based resources has initiated the efforts to develop biodegradable plastics (John and Thomas, 2008).

2.2 Biodegradable Plastics

Plastics with biodegradable labelling have been commercially available since 1990 and can be produced from plant origins or bacteria (Mohee et al., 2008). Although these biodegradable plastics have been introduced into the market for years, none of them is efficiently biodegradable in landfills (Shah et al., 2008). As they only disintegrate and did not completely biodegrade (Mohee et al., 2008), none of the products has gained widespread use (Shah et al., 2008).

To avoid misconceptions on the term biodegradability, several standards in the area of degradable as well as biodegradable plastics have been developed by national standard bodies, including the American Society for

Testing and Materials (ASTM) and the International Organization for Standardization (ISO).

ISO defines degradable plastic as a plastic designed to undergo a significant change in its chemical structure under specific environmental conditions, resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application over a period of time that determine its classification (Mohee et al., 2008).

According to ASTM, a biodegradable polymer is a degradable polymer in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae; whereas environmentally degradable plastics are materials that retain the same formulations as conventional plastics during use, degrade after use into low molecular weight compounds by the combined actions of physico-chemical agents and microorganisms existing in nature and the materials ultimately break-down to carbon dioxide and water (Agamuthu and Faizura, 2005).

More research activity has been promoted worldwide to either modify current products to promote degradability or to develop new alternatives that are degradable by biodegradation, photo degradation, environmental erosion and/or thermal degradation (Shah et al., 2008). One of the many strategies to minimise the environmental impact of petroleum-based plastics is the use of biodegradable plastics or bioplastic and resources (Sanchez-Garcia et al., 2008). There have been attempts to solve these problems by including biodegradability into polymers through slight modifications of their structures (Lanthong et al., 2006). While most commodity plastics used at present either take decades to degrade or are non-biodegradable at all, plastics such as polyethylene with starch blend, are able to biodegrade (Shah et al., 2008). The global manufacturing capacity of renewable raw material for biopolymer production has been increasing steadily years after years and it was estimated to reach 901 000 tonnes in 2010 (Figure 2.2).

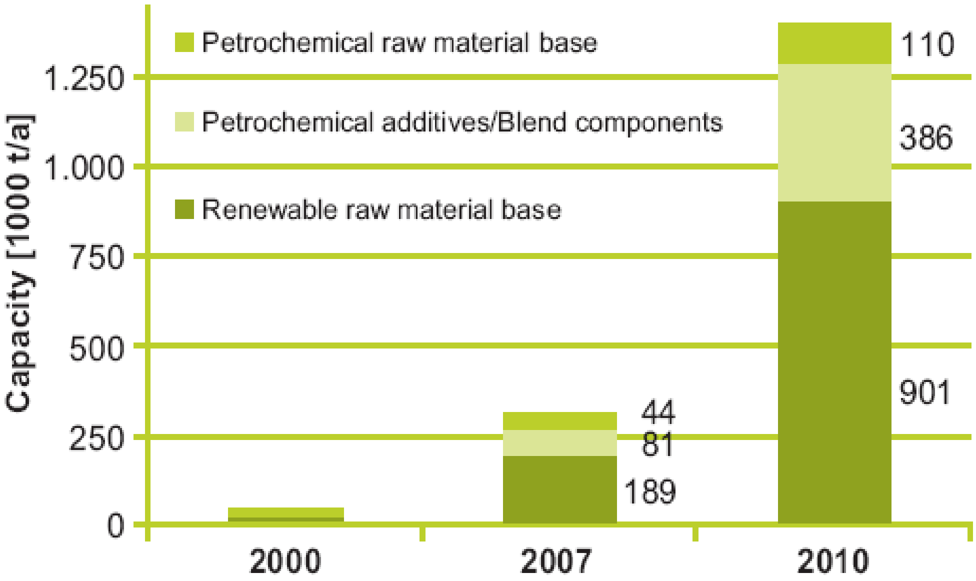


Figure 2.2: World manufacturing capacity of petrochemical raw material base, petrochemical additives/blend components and renewable raw material base 2000 – 2010 (Nachwachsende-rohstoffe.de, 2007)

Several methods have been developed to evaluate and quantify biodegradability under different disposal conditions like composting, soil, marine, wastewater treatment and anaerobic digestion (Mohee et al., 2008). Compostability of polyethylene and pro-oxidant additive-based environmentally degradable plastics was investigated by Agamuthu and Faizura (2005). They found that the polyethylene-based samples were not hydrolytically degradable at 60 °C and only degraded oxidatively when exposed to air for 60 days. Thus, these environmentally degradable plastics were biodegradable and hence safe to use (Agamuthu and Faizura, 2005).

2.3 Natural Polymers Used in Composites

2.3.1 Starch

Starch can be processed into thermoplastic starch (TPS) under the action of high temperature and shear. Conventional TPS materials are susceptible to aging and starch retrogradation. Starch retrogradation is re-crystallisation of its molecules, which makes TPS fragile. The use of glycerol as plasticiser tends to cause TPS retrogradation after it has been stored for a period of time (Ma et al., 2005). Preliminary studies by Ma et al. (2005) showed that a combination of formamide and urea did effectively restrain TPS retrogradation and make thermoplastic starch flexible. Avella et al. (2005) prepared nanocomposite films by homogeneously dispersing functionalised layered silicates (clay minerals) in TPS via polymer melt processing techniques. These films were made by using different starch matrices, such as a mixture of potato starch with biodegradable polyester, and neat potato starch. Generally, a plasticiser was required to make them suitable for engineering applications as starch is highly water soluble and it exhibits poor melt processability (Satyanarayana et al., 2009).

Multilayer films based on various biodegradable aliphatic polyesters and plasticised wheat starch had been prepared through flat film coextrusion and compression moulding (Ma et al., 2005). Attempts had been made to chemically modify wheat starch using glycol, leading to the development of cross-linked networks, which improved processing and doubled the tensile strength from 8 to 15 MPa, with 130–140% in elongation (Satyanarayana et al., 2009).

2.3.2 Alginate

Alginate is a salt of alginic acid, a polymer of β-D-mannuronic acid (M) and α-L-guluronic acid (G), which is isolated from brown seaweeds (Olivas and Barbosa-Canovas, 2008). As sodium alginate is a good chelator, it can be used to remove radioactive toxins such as iodine-131 and strontium-90 from the body (Carneiro-da-Cunha et al., 2010). Alginate is frequently used as matrix polymer for encapsulation of proteins, drugs and cells. Alginate is deemed suitable for fabrication into film for use as a transdermal drug delivery system, owing to its excellent film forming, biocompatible, and non-toxic properties (Ashikin et al., 2010).

Combined with the polyelectrolyte nature of the alginate molecule (Draget and Taylor, 2011), the G-block segments provide rigid and folded structural conformations, which are responsible for a pronounced stiffness of the molecular chains (Avella et al., 2007). Avella et al. (2007) did a study on the interaction among sodium alginates of different molecular compositions, water and glycerol. Polymer with the higher amount of guluronic acid had shown to give a lower value of stress at break compared to lower amount of guluronic acid, which was contrary to what was expected theoretically.

Many researchers had studied sodium alginate for its mechanical properties and its potential as composite film. The effect of plasticiser on sodium alginate film also had been investigated. Plasticised microcomposite films were developed by incorporating hydrophilic small molecules, such as glycerine, into the composite. The addition of plasticisers had shown to cause changes in thermal behaviour, matrix structure, mechanical properties, and permeability on water vapour and drugs (Pongjanyakul and Puttipipatkhachorn, 2008). Olivas and Barbosa-Canovas (2008) soaked alginate film in calcium chloride solutions and analysed the effect of different plasticiser and relative humidity on the mechanical properties of the alginate–calcium-based films. In the study, it was noted that as relative humidity increased, tensile strength decreased and elongation increased for all films; whereas films plasticised with glycerol gave the highest tensile strength and elongation compared to those plasticised with fructose, sorbitol or polyethylene glycol (Olivas and Barbosa-Canovas, 2008). The effect of the plasticiser (glycerol) concentration on the solubility in water, swelling degree and mechanical properties of alginate/pectin composite films cross-linked with calcium ions was also studied by da Silva et al. (2009). Da Silva et al. (2009) found that increasing the glycerol concentration increased film solubility in water, moisture content, volumetric swelling and flexibility but decreased the resistance of the film to tensile stress.

The mechanical strength of the composite film was also found to be greatly affected by different drying condition. Ashikin et al. (2010) investigated plasticity of hot air-dried guluronate-rich and mannuronate-rich alginate films prepared from 2% and 4% (w/w) alginate solutions. Drying parameters, such as time, temperature, drying rate and relative humidity, were investigated with respect to their influences on film integrity. It is known that guluronate-rich alginate is conformationally less flexible than mannuronate-rich alginate. Therefore, theoretically, mannuronate-rich alginate could respond differently from guluronate-rich alginate in their interaction and molecular rearrangement during film formation while drying at different polymer concentrations and drying temperatures would affect the mobility of the polymer chains in liquid (Ashikin et al., 2010).

The most unique and useful property of alginates is their ability to react with polyvalent metal cations, specifically calcium ions, to produce strong gels or insoluble polymers (Rhim, 2004). Olivas and Barbosa-Canovas (2008) had developed a method to increase the polymer gel strength by immersing it into aqueous solutions of multivalent cations. Because of its hydrophilic nature, alginate exhibit poor water resistance even though strong films can be prepared from it. Such weakness of the alginate films can be improved by utilising the ability of alginate to form strong and insoluble gels with calcium ions. Incorporation of calcium can reduce the water vapour permeability of these films, thus making them water insoluble. However, as the rate of gel formation between alginate and calcium ions is very high, film casting in some cases is prevented.

Rhim (2004) researched on the properties of sodium alginate films modified using two different methods of $CaCl_2$ treatment; direct addition of $CaCl_2$ into the film making solution (mixing films) and the immersion of alginate films into $CaCl_2$ solutions (immersion films). The researchers noted that tensile strength and elongation of the mixing films were not changed considerably with different $CaCl_2$ concentrations (0.04 - 0.12 g $CaCl_2$/4 g alginate); whereas those of the immersion films in different concentrations of $CaCl_2$ solutions (1 - 5 g $CaCl_2$/100 ml distilled water) changed considerably with significant increase in tensile strength and decrease in elongation.

Besides $CaCl_2$, other particles and additives had been added into sodium alginate to form composite film. Recently, magnesium aluminum silicate (MAS) was used to improve rheological properties of sodium alginate gel. In the presence of MAS, the flow type of the sodium alginate gels had shifted from Newtonian to pseudoplastic. This led to a further study on the physicochemical properties of the sodium alginate–MAS composite films conducted by Pongjanyakul et al. (2005). It was found that sodium alginate and MAS could form a microcomposite film with improved mechanical properties, retarded water uptake and drug permeability (Pongjanyakul and Puttipipatkhachorn, 2008). Compared with sodium alginate films, composite films in the sodium alginate to MAS ratios of 1:0.5 and 1:1 showed an increase in tensile strength and elongation percentage.

2.3.3 Soy Protein

In soy protein, there are 18 amino acids with polar functional groups that are capable of chemical reaction. The mechanical and physical properties of protein can be improved by utilising these reactive groups for chemical modification and thus improve the properties of the composites obtained (Huang and Netravali, 2009). Soy protein plastics of different compositions had been prepared by injection moulding (John and Thomas, 2008). Huang and Netravali (2009) reinforced soy protein concentrate with the micro/nano-sized bamboo fibrils. The fibrils were uniformly dispersed into the soy protein resin and formed into isotropic composite sheets.

Some researchers had investigated the effect of stearic acid on the thermal and tensile properties of ramie fibre reinforced soy protein isolate (SPI) resin green composites. It was observed that part of the stearic acid had crystallised in SPI resin and that the crystallisability was affected by the addition of glycerol as a plasticiser. The fabricated green composite was found to have enormous potential for certain indoor applications, such as featherweight circuit boards in computers using waste chicken feathers and soy based resin (John and Thomas, 2008, Lodha and Netravali, 2005a).

2.4 Chemical Modification of Natural Polymers

Natural polymers such as alginates suffer from limitations in fabrication, which limits its application in some fields such as in controlled-release technology due to its tendency to enzymatic degradation. Efforts have been made to develop chemically modified matrices to overcome this problem. One of the techniques used to modify chemical properties of these natural polymers is by means of graft copolymerisation (Işıklan et al., 2010). In principle, graft co-polymerisation is an attractive method to impart a variety of functional groups to a polymer (Bhattacharya and Misra, 2004).

In the last decade, there have been studies on synthesis and characterization of graft copolymers of these natural polymers. Grafting is a well-established method for the development of natural-synthetic polymer materials. Graft copolymerisation of vinyl monomers onto alginate give certain properties and expand the field of potential application of the modified alginate by attaching various types of side chains (Işıklan et al., 2010). Graft copolymers of sodium alginate with itaconic acid were prepared by Işıklan et al. (2010) in aqueous solution using benzoyl peroxide as the initiator. There were studies on graft copolymerisation of polystyrene, styrene, methyl methacrylate, methyl acrylate and butyl acrylate onto starch. Graft copolymerisation can be performed by irradiation or free-radical graft copolymerisation (Kaewtatip and Tanrattanakul, 2008).

Graft copolymerisation is also an effective method of chemical modification of natural fibres (Ibrahim et al., 2010). Due to their non-abrasive nature, natural fibres are comparatively easy to process, which permits high filling levels, significant cost savings, and relatively high reactive surface, which facilitates the grafting of specific groups (Sanchez-Garcia et al., 2008).

There is considerable interest from the standpoint of modification of cellulosic fibres although there has been little commercial exploitation. One example of a graft copolymer that has achieved some commercial interest is cellulose acetate grafted with vinyl acetate using a cobalt-60 gamma ray source (Stevens, 1999). In recent years, a number of monomers such as ethyl acrylate, styrene and allyl-dimethylhydantion were successfully grafted onto cellulose by copolymerisation (Wan et al., 2011).

Through graft copolymerisation, the physical and chemical properties of the fibres are altered by cellulose modification (Stevens, 1999). Graft copolymerisation of methyl methacrylates onto different back-bones such as poly(butyl acrylate), poly(methyl acrylate), poly(acrylic acid) and cellulose resulted in increased chemical resistance, hydrophobicity and physical strength of the material (Kaith et al., 2010). According to Dahou et al. (2010), chemical modification can also be used to vary certain properties of cellulose such as its elasticity, water absorbency, adsorptive or ion-exchange capability, resistance to microbiological attack and thermal resistance.

Kaith et al. (2010) reinforced corn starch based green composites with graft copolymers of *Saccharum spontaneum L.* fibre and methyl methacrylates and prepared its mixture with acrylamide, acrylonitrile, acrylic acid. *Saccharum spontaneum L.* fibre-reinforced composites were found to exhibit better tensile strength. It is well established that potassium persulfate, manganic pyrophosphate, ceric ammonium nitrate, potassium permanganate, benzoyl peroxide and redox couples such as ferrous ammonium sulfate –

hydrogen peroxide are effective for grafting vinyl monomers onto starch via free radical graft copolymerisation (Kaewtatip and Tanrattanakul et al., 2008). Kaewtatip and Tanrattanakul et al. (2008) grafted cassava starch with polystyrene with potassium persulfate as initiator, via free-radical polymerisation of styrene by suspension polymerisation technique.

2.5 Research on Particulate Filler-Reinforced Polymer Composites

The use of inorganic fillers in both elastomers and plastic materials has been practiced for many decades. With regard to elastomers, the key aim is either to cheapen the compounds using clay and other materials or to provide a major reinforcement such as in synthetic elastomers using carbon black and silica (Kemal et al., 2009). There is a new concept in using filler particles as toughening agent. The general idea behind this study is to mimic the rubber toughening mechanism using rigid filler particles. Rigid particles must debond and create free volume in the blend on a sub-micron size level such as cavitation mechanism in rubber toughened systems (Zuiderduin et al., 2003).

The application of different type of particulate filler in composite has been widely studied. According to Mirmohseni and Zavareh (2010), an alternative approach for toughening is to fill epoxy cured polymers with inorganic nano-fillers to achieve nanocomposites. In addition to layered nano-fillers, various particulate fillers such as; alumina (Al_2O_3), titania (TiO_2), silica (SiO_2) and calcium carbonate ($CaCO_3$) are also employed for this purpose. Incorporation of inorganic nano-fillers improves fracture toughness to some extent (Mirmohseni and Zavareh, 2010). Mirmohseni and Zavareh (2010) incorporated poly(acrylonitrile-co-butadiene-co-styrene), clay (layered nano-filler) and nano-TiO_2 (particulate nano-filler) into epoxy matrix. It was found that the tensile and impact strength of the quaternary nanocomposite with optimum composition increased by 64% and 168% compared to neat epoxy, respectively.

Barium sulfate ($BaSO_4$) filled polymer systems have been studied extensively (Wang et al., 2003). The effect of interfacial interaction on the mechanical performance of a series of polypropylene (PP) / barium sulfate ($BaSO_4$) composites were studied by Wang et al. (2003). It was concluded that PP can be toughened with specially treated $BaSO_4$ particles. For PP, it was already known that a moderate impact improvement with rigid particles was possible. Complete toughened systems of PP with $CaCO_3$ with notched fracture energies rising to 40–50 kJ/m^2 were reported. There were also reports on polyketone polymers toughened with $CaCO_3$ that gave complete ductility at room temperature and notched impact strength of 80 kJ/m^2 (Zuiderduin et al. 2003).

Because of silicon carbide’s commercial availability and outstanding high-temperature properties, it has been most frequently used in manufacturing carbon fibre reinforced ceramic matrix composites. In one investigation by Cai et al. (2010), graphite filler, acting as a carbon source, was mixed with a resin matrix to tailor the properties of the matrix and fibre/matrix interface. The results showed that the material had an average strength of 120 MPa.

The effects of iron fillings particles on the microstructure and properties of fibre–polyester composites had been analysed. Ultimate tensile and compressive strength increased by 41.3 and 20.8% up to a maximum of 12 wt% of iron fillings addition (Madugu et al., 2009).

Fused silica has been widely used as filler in polymer composites due to its high chemical and thermal stability. As the price of fused silica is quite high compared to other types of silica such as silica mineral, attempts have been made to find an alternative filler to be used in underfill materials. (Underfill material is used to fill the gap between the chip to reduce the thermal stresses imposed on the solder joints and further improving the long-term reliability of electronic device.) Ahmad et al. (2008) carried out a study to evaluate the performance of silica mineral composites in comparison with conventional fused silica composites, which is commonly used as underfill material. In general, it was noted that the addition of particulate filler loading increased the tensile strength and modulus, flexural strength and modulus. Besides, the investigation also revealed that elongated silica mineral particles exhibited higher flexural and tensile properties in comparison with fused silica filler composites.

Hartikainen et al. (2005) observed that by incorporating filler particles into the matrix of fibre reinforced composites, though synergistic effects might be achieved in the form of higher modulus and reduced material costs, it was accompanied with decreased strength and impact toughness. From the research of Hartikainen et al. (2005), it was concluded that the addition of $CaCO_3$ in long glass fibre reinforced polypropylene increased the stiffness but decreased the strength and toughness.

Rong et al. (2003) discovered that it was very difficult to uniformly disperse nanoparticles in polymers due to the strong attraction between the particles and the limited shear force during compounding. In another study done on the toughening of isotactic PP using ultrafine calcium carbonate (average particle size 70 nm), only a limited increase in fracture toughness was obtained due to insufficient dispersion of the particles at higher filler loadings (Lazzeri et al., 2005).

A recent research by Gao et al. (2009) also showed the negative effect of particulate filler. Gao et al. (2009) compounded nano-$CaCO_3$ incorporated polystyrene composites by twin-screw extrusion. Compact tensile and tensile tests showed that the strength and toughness of polystyrene had decreased after the addition of nano-$CaCO_3$ particles. Fracture surface analysis suggested that interfacial debonding and nano-filler agglomerations were the key factors responsible for the declined strength and toughness.

2.5.1 Calcium Carbonate

Lazzeri et al. (2005) stated that calcium carbonate was used in their research because it is the most widely used filler for plastics and it can be used at high loading. It is available in different grades: dry processed, wet or water ground and surface treated. Precipitated calcium carbonate can be produced in three polymorph forms (vaterite, calcite or aragonite), with a wide variety of particle sizes and shapes, including acicular and plates forms. However, only the calcite form with a rhombohedric cell and a low aspect ratio was found to have much commercial application in polymers. Jin and Park (2008) mentioned that nano-$CaCO_3$ is the cheapest commercially available calcium carbonate, which has the additional advantages of a low aspect ratio and a large surface.

According to Kemal et al. (2009), ground calcium carbonate of particle size greater than 1 mm was often added to poly(vinyl chloride) (PVC) compounds to reduce cost, but at the expense of performance with reduction in tensile and impact strength. It has been found that the addition of nanometer-sized calcium carbonate has significantly improved both the toughness and stiffness of PVC, although it has little effect on the tensile strength. New techniques for cheap processing of nanometer-sized calcium carbonate have been developed, which have potential applications in commodity applications of PVC such as piping materials (Kemal et al., 2009).

There had been investigation on the effect of the addition of about 10 wt% of nano-sized calcium carbonate to polyethylene (PE) on tensile properties, viscosity and dimensional stability of the polymer (Sahebian et al., 2009). Lazzeri et al. (2005) showed that the Young's modulus of polyethylene had increased by about 70% as 10% of nano-sized calcium carbonate was added to it. Sahebian et al. (2009) found that dimensional stability of high density polyethylene was augmented by the addition of nano-sized calcium carbonate. Sahebian (2007) also illustrated that the creep behaviour of PE nanocomposites reinforced with different nano-sized calcium carbonate depends strongly on calcium carbonate content. It was found that the best creep resistance of PE nanocomposites was achieved with 10% of calcium carbonate loading (Sahebian et al., 2009).

Several researchers have used nano-$CaCO_3$ to prepare nano-$CaCO_3$-reinforced rubber composites and studied on their mechanical properties. However, only a few studies on the same properties of butadiene rubber/nano-$CaCO_3$ composites have been reported (Jin and Park, 2008). Jin and Park (2008) investigated the mechanical interfacial properties of butadiene rubber (BR) reinforced with nano-$CaCO_3$ and noticed that the mechanical interfacial properties of BR/nano-$CaCO_3$ composites were improved with the addition of nano-$CaCO_3$ as were the tensile strength and elongation. All of the results indicated that nano-$CaCO_3$ is a good candidate for the use as a butadiene rubber-reinforcing agent (Jin and Park, 2008).

Rai and Singh (2003) prepared polymer-matrix composites by mixing different amounts of calcium carbonate and white cement with polystyrene to give uniform slurry of inorganic and organic phases and casting it in an aluminium mould. The fracture toughness, flexural strength and elastic modulus were found to increase with increasing amount of the inorganic component in the polymer.

Zuiderduin et al. (2003) prepared PP–$CaCO_3$ composites with the particle content of 0–32 vol% and studied the influence of particle size (0.07–1.9 mm) on the toughening properties of the composites. The impact resistance of the composites had shown large improvement with increasing particle content.

2.6 Research on Natural Fibre-Reinforced Polymer Composites

Plant fibres are considered as naturally occurring composites consisting mainly of cellulose fibrils embedded in lignin matrix (John and Thomas, 2008). Cellulose is the most abundant biomass resource that possesses excellent mechanical and thermal properties (Nishino et al., 2004). Micro-fibrillated cellulose with high aspect ratio and high tensile properties can be obtained by mechanical shearing of cellulose fibres. It has been used for fabrication of composites with excellent mechanical properties (Huang and Netravali, 2009). There are technologies that can reduce fibre cross-section to the nanometer level as in the case of micro-fibrillated cellulose (Sanchez-Garcia et al., 2008). The studies of Alemdar et al. (2008) showed that nano-size fibres with increased cellulose content and improved thermal and mechanical properties from soya hulls and wheat straw could be produced for potential use as reinforcement fibres in composite applications.

The ability of fibre to increase mechanical strength of bio-composites was agreed by many researchers. According to Nishino et al. (2004), when both fibre and matrix are composed of the same material, some benefits relevant to recyclability and better adhesion at interface can be expected. Reinforcement of bioplastics with lignocellulosic fibres was carried out to enhance mechanical properties, leading to considerable improvement in the composite tensile strength (Sanchez-Garcia et al., 2008).

Mechanical properties of natural fibre-reinforced thermoplastic starch (TPS) composites were studied by Ma et al. (2005). From the comparison of the tensile strength and elongation percentage of the fibre reinforced TPS with different fibre contents to those of pure TPS matrix, it was found that as fibre content increased, the initial tensile strength was increased. However, the application of fibre made the elongation percentage decrease. The increase in tensile strength was due to the strong intrinsic adhesion of the fibre–matrix interface caused by chemical similarity of starch and cellulose fibre (Ma et al., 2005). It was also observed in the study that with the increase of fibre contents, TPS gave a reducing elongation percentage over the whole range of water contents. This behaviour was due to the highly crystalline hydrophobic character of the cellulose fibres compared to starch hydrophilic property. TPS with improved thermal stability was also obtained, probably due to the higher and longer thermal resistance of cellulose fibre (Ma et al., 2005).

According to Kim et al. (2008), with increasing wt% of wood fibres, the tensile strength of the PP/wood fibre composites decreased due to the weak interaction between PP and wood fibre. With an addition of 10 wt% cotton fibre in PP/cotton composites, the resulted tensile strength decreased. However, the tensile strength increased with the addition of 20 and 30 wt% cotton fibres, which was said being due to the entanglement of cotton fibre when its content was above 10 wt%.

Alemdar et al. (2008) mentioned that a way to improve the thermal and mechanical properties of starch was by the addition of natural fillers. The mechanical properties of a fibre-reinforced polymer composite are dependent on both the properties of the constituents and the properties of the region surrounding the fibre known as the interphase. As stress transfer from the matrix to the fibre takes place at such interphase, it is vital to characterise its properties to better understand the performance of the composites (Herrera-Franco and Valadez-Gonzalez, 2005).

As a flaw-free material is extremely difficult to produce and cracks may be introduced during service, the understanding on crack resistance ability is also essential. Crack stopping capability and good toughness are particularly important. Wong et al. (2010) mentioned that toughness of a brittle thermosetting polymer such as epoxy and polyester can be improved through natural fibre reinforcement.

Kenaf/poly(L-lactide) (PLA) composites were investigated with different fibre proportions. It was found that tensile and bending strength as well as Young’s modulus increased linearly up to the fibre content of 50%. Kenaf/PLA composites had also been produced by melt-mixing and injection moulding with fibre mass contents ranging between 0% and 30%. At 30% of fibre mass contents, the tensile strength improved by 30% (John and Thomas, 2008; Graupner et al., 2009).

Compression-moulded PLA laminated composites reinforced with kenaf produced by film stacking method was examined for the influence of silane-treatment and alkalization of kenaf fibre on the composites’ mechanical and thermal properties. The mechanical properties were improved by both treatments. Better adhesion between treated fibres and matrix was shown in scanning electron microscopy (SEM). In the study of the mechanical properties of compression moulded composites with different volume fractions and the effects of alkali treatment on the fibre surface morphology of hemp, the best results were obtained with 40% volume fraction of the alkali-treated fibre bundles (Graupner et al., 2009).

Thermal properties of green composites have been studied intensively by researchers. For instance, the thermal stability of PLA composites with rice straw fibre modified by poly(butyl acrylate) was investigated by Qin et al.

(2011). Thermogravimetric analysis results confirmed that thermal stability of PLA/rice straw fibre composites increased with increasing amount of PBA. In the analysis of sisal fibre-reinforced rubber seed oil-based polyurethane composites, it was observed that good fibre–matrix interaction caused improved thermal stability of the composite (Bakare et al., 2010).

Besides mechanical and thermal properties, lignocellulosic materials appear to be suitable reinforcing agents or fillers for biodegradable matrices due to other criteria such as a wide variety of feedstocks available throughout the world, non-food agricultural-based economy and low energy consumption (Sanchez-Garcia et al., 2008).

However, studies have shown that the presence of moisture could cause degradation of the mechanical properties of natural fibre reinforced composites to a larger extent compared to synthetic fibre reinforced composites, as a result of the organic nature and the higher moisture sorption behaviour of natural fibres (Thwe and Liao, 2003). In addition, low microbial resistance and susceptibility to rotting were also a restriction to the successful exploitation of biofibres for durable composite application. These properties cause serious problems during shipping, storage and processing of composite. Moreover, as vegetable fibres degrade at higher temperatures, processing temperature of composites is usually restricted to 200 ^{o}C. This limitation restricts the choice of matrix material (John and Thomas, 2008). According Nishino et al. (2004), the fact that incorporated fibres would overheat and lose their high-performance characteristics during processing of the melted matrix has become the biggest problem faced in the manufacturing of these types of composites.

Plant fibres cannot be processed like thermoplastic polymers in general due to the high degree of crystallinity of cellulose and the three-dimensional net structure of lignin. They have to be converted into thermally formable materials through certain substitution reactions on the side chains of cellulose in association with partial removal of lignin (Zhang et al., 2005). Moreover, the usually polar fibres have inherently low compatibility with non-polar polymer matrices, especially with hydrocarbon matrices such as polyethylene and polypropylene (Xie et al., 2010b). With the presence of hydroxy and other polar groups in natural fibre, weak interfacial bonding between fibres and hydrophobic polymer matrices due to high water uptake would result in low mechanical properties of the composite (Thwe and Liao, 2003). When composites are composed of two chemically foreign components, an interface is needed between the fibre and the matrix. The interface often brings serious problems such as poor adhesion and water uptake by the composites (Nishino et al., 2004).

2.6.1 Bamboo Fibre

Bamboo fibres are more popular among the natural fibres due to their high strength (Kinoshita et al., 2009). They are known as one of the most attractive reinforcement in polymer matrix (Nayak et al., 2009). Bamboo fibre is recognized as an attractive candidate as a strengthening natural fibre and may play an important role in forming future organic structures and composites (Liu et al., 2010). Kinoshita et al. (2009) mentioned that the excellent mechanical properties of bamboos should be effectively utilised from the viewpoint of the effective utilisation of natural resources.

There were studies on properties such as tensile strength, modulus, tear strength and elongation at break of bamboo-fibre-reinforced natural rubber composites, with and without the presence of a bonding agent. It was found that the presence of bonding agent gave shorter curing time and enhanced mechanical properties. The flexural strength value of laminates, with reformed bamboo plate at the bottom as a tensile layer and fibre-reinforced mortar sheet on top as a compressive layer, was improved to greater than 90 MPa. Recently, analysis on PP based composites using steam exploded bamboo fibres showed that tensile strength and modulus increased by about 15% and 30%, respectively (Rao and Rao, 2007). In fact, Rao and Rao (2007) stated that the use of silane coupling agent has positive effect on curing characteristics and mechanical properties of bamboo fibre filled natural rubber. It was concluded that the presence of a silane coupling agent improves the adhesion between the fibre and rubber matrix and consequently enhances the tensile strength, tear strength, hardness and tensile modulus. The use of bamboo fibre as reinforcement in structural concrete elements has also been explored by researchers recently (John and Thomas, 2008).

2.7 Mechanical Properties of Some Commercial Polymers and Biopolymers

For the great bulk of commercial polymer, mechanical properties are of fundamental interest. Although other properties, such as thermal stability, flame resistance and chemical resistance are of concern in more specialised applications, all polymers regardless of use must exhibit a specified range of mechanical properties suitable for application (Stevens, 1999). Polystyrene, poly(methyl methacrylate) and unmodified unplasticised PVC are rated as brittle, breaking with sharp fracture, whereas low-density polyethylene and plasticised PVC are considered tough (Brydson, 1999).

Many proteins and polysaccharides form materials with useful material properties. Materials from native biopolymers generally have good mechanical properties (Emmambux et al., 2003). Polycaprolactone has low tensile strength but high elongation at breakage. Poly(L-lactide), an optically active form of PLA, has good tensile strength, low extension and a high modulus (Nair et al., 2007).

Table 2.1: Mechanical properties of some commercial polymers (Stevens, 1999)

Polymer	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)
Polyethylene, low density	31	283	650
Polyethylene, high density	31	1090	1200
Polypropylene	41	1720	600
Poly(vinyl chloride)	52	4140	80
Polystyrene	52	3280	3
Poly(methyl methacrylate)	76	3240	10
Polytetrafluoroethylene	34	552	400
Nylon 66	83	-	300
Poly(ethylene terephthalate)	72	4140	300
Polycarbonate	66	2380	110

Table 2.2: Mechanical properties of some commercial biopolymers (Averous, 2012)

Biopolymer	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)
Polylactic acid	-	2050	9
Poly(hydroxybutyrate-valerate)	-	900	15
Polycaprolactone	14	190	>500
Poly(ethyl acrylate)	17	262	420
Poly(butylene adipate-co-terephthalate)	9	52	>500

2.8 Research and General Applications of Biopolymer and Biopolymer Composite

A variety of renewable biopolymers such as proteins, polysaccharides, lipids, and their composites, derived from animal and plant resources have been investigated for the development of edible/biodegradable packaging materials to substitute for their non-biodegradable petrochemical-based counterparts (Rhim and Ng, 2007). The use of biopolymer and biopolymer composite has extended to almost all fields.

The construction industry has become a major field of use for biopolymers. Bio-based composite roof structures were successfully fabricated from soy oil-based resin and cellulose fibres in the form of paper sheets made from recycled cardboard boxes. This recycled paper was previously tested in composite sheets and structural unit beams and was found to give the required stiffness and strength required for roof construction (John and Thomas, 2008).

Bioplastic has been developed as films packaging for food products, loose film used for transport packaging, service packaging like carry bags, cups, plates and cutlery, biowaste bags, in agri- and horticultural fields like bags and compostable articles (Siracusa et al., 2008). The use of degradable plastics in mulching films for the growing of vegetables and soft fruits has become an important economic tool in commercial horticulture. Mulching films made from conventional plastics have to be removed from the fields before the next planting season as they would interfere with root growth and reduce crop yields. However, with degradable films, disintegration is programmed to commence at the time of cropping (Scott, 2002). Bilck et al. (2010) developed biodegradable film by extrusion from cassava starch and poly(butylene adipate-co-terephthalate) blends to use as mulching film in strawberry production. They found out that the film produced very similar quality and average fruit fresh weight (weight of fruit when sampled without losing water) to polyethylene film. Degradable mulch is also used in cereal growing, in forestry and environmental improvement schemes (Scott, 2002).

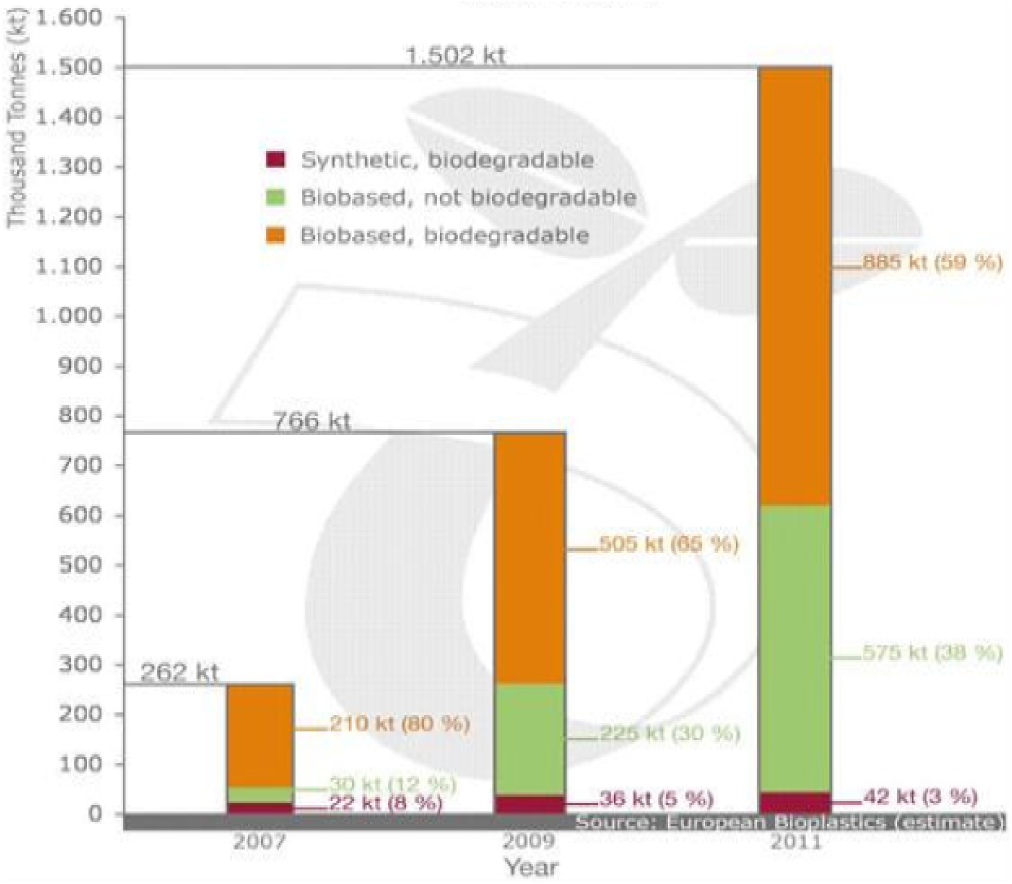


Figure 2.3: World bioplastics production (estimated) 2007 – 2011 (Interplast, 2007)

Biopolymer-based packaging materials have some beneficial properties as packaging materials in improving food quality and extending the shelf-life through minimizing microbial growth in the product. A variety of active packaging technologies have been developed to provide better quality and safe foods and also to limit package-related disposal problems and environmental pollution. Active packaging is a type of packaging that changes the condition of the packaging to improve the safety or sensory properties or to extend shelf-life while maintaining the quality of the food (Rhim and Ng, 2007).

Currently, several types of bio-based polymers found in the market such as starch materials, cellulose materials, PLA and polyhydroxy acid, are produced by different manufacturers. They are used principally as films or moulding materials. Until now, polyhydroxy acid polymer is a very expensive polymer because it is commercially available in very limited quantities. PLA is becoming a growing alternative as green food packaging materials because it was found that in many situations it performs better than the synthetic ones, such as oriented polystyrene and PET materials. Starch can be transformed into a foamed material using water steam, thus replacing the polystyrene foam as packaging material. Polycaprolactone is a thermoplastic polymer with good chemical resistance. It is easy to process and has a very short degradation time. It could be mixed with starch to obtain a good biodegradable material at a relatively low price, for the use as trash bags (Siracusa et al., 2008).

Polysaccharide-derived films have excellent gas permeability properties, resulting in desirable modified atmospheres that enhance the shelf life of the product without creating anaerobic condition. Besides, polysaccharide coatings and films can be used to extend the shelf-life of muscle foods by preventing surface browning, dehydration and oxidative rancidity. Although these films can exhibit low gas permeability, their hydrophilic nature makes them poor barriers for water vapour. Polysaccharide films have been available commercially for the Japanese meat industry for a number of years. When applied to wrapped meat products and subjected to steam and smoking, the films actually dissolves and becomes integrated into the meat surface. Meats treated with the polysaccharide film in this manner exhibited higher yields, improved structure and texture, and reduced moisture loss (Cutter, 2006).

Nature Seal, a type of cellulose based coating that was adjusted to a pH of 2.5-3.0 with an acidulant had been used to coat fresh cut potato and apple for better browning and microbial control. Chitosan was coated on fresh strawberries to form firmer fruit with high titratable acidity, better colour retention and decrease in respiration rate and fruit decay. Moreover, significant decrease in inoculated *Salmonella montevideo* by two log cycles on fresh tomato skin was achieved by the use of cellulose based coating with acetic and citric acid. The application of mineral oil based coating was proven to lower respiration rate and better colour firmness retention in green bell peppers (Emmambux et al., 2003).

CHAPTER 3

MATERIALS & METHODS

3.1 Materials

Sodium alginate was obtained from Sigma–Aldrich, USA. The monomers, acrylamide and butyl acrylate and the crosslinker, *N*,*N*-methylenebisacrylamide (*N*-MBA) were obtained from Sigma–Aldrich, USA. Calcium carbonate (Uni-Chem Chemical Reagents, USA) and calcium chloride (Systerm, Malaysia) were used as particulate filler. Dry bamboo leaves collected from the campus of Universiti Tunku Abdul Rahman, Kampar, Perak, Peninsular Malaysia were used as fibrous filler while oxalic acid (Merck, Germany) was employed to extract fibre from the bamboo leaves.

Potassium persulfate (Systerm, Malaysia) and sodium formaldehyde sulfoxylate (Sigma–Aldrich, USA) were used as redox initiators. Both glycerol and ammonia 25% were provided by Merck, Germany. Acetonitrile (Mallinckrodt Chemicals, USA), dimethylformamide (Fischer Scientific, USA), chloroform (Systerm, Malaysia) and toluene (J. T. Baker, Mexico) were used as solvents in solubility test.

3.2 Gelatinisation of Sodium alginate

Sodium alginate was mixed with 120 mL of distilled water in different addition sequence (water added into sodium alginate, W+SA and sodium alginate added into water, SA+W). The mixture was stirred and heated at 80 ^{o}C for 30 minutes to form gelatinised sodium alginate. The gelatinised sodium alginate was adjusted to pH 9 by adding 2 mL of liquid ammonia into it. The solution was cooled to 45 ^{o}C for later use.

3.3 Preparation of Hybrid Polymer (HP)

HP was prepared by mixing in sequence 260 mL of distilled water, different amount of acrylamide and butyl acrylate (1: 9 – 9: 1 acrylamide to butyl acrylate ratio), variable amount of *N*-MBA (1, 2, 3, 4, 5 and 10 wt% of total monomer), 1 g potassium persulfate and 1 g SFS, into the gelatinised sodium alginate of variable amount (1: 0.16 – 1: 0.73 monomer to sodium alginate ratio) with variable stirring speed (300 – 1400 rpm) for a certain duration (30 and 90 minutes) and at a certain reaction temperature (50, 60, 70 and 80 ^{o}C). The hybrid polymer solution was then filtered to remove any un-dissolved particles.

3.4 Preparation of Hybrid Polymer-Fibre Composite (HPFC)

3.4.1 Preparation of Bamboo Leaves

The dry bamboo leaves (Figure 3.1) were washed with water to remove impurities such as sand and dried in air. Then, they were cut into 2 – 5 cm in size for storage in a refrigerator.

Figure 3.1: Dry bamboo leaves

To extract fibre from bamboo leaves, dry bamboo leaves with 2 – 5 cm in size were cooked with oxalic acid (at 6% of raw material dry weight) and distilled water (at distilled water to raw material ratio of 112.5) at 100 ^{o}C for 75 minutes under proper stirring. Cooked sample was washed with distilled water to remove residual cooking liquor. It was then blended at 22000 rpm for 10 minutes to form a fibre-water mixture. Excess water was removed by centrifugation and the fibre was dried in an oven. Fibre with different sizes was obtained by sieving it through different mesh sizes (100, 150 and 300 μm).

3.4.2 Fibre In-situ Addition

In preparing HPFC by fibre in-situ addition, the mixture of 260 mL of distilled water, variable amount of bamboo leaf fibre (5, 10, 15 and 20 wt% based on theoretical total solid content of hybrid polymer, 1.42 g of acrylamide (0.01mol), 23.08 g butyl acrylate (0.09 mol), 5 wt% *N*-MBA, 1 g potassium persulfate and 1 g SFS was added into the gelatinised sodium alginate slowly and stirred for 90 minutes at 50 ^{o}C. The HPFC solution was filtered to remove any un-dissolved or large particles.

3.4.3 Fibre Post Addition

In preparing HPFC by fibre post addition, variable amount of bamboo leaf fibre (5, 10, 15 and 20 wt% of polymer total solid) was incorporated into the synthesised HP with 5 wt% *N*-MBA and stirred (1000 rpm) for 90 minutes at 50 ^{o}C. The HPFC solution was filtered to remove any un-dissolved or large particles.

3.5 Preparation of Hybrid Polymer-$CaCO_3$ Composite (HPCC)

HPCC was prepared by mixing 260 mL of distilled water, 1.42 g of acrylamide (0.01 mol), 23.08 g butyl acrylate (0.09 mol), variable amount of

$CaCO_3$ (1, 2, 3, 4, 5 and 10 wt% of total monomer), 1 g potassium persulfate and 1 g SFS into the gelatinised sodium alginate slowly and stirred (1000 rpm) for 90 minutes at 50 ^oC. The HPCC solution was then filtered to remove any un-dissolved particles. The pH of HPCC was adjusted with ammonia (25%) to pH 7, 8, 10 and 12.

3.6 Preparation of HP and Composites Film

HP and composites solution was poured into a shallow rectangular plastic mould and left to dry at 27 ^oC or 50 ^oC to form a thin film of about 0.05 – 0.2 mm in thickness.

3.7 Ca^{2+} and Glycerol Post-treatment

3.7.1 Surface Treatment with $CaCl_2$ and Glycerol

HP films were immersed in a solution containing $CaCl_2.2H_2O$ (1 – 10 wt% of dry polymer) and glycerol (5 and 10 wt% of dry polymer), respectively, for 10 minutes and left to dry at 50 ^oC.

3.7.2 Homogeneous Mixing with Ca^{2+} and Glycerol

HP emulsion was added with $CaCl_2.2H_2O$ or $CaCO_3$ (1 – 30 wt% of dry polymer) and glycerol (10 wt% of polymer total solids content), respectively, and stirred for 10 minutes to give a homogeneous mixture. A film was then prepared as described in Section 3.6.

3.8 Products Characterisation

3.8.1 Mechanical Properties

The tensile strength, percentage elongation at break and Young's modulus of the HP and composites films were measured with Instron Microtester 5848 (static load cell of +/- 2 kN) at room temperature, 27 ^{o}C. All measurements were performed with at least three replicates of rectangular specimen (50 mm long, 15 mm wide and 0.05 – 0.2 mm thick) at the extension rate of 1.5 mm/min. Measurements of three replicates with the closest values were averaged to give the final results.

3.8.2 Swelling and Solubility in Various Solvents

The HP and HPCC films were weighed (W_0), immersed in 50 mL each of 5 different solvents; water, acetonitrile, dimethylformamide, chloroform and toluene, at 25 ^{o}C, and shaked with an orbital shaker at 200 rpm for 24 hours. After that, the wet samples were carefully blotted between filter paper to remove the excess solvent from the surface, immediately weighed (W_1) and then dried at 50 ◦C to constant weight (W_2). The extend of swelling and solubility of the films were calculated according to the following equations:

$$\text{Swelling (\%)} = [(W_1 - W_2) / W_2] \times 100 \qquad \text{(Eq. 3.1)}$$

$$\text{Solubility (\%)} = [(W_0 - W_2) / W_0] \times 100 \qquad \text{(Eq. 3.2)}$$

where W_0, W_1 and W_2 are the original, wet and dry weights of the samples, respectively.

3.8.3 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of HP and composites films were taken in the wavenumber region between 400 and 4000 cm^{-1} at room temperature, using a Perkin Elmer Fourier transform infrared spectroscopy Spectrum RX1. FTIR analysis of bamboo leaf fibre was done with KBr disc.

3.8.4 Thermo Gravimetric Analysis (TGA)

TGA analysis on HP and composites films was carried out with Mettler Toledo thermo gravimetric analyser TGA/SDTA851^{e}. Analyses were performed with 2-3 mg of HP, HPFC and bamboo leaves fibre samples under nitrogen atmosphere at a heating rate of 10 ^{o}C/min from 30 to 600 ^{o}C. HPCC sample of 2 to 3 mg was scanned from 30 to 900 ^{o}C at the same heating rate in nitrogen atmosphere.

3.8.5 Scanning Electron Microscopy (SEM)

SEM images of HP and composite films were taken with JEOL field emission scanning electron microscope JSM-6701F to examine the morphology and surface features of the samples at room temperature. The samples were deposited on a brass holder and sputtered with a thin coat of platinum under vacuum. The acceleration voltage was 2 kV for HP and 10 kV for HPFC and HPCC with the secondary electron image as a detector.

CHAPTER 4

RESULTS & DISCUSSION

4.1 Preparation of Hybrid Polymer (HP) and Composites

4.1.1 Gelatinisation and Graft Polymerisation

In the preparation of HP and composites, sodium alginate was chosen as the grafting matrix because it can form strong and flexible films compared to other type of polysaccharides. Although sodium alginate has poor resistance to water due to their hydrophilic nature, it can react with divalent cations to form insoluble solids (da Silva et al., 2009). Active groups, such as hydroxyl and carboxyl, in the carbohydrate can form hydrogen bonding or undergo condensation reaction to form a cross-linked structure. It was found that better mechanical properties of sodium alginate film is due to a more effective crosslinking by alginate polymeric matrix compared to pectin (da Silva et al., 2009). Comparing to starch films that are typically very brittle, the use of too much starch in composite preparation lowered the flexibility of the film and affects its mechanical properties (Xu et al., 2005).

Similar to the concept of starch gelatinisation, sodium alginate was cooked in water at 80 ^{o}C for half an hour to break down the granules into a mixture of polymers-in-solution (Ratnayake and Jackson, 2009). Fang and Fowler (2003) explained that no depolymerisation occurs when gelatinisation takes place in an abundance of water at temperatures below 100 °C. In the presence of water and heat, gelatinisation is vital to break down the intermolecular bonds of the molecules and form thermoplastic material (Prachayawarakorn et al., 2010) that mix well with monomers and fibres. As the gelatinised alginate cooled to 45 ^{o}C, the dispersed matrix forms a paste like mass that functioned as an adhesive or binding agent (Said, 2010).

Graft copolymerisation of acrylamide and butyl acrylate monomers on alginate backbones was achieved by using chemical means. In the chemical process, the role of initiator is very important in determining the path of the grafting process (Bhattacharya and Misra, 2004). The use of redox initiators, namely oxidising ion, potassium persulfate ($K_2S_2O_8$) and reducing agent, sodium formaldehyde sulfoxylate (CH_3NaO_3S) is useful in initiation of low-temperature polymerisation and emulsion polymerisation. According to Li et al. (2010), redox initiators can produce radicals at reasonable rates to initiate radical vinyl polymerisation even at low temperature.

Graft copolymerisation is started with the creation of active centres on alginate by radicals resulting from the redox reaction between reductant and oxidant. It is possible that free radicals are produced by one-electron transfer reactions in the aqueous phase of the emulsion polymerisation (Stevens, 1999). Lanthong et al. (2006) stated that the mechanism of graft copolymerisation of acrylamide and itaconic acid onto cassava starch via the redox system involved chain transfer reaction. Side chain grafts of acrylamide and butyl acrylate are covalently attached to the main chain of alginate backbone through these active centres to form branched copolymer (Dahou et al., 2010). The use of crosslinker was vital to link sodium alginate-*graft*-poly[acrylamide-*co*-(butyl acrylate)] polymer chains together to form three-dimensional network. According to Lanthong et al. (2006), crosslinking reaction takes place through any site in the growing polymer chains by opening the double bonds of the two vinyl groups of *N,N*-methylenebisacrylamide. Whereas, calcium ion binds with carboxylate groups of alginate in a planar two-dimensional manner, producing the so-called "egg-box" structure (Pathak et al., 2010).

The use of higher ratio of butyl acrylate to acrylamide (9:1) was justified in creating HP and composites films that were flexible enough to be peeled off from the mould. Preliminary attempts of using butyl acrylate-acrylamide at the ratios of 1:9 and 5:5 in polymerisation were found to form films that were too brittle to be useful. Butyl acrylate was found to have the ability to modify the compatibility between the hydrophilic cellulose fibre and the hydrophobic polymer. Poly(butyl acrylate) is a very soft polymer that could be adsorbed and coated on polysaccharide (Qin et al., 2011).

4.1.2 Fibre Extraction

In extracting fibre from bamboo leaves, semi-chemical pulping, which combines both chemical and mechanical pulping, was applied to produce high yield of good quality pulp. Bamboo leaves were reduced to 2-5 cm in length as appropriate size is important for effective cooking process. Oxalic acid was used to remove pulp from the bamboo leaves chemically during cooking before the cooked material was mechanically defibreised by blending at high speed.

Extracted fibre was added together with the monomers while the latter was graft-polymerised onto sodium alginate. The fibre acts as reinforcement to the prepared polymer film.

4.1.3 Thin Film Formation and Post Treatment

HP and composites films were prepared using casting and solvent evaporation method. HP films crosslinked with *N*-MBA were more transparent than the composite films crosslinked with Ca^{2+}. Brown-coloured films were obtained when the polymer was incorporated with bamboo fibre.

Polymer films post treated with different concentrations of $CaCl_2$ were also prepared. However, these films were found too brittle and too hard for analysis using microtester for mechanical properties. Hence, glycerol, which served as plasticiser, was added to improve film flexibility and to decrease brittleness, as suggested by da Silva et al. (2009) and Guerrero and de la Caba (2010). Glycerol was also used to treat the films for the purpose to increase the extension ability of the films.

In the preparation of the post treated homogenous films, the viscosity of HP mixture increased rapidly as the concentration of $CaCl_2$ and $CaCO_3$

increased. The polymer mixture has become too viscous to be further processed when more than 5 wt% of $CaCl_2$ was added into it. Comparatively, up to 30 wt% of $CaCO_3$ could be added into the polymer mixture without causing it to become too viscous. Similar findings were also reported by Rhim (2004).

4.2 Characterisation on Mechanical Properties

Tensile strength of HP and composites films measures the mechanical resistance due to the cohesion between polymer chains. Plasticity of the films are analysed by the elongation at break value, which is the capacity of the film to extend before breaking (da Silva et al., 2009). The stiffness or the ratio between stress and strain of a material at the elastic stage of a tensile test is indicated by Young's modulus (Ibrahim et al., 2010).

4.2.1 Effect of Monomer to Sodium Alginate Ratio

The mechanical properties of the polymer films with different monomer to sodium alginate ratios are shown in Table 4.1. It was found that the monomer to sodium alginate ratio of 1: 0.24 gave the highest tensile strength of 17.7 MPa with Young's modulus of 700.8 MPa. Attempts with monomer to sodium alginate ratios of 1: 0.49 and 1: 0.73 failed to increase the tensile strength and Young's modulus (Table 4.1). Isiklan et al. (2010) observed that grafting parameter increased initially with an increasing percentage of sodium alginate up to 1.5 g/dL and thereafter decreased with further increase in its percentage.

The increase in grafting efficiency could be attributed to the increase in the number of sodium alginate macro radicals available for grafting with the increase in sodium alginate quantity (Isiklan et al., 2010). Therefore, with higher grafting parameter of acrylamide and butyl acrylate to sodium alginate, the affinity and dispersion of monomers in the matrix are better as more of the monomers could form three-dimensional cross-link networks with sodium alginate. Thus, mechanical strength is increased. Similar explanation has been stated in the grafting of poly-glycidyl methacrylate and aluminum oxide onto epoxy resin (Jiao et al., 2009).

Table 4.1: Mechanical properties of HP grafted with different monomer to sodium alginate ratio

Monomer to sodium alginate ratio	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
1 : 0.16	2.2 ± 0.2	14.5 ± 3.7	43.5 ± 2.6
1 : 0.24	17.7 ± 2.3	7.8 ± 4.2	700.8 ± 152.4
1 : 0.49	7.4 ± 1.1	47.3 ± 11.8	28.2 ± 8.2
1 : 0.73	14.0 ± 2.2	29.7 ± 13.7	192.3 ± 64.2

Reduction in the grafting value could be due to the increase in the viscosity of the reaction medium, which limits the movement of the initiators. Besides, high amount of sodium alginate macro radicals could interact with one another to terminate the reaction, thus lowering both graft yield and grafting efficiency (Isiklan et al., 2010). More sodium alginate intra-molecular bonds rather than inter-molecular bonds are formed resulting in a phase separation between sodium alginate and monomers. Thus, tensile strength decreased beyond the optimum quantity of the carbohydrate.

The elongation at break of the HP film with different quantity of sodium alginate gave an opposite result as compared to the tensile strength value. The maximum, 47.3% was obtained at monomer-sodium alginate ratio of 1: 0.49. When the ratio increased to 1: 0.73, the elongation at break decreased to 29.7%. At the monomer to sodium alginate ratio of 1: 0.24, the film had the lowest value of elongation at break, 7.8%, as compared to its highest tensile strength. According to da Silva et al. (2009), it is normal for films with high tensile strength to have low elongation at break as shown in Table 4.1.

4.2.2 Effect of Addition Sequence of Water and Sodium Alginate

The effect of different addition sequence of water and sodium alginate during gelatinisation, before the grafting process, on the mechanical properties of the composite films was investigated. Hybrid polymer-$CaCO_3$ composites (HPCC) prepared with the addition of sodium alginate into water had better tensile strength (Figure 4.1) and elongation at break (Figure 4.2) than the composites synthesised with the opposite sequence. The addition of sodium alginate powder into water (SA+W) during the gelatinisation process was found to give positive effect in terms of tensile strength due to better dispersion and dissolution of sodium alginate.

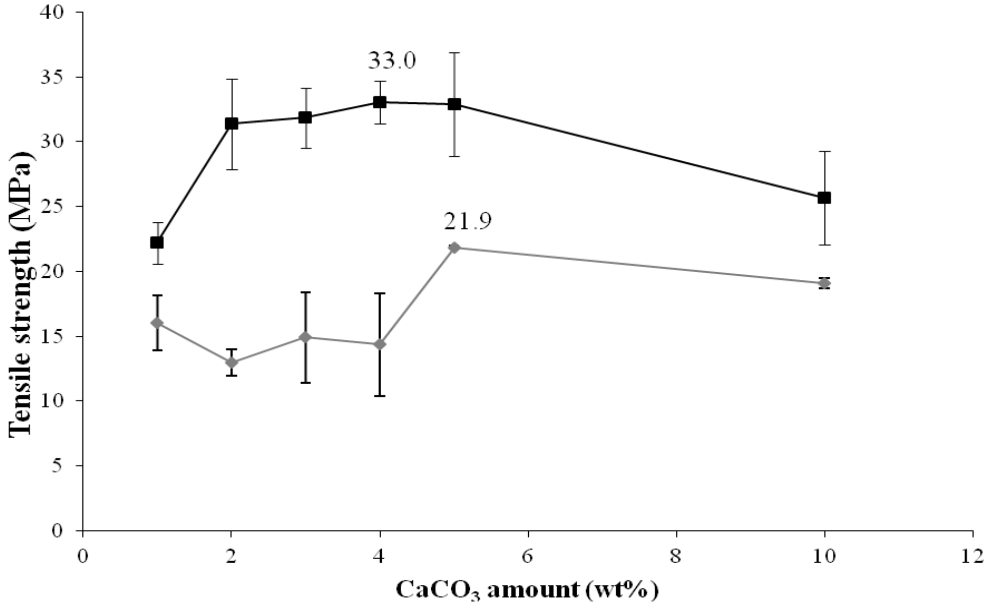


Figure 4.1: The effect of addition sequence of water (W) and sodium alginate (SA); W+SA (▲) and SA+W (■) on the tensile strength of HPCC against different amount of calcium carbonate

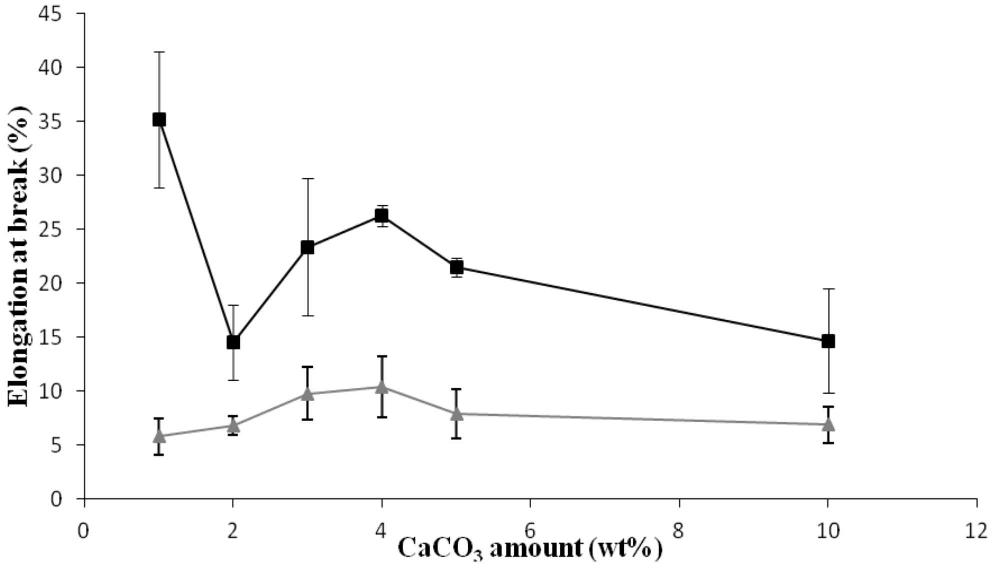


Figure 4.2: The effect of addition sequence of water (W) and sodium alginate (SA); W+SA (▲) and SA+W (■) on the elongation at break of HPCC against different amount of calcium carbonate

4.2.3 Effect of Reaction Time

In graft copolymerisation, reaction time plays an important role. Grafting of sodium alginate was carried out with two polymerisation times, with monomer to sodium alginate ratio of 1: 0.24, and the results are shown in Table 4.2. The results show that 30 minutes of reaction time gave film with lower tensile strength, 10.8 MPa and Young's modulus, 235.4 MPa compared to that polymerised for 90 minutes with the tensile strength of 17.7 MPa and Young's modulus of 700.8 MPa. Longer polymerisation duration allows the chain length of branches grafted on the sodium alginate backbone to grow longer. Thus, the addition of monomer molecules to the growing grafted chains increases (Isiklan et al., 2010) and the mechanical properties of the polymer improved.

Table 4.2: Mechanical properties of HP processed with different reaction time

Reaction time (minutes)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
30	10.8 ± 1.0	20.7 ± 2.7	235.4 ± 33.6
90	17.7 ± 2.3	7.82 ± 4.2	700.8 ±152.4

In graft polymerisation of acrylamide onto xanthan gum, Behari et al. (2001) suggested that there may be an addition of a greater number of monomer molecules to the growing grafted chain with increasing time. Pulat and Babayigit (2001) grafted acrylamide and itaconic acid were grafted onto polyurethane using benzoyl peroxide as the initiator. They reported that the optimum reaction time for acrylamide and itaconic acid was 1 and 2 hours, respectively.

4.2.4 Effect of Processing Temperature

4.2.4.1 Reaction Temperature

With the monomer to sodium alginate ratio of 1: 0.24, graft polymerisation was carried out at different temperature (50 – 80 ^{o}C) for 90 minutes. The HP films obtained were then tested mechanically in order to identify the optimum polymerisation temperature. It was found that the reaction temperature of 50 ^{o}C produced film with the highest tensile strength, 20.5 MPa (Figure 4.3).

The kinetics of graft copolymerisation is controlled by the reaction temperature. Although monomeric diffusion processes in the backbone increases with increasing temperature, molecular motion of the system also increases with increased temperature, resulting in increased radical decay. Thus, the number of radicals available for grafting decreases (Bhattacharya and Misra, 2004) and results in lower mechanical strength. Ghosh and Ganguly (1994) explained that at temperature beyond 40 °C, homopolymer formation is more prominent. The grafted-on polymer, formed on the grafting surface at the early stage of the reaction, acts as a physical barrier preventing monomer penetration in the grafting structure in the later stage. Therefore, less graft copolymer is formed while formation of the homopolymer in the aqueous medium increases. With less graft copolymer, less crosslinking would occur between polymer chains.

In addition, further increase in temperature could also result in reaction termination due to enhanced mobility of macroradicals. Above this optimum temperature, the grafting parameters might show a decrease (Behari et al., 2001) and hence, the tensile strength of the polymer would decrease.

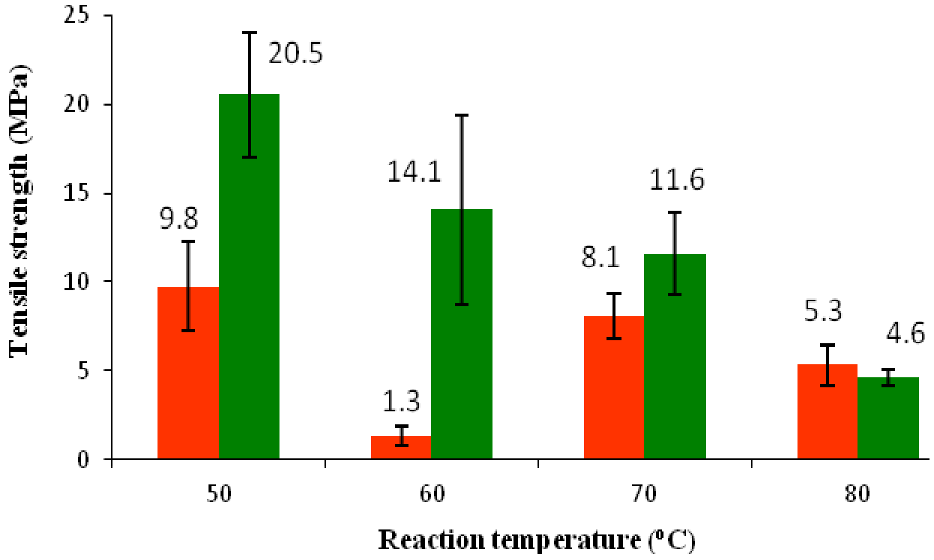


Figure 4.3: The effect of reaction and drying temperatures on the tensile strength of HP dried at 27 °C (🟥) and 50 °C (🟩) respectively

4.2.4.2 Drying Temperature

The polymer prepared at different reaction temperature was cast into film and dried at 27 ^{o}C and 50 ^{o}C respectively. Figure 4.3 shows that drying at 50 ^{o}C formed films with better tensile strength. Figure 4.4 shows that lower drying temperature favoured the formation of film with higher extension ability. According to Ashikin et al. (2010), the plasticity of alginate films increased with a decrease in drying temperature from 60 ^{o}C to 40 ^{o}C. Application of higher drying temperature and relative humidity are vital to the formation of more compact structure and allow reorganisation of the crystalline structure of resistant starch (Yue et al., 1999).

Denavi et al. (2009) found that in the preparation of films from laboratory soy protein isolate, the drying process acts like a thermal treatment for the protein where the unfolding of the molecule occurs.

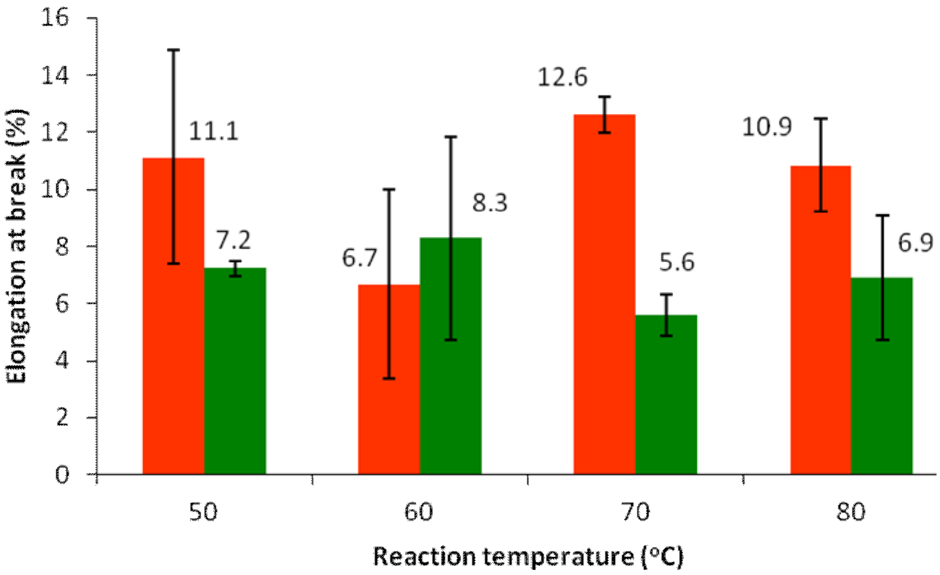


Figure 4.4: The effect of reaction and drying temperatures on the elongation at break of HP dried at 27 °C (🟥) and 50 °C (🟩) respectively

4.2.5 Effect of Stirring Speed

Further analysis was carried out to study the impact of stirring speed on the mechanical properties of the HP film. From Table 4.3, it was found that the stirring speed of 1000 rpm produced the best film in terms of tensile strength (22.6 MPa) and Young's modulus (1098 MPa). Homogeneity of the reaction mass is largely maintained by good bulk movement of the fluid (Choi and Lee, 2010). Thus, the films prepared would have equally distributed network bond with better strength and modulus.

Properties of a heterogeneous system are influenced by its processing and initial turbulence play (Oprea and Dodita, 2001). Good mixing is essential to prevent high local concentrations of the water-soluble monomers in the reaction mixture, as certain components of the reaction are added continuously. Polymer solution that was not homogenous was found to form agglomerates due to insufficient stirring. As monomers could not bond to the polymer backbone efficiently, less crosslinking or grafting was formed between polymer chains. Thus, the mechanical strength of the film suffered (Table 4.3).

Oprea and Dodita (2001) stated that the establishment of the optimum agitation is vital to provide a good dispersion of monomers and at the same time, to avoid foaming and coalescence. In the current research, stirring speed beyond 1000 rpm failed to produce HP films with tensile strength higher than

22.6 MPa. This was probably due to the formation of foam during the polymerisation process.

Table 4.3: Mechanical properties of HP prepared at different stirring speed

Stirring speed (rpm)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
300*	4.5 ± 0.6	7.8 ± 4.2	564.6 ± 142.2
400*	2.4 ± 0.4	36.5 ±13.9	14.1 ± 4.9
600*	2.8 ± 0.8	14.6 ± 5.8	66.4 ± 7.3
800	4.7 ± 1.4	20.4 ± 5.8	82.5 ± 12.4
1000	22.6 ± 0.6	17.9 ± 1.4	1098.0 ± 70.3
1200	20.5 ± 3.5	8.6 ± 1.2	930.8 ± 115.9
1400	8.4 ± 2.1	10.9 ± 2.6	287.2 ± 139.8

*Inhomogeneous product with agglomerates

4.2.6 Effect of Bamboo Leaves Fibre

4.2.6.1 Amount of Fibre

Different amount of bamboo leaf fibre was added into the HP solution with 5 wt% of *N*-MBA at 50 ^{o}C for 90 minutes to form hybrid polymer-fibre composites (HPFC). The results show that increasing amount of fibre had impaired the mechanical properties of the HPFC film (Figures 4.5 – 4.7). According to Mamoor et al. (2009), elongation at break decreases with increase in fibre contents due to resistance offered by fibres in uncoiling of chains. Decreasing Young's modulus and tensile strength might be due to poor adhesion between the fibrous filler and the matrix and thus, poor stress transfer from the matrix to the filler (Ibrahim et al., 2010).

Theoretically, with increase in fibre concentration stress distributes evenly and fibres give reinforcing effect (Mamoor et al., 2009). Herrera-Franco and Valadez-Gonzalez (2005) stated that when fibres are loaded through the matrix, the load must be transferred effectively to the fibre, and in order to achieve that, a strong fibre/matrix bond is required. It was explained that hydrophilic nature of natural fibres adversely affects adhesion to a hydrophobic matrix and may cause a loss of strength. The fibre surface has to be modified in order to promote adhesion (Herrera-Franco and Valadez-Gonzalez, 2005). Chemical treatments with suitable coupling agents are vital to enhance hydrophobicity of natural fibre (Thwe and Liao, 2003). Nishino et al. (2004) proved that mechanical properties were higher for craft pulp composite with pre-treated and impregnated ramie fibres than untreated ones. These were due to the increased interfacial strength resulting from the partial surface dissolving of the pre-treated fibre.

Graft copolymerisation of monomers onto the fibre surface was proposed as one of the ways to modify the natural fibre surface (Herrera-Franco and Valadez-Gonzalez, 2005). In fact, when the matrix and the fibre are composed of the same material, better adhesion at interface can be expected (Nishino et al., 2004). Since both bamboo leaves fibre and sodium alginate are both polysaccharides, good adhesion between these two materials was anticipated. However, in the current study, mechanical properties of the composite film were not improved with fibre. It was assumed that graft polymerisation with butyl acrylate had impaired the bonding between sodium alginate and bamboo leaf fibre.

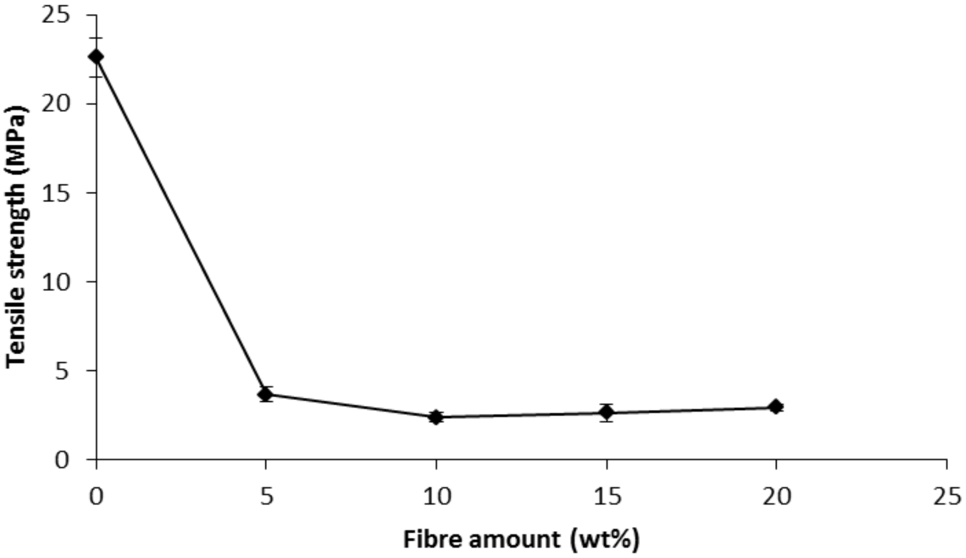


Figure 4.5: The effect of fibre content on the tensile strength of HPFC

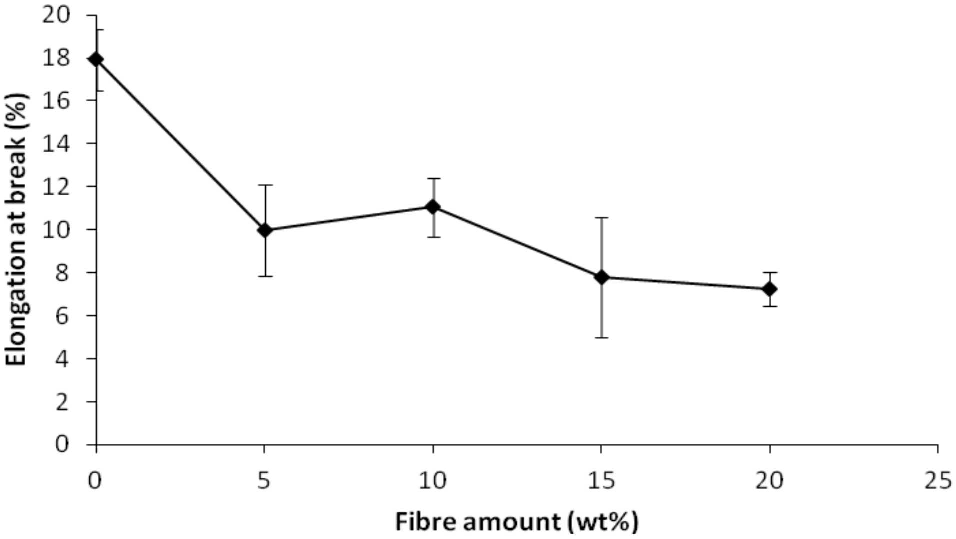


Figure 4.6: The effect of fibre content on the elongation at break of HPFC

Besides, poor strength with the existence of fibre might be due to accumulation of stresses and strains in excess of a threshold level that cause non-uniform anchorage (Ghosh and Ganguly, 1994). Sanchez-Garcia et al. (2008) stated that the tendency of filler to form hydrogen bonding with each other causes a composite with high fibre content in the matrix to form fibre agglomeration, thus poorer mechanical.

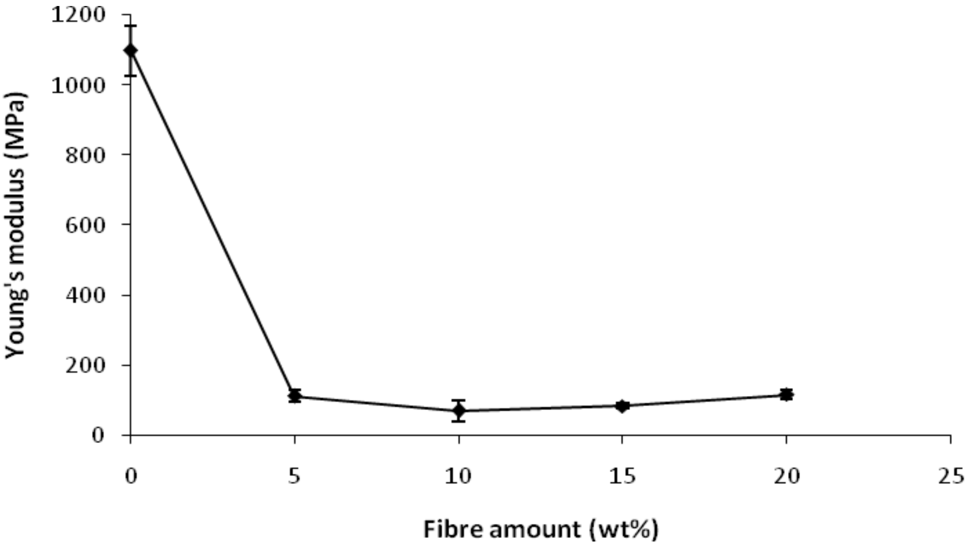


Figure 4.7: The effect of fibre content on the Young's modulus of HPFC

4.2.6.2 Size of Fibre

The effect of fibre size on mechanical properties of the polymer film was investigated by incorporating fibre of different sizes into the polymer matrix. From Table 4.4, the fibre size of 300 μm gave the highest tensile strength of 10.1 MPa and the highest Young's modulus of 408.5 MPa. As the fibre size decreased from 300 to 100 μm, tensile strength and Young's modulus decreased. This may be attributed to insufficient fibre length to enable proper tensile load transfer from the matrix (Thwe and Liao, 2003). According to Barbosa Jr. et al. (2010), for the same proportion of fibre in a composite, a larger number of tips due to shorter fibres can act as tension points, hindering the transfer of the applied load from the matrix to the fibre. Nevertheless, short fibres provide high flexibility in the final product. Besides, Wong et al. (2010) explained that fibre orientation might be a factor to the tensile strength of the composite. Fibre distribution could be affected by fibre length and there is less likely that longer fibres are distributed in transverse direction. As fibre reinforcing effect is always the weakest in transverse direction, poorer tensile properties are often exhibited by shorter fibre length compared to longer fibre length (Wong et al., 2010).

Mechanical improvement could be achieved by reinforcing the matrix at a critical fibre length (Wong et al., 2010), which is 300 μm in this study. In the research of Thwe and Liao (2003), it was observed that further increase in bamboo fibre length to more than 6 mm did not result in an increase in tensile strength and modulus of the polypropylene-bamboo fibre composite. A slight drop in tensile strength and modulus was observed instead. Although tensile stress transfer to the fibre improves with increment in fibre length (Wong et al., 2010), fibre failures may readily occur in a brittle manner (Thwe and Liao, 2003). Further increase in the fibre length leads to no further increase in the transferred stress when the tensile stress in the fibre reaches a maximum. Larger average size of bamboo fibre may lead to poorer compatibility with the matrix (Thwe and Liao, 2003).

Table 4.4: Mechanical properties of HPFC with different fibre size of 5 wt%

Fibre size (µm)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
100	8.2 ± 1.1	8.6 ± 0.8	255.1 ± 81.2
150	8.8 ± 0.6	6.6 ± 0.6	329.3 ± 16.6
300	10.1 ± 0.7	6.9 ± 0.1	408.5 ± 14.9
>300	3.7 ± 0.4	10.0 ± 2.1	112.1 ± 17.1

4.2.6.3 Sequence of Fibre Incorporation

Incorporation of bamboo fibre (with fibre size of 300 µm) during polymerisation (in-situ addition) and after the polymerisation (post addition) was conducted in this study. It was found that post addition of fibre gave better result in terms of tensile strength compared to in-situ fibre addition (Figures 4.8). This indicates that the grafted alginate has better adhesion with bamboo fibre after it has been polymerised with acrylamide and butyl acrylate monomers. For both of the incorporation methods, increasing the amount of fibre impaired the tensile strength (Figure 4.8), elongation at break (Figure 4.9) and Young's modulus (Figure 4.10) of HPFC.

In the in-situ addition, fibre was added together with monomers into gelatinised sodium alginate with the intention to create better adhesion between the matrix and fibre since both fibre and acrylamide monomer are relatively hydrophilic. However, the attempt has failed to improve the mechanical properties of the film. This is probably due to the presence of the more hydrophobic monomer, butyl acrylate, in the system.

In the preparation of poly(lactic acid) composites with rice straw fibre modified by poly(butyl acrylate) (Qin et al., 2011), it was found that excess poly(butyl acrylate) could not be dispersed well in the matrix and caused stress defects. This resulted in poor interfacial adhesion between poly(lactic acid) and modified rice straw fibre, which reduced the mechanical strength of the composite. When the fibre and the matrix are chemically alike, a better adhesion at interface is expected (Nishino et al., 2004).

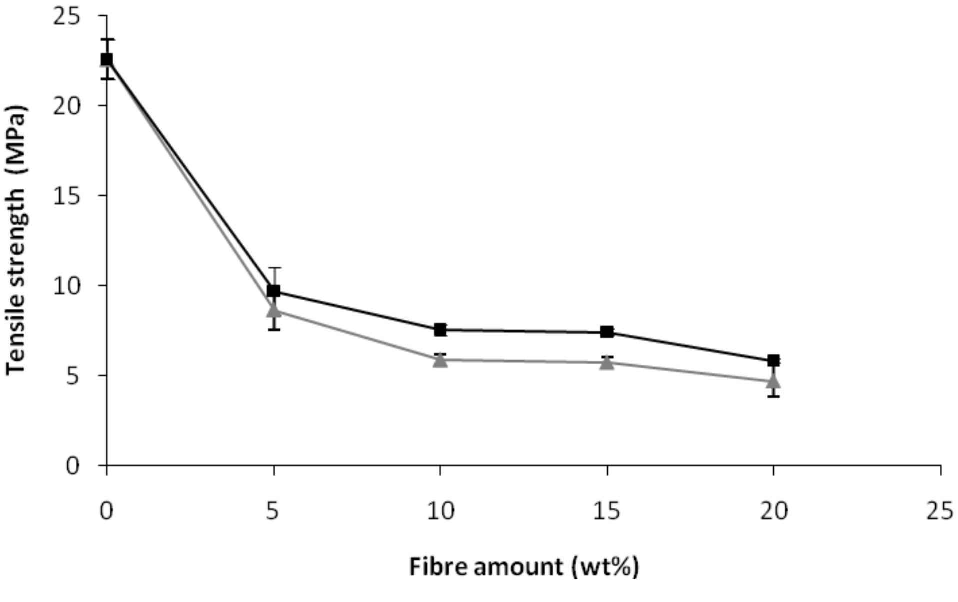


Figure 4.8: The effect of fibre incorporation sequence, insitu (▲) and post (■) addition on the tensile strength of HPFC

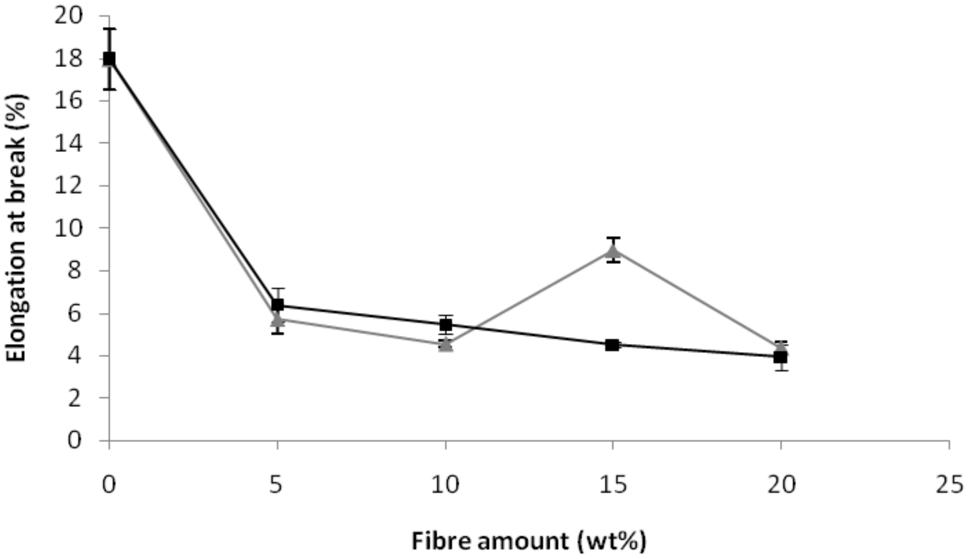


Figure 4.9: The effect of fibre incorporation sequence, insitu (▲) and post (■) addition on the elongation at break of HPFC

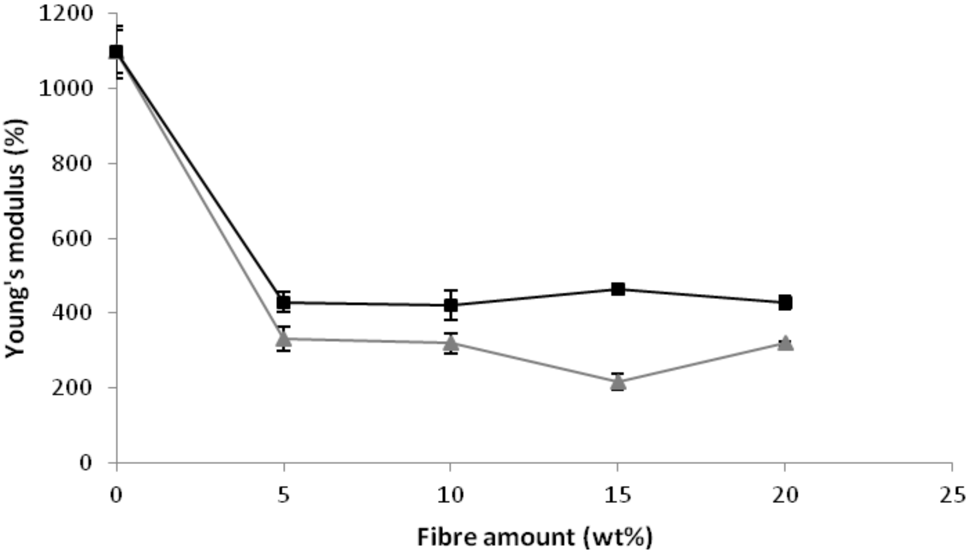


Figure 4.10: The effect of fibre incorporation sequence, insitu (▲) and post (■) addition on the Young's modulus of HPFC

4.2.7 Effect of Crosslinker

4.2.7.1 Type of Crosslinker

Different types of crosslinker, namely *N*,*N*-methylenebisacrylamide (*N*-MBA), calcium carbonate ($CaCO_3$) and calcium chloride ($CaCl_2$) were incorporated at the amount of 1 wt% during the graft polymerisation of acrylamide and butyl acrylate with sodium alginate. Hybrid polymer composite incorporated with calcium carbonate had the highest tensile strength of 22.20 MPa and Young's modulus of 674.88 MPa (Table 4.5). The use of calcium chloride as crosslinker gave the highest extending ability, which was 23.69% (Table 4.5).

Table 4.5: Mechanical properties of HP incorporated with 1 wt% of different types of crosslinker

Type of crosslinker (1wt%)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
N-MBA	10.4 ± 0.8	20.9 ± 1.7	177.3 ± 77.8
$CaCO_3$	22.2 ± 1.6	5.8 ± 2.9	674.9 ± 55.2
$CaCl_2$	9.6 ± 1.7	23.7 ± 6.7	180.1 ± 49.3

The better results in terms of tensile strength and modulus shown by calcium carbonate is due to the strong interaction between calcium ions and guluronate blocks in alginate. Calcium ion is confined in the interstices of a three dimensional network linked by junction zones that involve cooperative association of extended segments of the polymer chains (da Silva et al 2009). Calcium helps to hold the alginate molecules together as their polymeric nature and their aggregation bind the calcium more firmly (McHugh, 1987). Rhim (2004) reported that the increase in tensile strength and the decrease in elongation at break by $CaCO_3$ treatment in alginate were mainly due to the development of crosslinking between carboxyl group of alginate and Ca^{2+}.

Although, technically, $CaCl_2$ should give comparable result on mechanical properties as $CaCO_3$, it was found otherwise in this study. In fact, the use of $CaCl_2$ as crosslinker resulted in film with higher elongation at break compared to that with $CaCO_3$. Rhim (2004) reported that the addition of $CaCl_2$ into alginate did not change the tensile strength and elongation at break of the resulted film considerably as compared to sodium alginate film. This might be due to inhomogeneous distribution of the crosslinker. Strong interactions between polymer matrix and reinforcement would contribute to the enhanced mechanical behaviour, whereas poor interaction leads to a decreasing trend as compared to the neat matrix.

4.2.7.2 Amount of Crosslinker

The amount of crosslinker used in polymerisation has significant effect on the mechanical properties of the polymer. Tables 4.6 shows that tensile strength increased with increasing amount of *N*-MBA from 1% to 2%. The increase of *N*-MBA amount from 2% to 3% impaired the tensile strength slightly but the tensile strength of the polymer improved as *N*-MBA amount increase from 3% to 5%. On the other hand, it is clearly showed in Table 4.7 that tensile strength increased with increasing amount of $CaCO_3$ (1 – 5%). This is basically due to the formation of more polymer chain network in the presence of higher amount of crosslinker. Similar result was obtained in the development of corn starch based green composites reinforced with *Saccharum spontaneum L* fibre and graft copolymers (Kaith et al., 2010).

With increasing amount of crosslinker, most of the monomers are used up in the crosslinking copolymerisation and free polymer contents decrease. Very high crosslink densities lead to polymer embrittlement (Stevens, 1999). Whereas, if the amount of crosslinker is too low in the polymer system, proper polymer network would not be produced. The findings in this study were consistent to show that both the incorporation of too little and too much crosslinker caused undesirable film formation.

The use of 5 wt% of both *N*-MBA and calcium carbonate had produced the best films in terms of tensile strength and Young's modulus (Tables 4.6 and 4.7). The rigidity of polymer is improved by higher crosslink density (Stevens, 1999). Polymer with lower rigidity has higher stretchability. Generally, polymer crosslinked with *N*-MBA had better elongation at break compared to that crosslinked with $CaCO_3$ (Tables 4.6 and 4.7) because ionic cross-linking reduced polymer segmental mobility (Rhim, 2004).

Table 4.6: Mechanical properties of HP incorporated with different amount of *N*-MBA

N-MBA (wt%)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
1*	10.4 ± 0.8	20.9 ± 6.7	177.3 ± 77.8
2	12.1 ± 1.7	39.3 ± 22.3	172.8 ± 166.3
3	9.9 ± 0.8	20.2 ± 1.1	207.7 ± 5.1
4	14.0 ± 1.6	13.9 ± 5.4	430.7 ± 145.9
5	22.6 ± 0.6	17.9 ± 1.4	1098.0 ± 70.3
10*	13.3 ± 0.1	12.6 ± 3.7	326.6 ± 47.1

*Polymer composite incorporated with 1 and 10 wt% of *N*-MBA could not form a continuous film

Table 4.7: Mechanical properties of HPCC incorporated with different amount of $CaCO_3$

$CaCO_3$ (wt%)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
1	22.2 ± 1.6	5.8 ± 1.7	674.9 ± 55.2
2	31.0 ± 1.2	6.8 ± 0.9	534.1 ± 41.7
3	31.8 ± 2.3	9.8 ± 2.4	437.3 ± 45.0
4	32.8 ± 1.3	10.4 ± 2.8	381.6 ± 30.7
5	32.9 ± 4.0	7.9 ± 2.3	763.8 ± 75.2
10*	26.1 ± 0.7	6.9 ± 1.7	638.7 ± 60.5

*Polymer composite incorporated with 10 wt% of $CaCO_3$ formed film with cracks

4.2.8 Effect of pH of the Composite

The HPCC prepared with 5 wt% $CaCO_3$ was adjusted to different pH and the films produced were tested for mechanical properties. For the study of the effect of pH on the composite, only HPCC was discussed. As observed in Table 4.8, the polymer solution at pH 8 formed film with the highest tensile strength (37.7 MPa) compared to the neutral or the more basic polymer solutions. The charge repulsion between ionised carboxylate $^{-}COO^{-}$ groups and the hydrogen bonding formed between carboxylic acid and ionised carboxylate groups play an important role in aqueous alginate solution. Whereas, in the formation of soy bean film, intra- and intermolecular interaction is promoted by basic pH, which contributes to the increased toughness observed at alkaline pH (Guerrero and de la Caba, 2010).

As pH increased beyond 8, tensile strength and Young's modulus of the HPCC decreased while elongation at break increased from 9.7% to 12.8%. At lower pH, the weakening of the electrostatic interactions promotes the development of intermolecular hydrogen bonds while at high pH, mutual repulsion of ionised carboxyl groups results in loosening of the network (Bu et al., 2005). Thus decrease the strength and increase the flexibility of the formed film.

Table 4.8: Mechanical properties of HPCC adjusted to different pH

pH	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
7	32.9 ± 4.0	7.9 ± 2.3	763.8 ± 75.2
8	37.7 ± 2.0	9.7 ± 3.1	448.0 ± 29.2
10	32.7 ± 1.5	10.0 ± 0.4	758.9 ± 28.4
12	16.0 ± 1.3	12.8 ± 1.4	78.2 ± 22.9

4.2.9 Effect of Ca^{2+} Post Treatment

4.2.9.1 Surface Treatment with $CaCl_2$

The film crosslinked with 5 wt% of *N*-MBA was immersed in calcium chloride and glycerol solution as part of the analysis on the effect of post treatment. $CaCO_3$ was not used as one of the Ca^{2+} source for surface treatment because $CaCO_3$ has very low solubility in water and thus could not treat the film properly. In general, tensile strength decreased as the film was treated with $CaCl_2$ (Figure 4.11). The highest tensile strength obtained was 24.7 MPa at the level of 5 wt% of $CaCl_2$ and 5 wt% of glycerol, which is only slightly higher than the non-treated film. On the other hand, elongation at break of the HP decreased (Figure 4.12) while its Young's modulus increased steadily (Figure 4.13) when it was treated with increasing concentration of $CaCl_2$.

The increase in tensile strength and the decrease in elongation at break with the increase of $CaCl_2$ concentration were mostly due to the development of cross-linking between carboxyl group of alginate and Ca^{2+} (Rhim, 2004).

Olivas et al. (2008) stated that by immersing film into $CaCl_2$ solution, linkage of calcium with carboxyl groups formed on the film's surface.

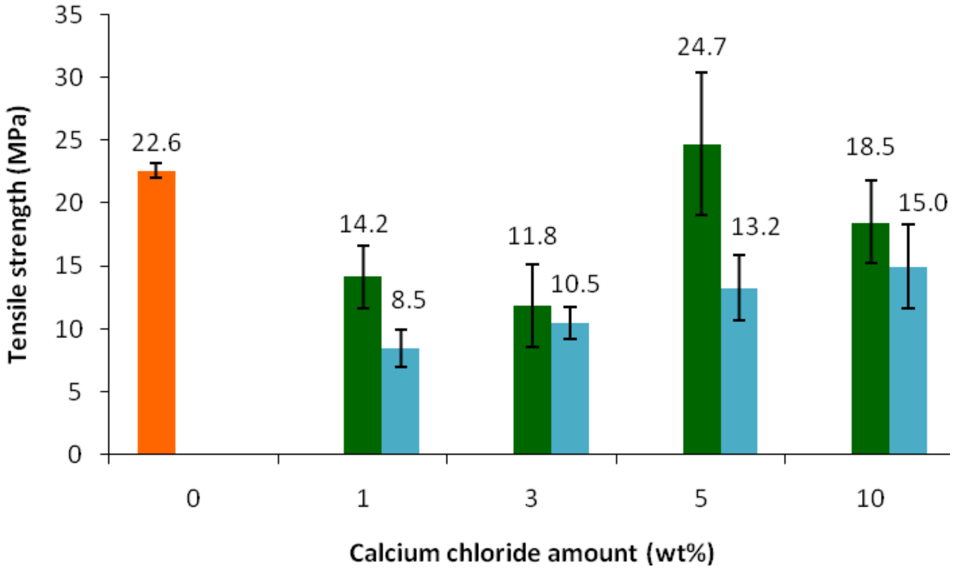


Figure 4.11: The effect of surface treatment with $CaCl_2$ and glycerol of 0 wt% (🟥), 5 wt% (🟩) and 10 wt% (🟦) on the tensile strength of HP

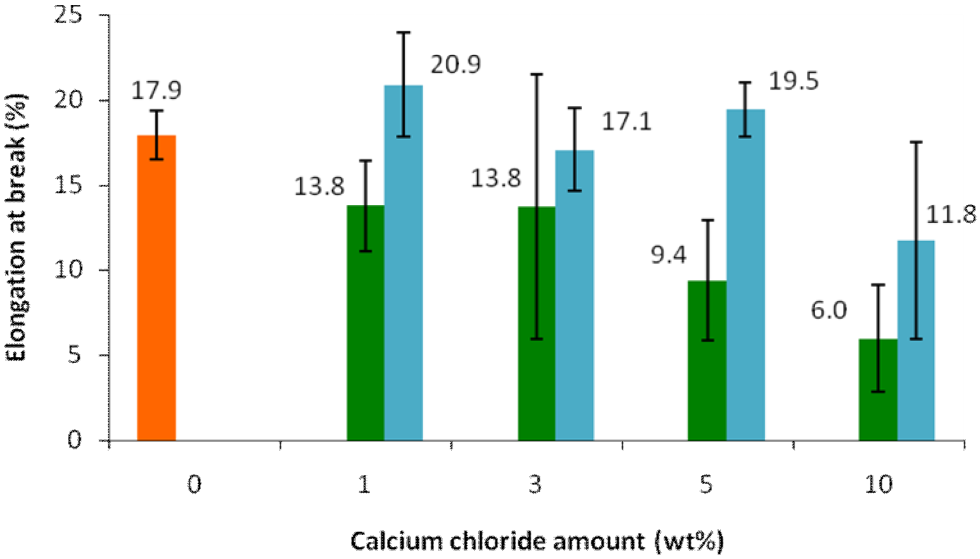


Figure 4.12: The effect of surface treatment with $CaCl_2$ and glycerol of 0 wt% (🟥), 5 wt% (🟩) and 10 wt% (🟦) on the elongation at break of HP

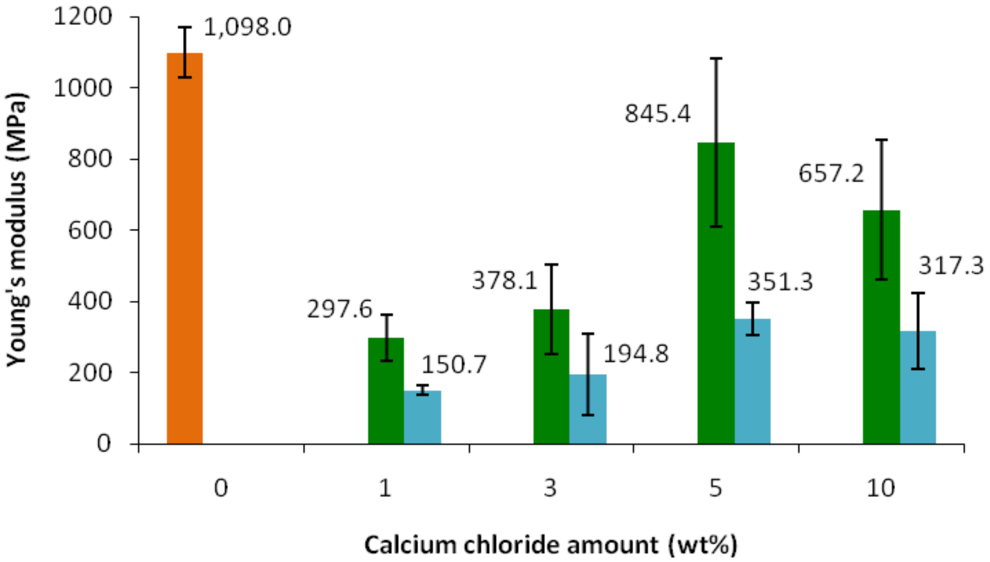


Figure 4.13: The effect of post treatment with $CaCl_2$ and glycerol of 0 wt% (🟥), 5 wt% (🟩) and 10 wt% (🟦) on the Young's modulus of HP

4.2.9.2 Homogenous Mixing with Ca^{2+}

The mechanical properties of the HP with 5 wt% of *N*-MBA mixed homogenously with different amount of calcium chloride and calcium carbonate have been evaluated. Treatment with Ca^{2+} (from either $CaCl_2$ or $CaCO_3$) has shown negative effect on both tensile strength (Figures 4.14 and 4.15) and Young's modulus (Figures 4.18 and 4.19) of HP film. Since the film was already crosslinked with *N*-MBA, further attempt to crosslink with Ca^{2+} might have caused disturbance to the chain network and decreased the strength of the film.

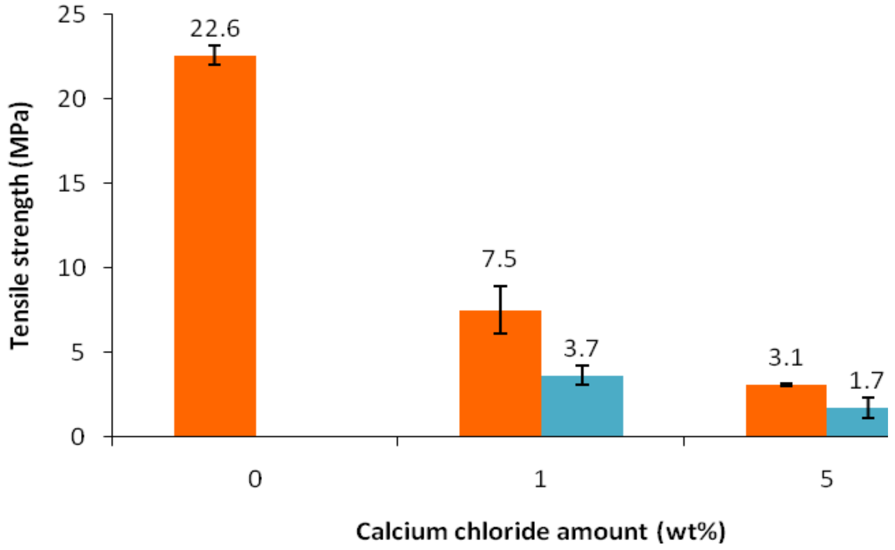


Figure 4.14: The effect of homogenous mixing with $CaCl_2$ and glycerol of 0 wt% (🟥) and 10 wt% (🟦) on the tensile strength of HP

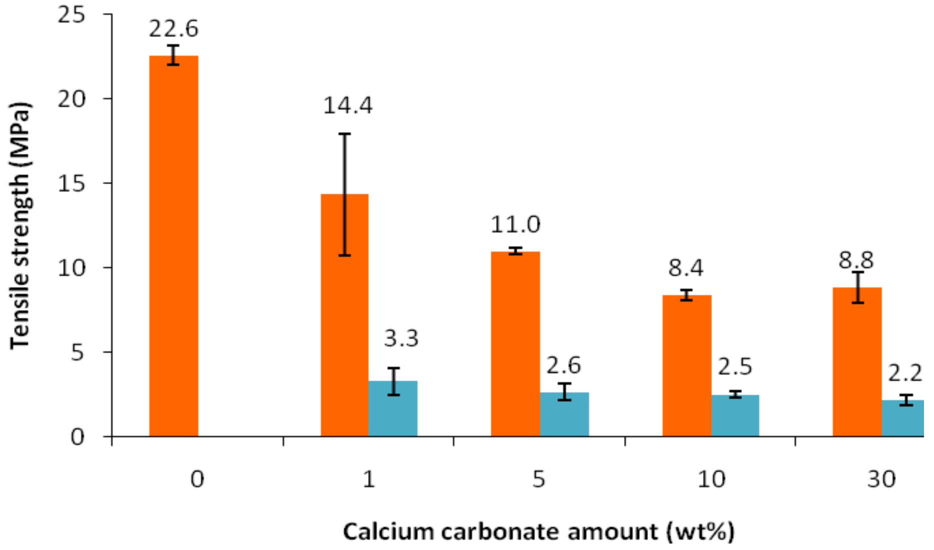


Figure 4.15: The effect of homogenous mixing treatment with $CaCO_3$ and glycerol of 0 wt% (🟥) and 10 wt% (🟦) on the tensile strength of HP

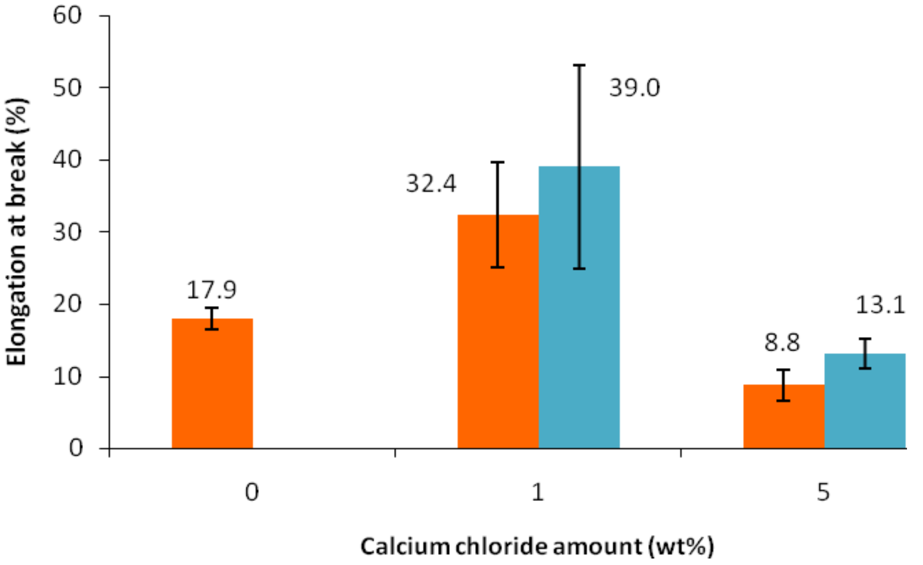


Figure 4.16: The effect of homogenous mixing with $CaCl_2$ and glycerol of 0 wt% (🟧) and 10 wt% (🟦) on the elongation at break of HP

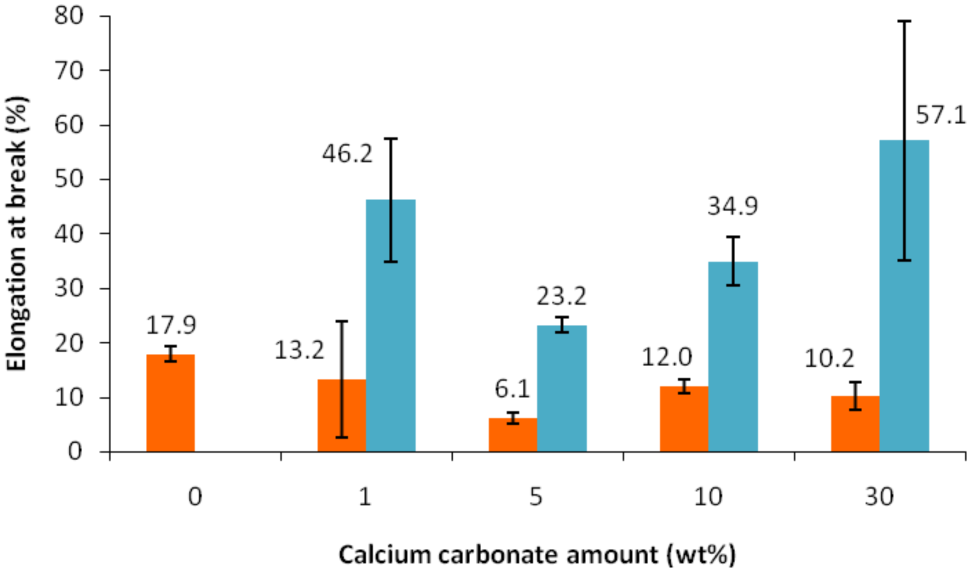


Figure 4.17: The effect of homogenous mixing with $CaCO_3$ and glycerol of 0 wt% (🟧) and 10 wt% (🟦) on the elongation at break of HP

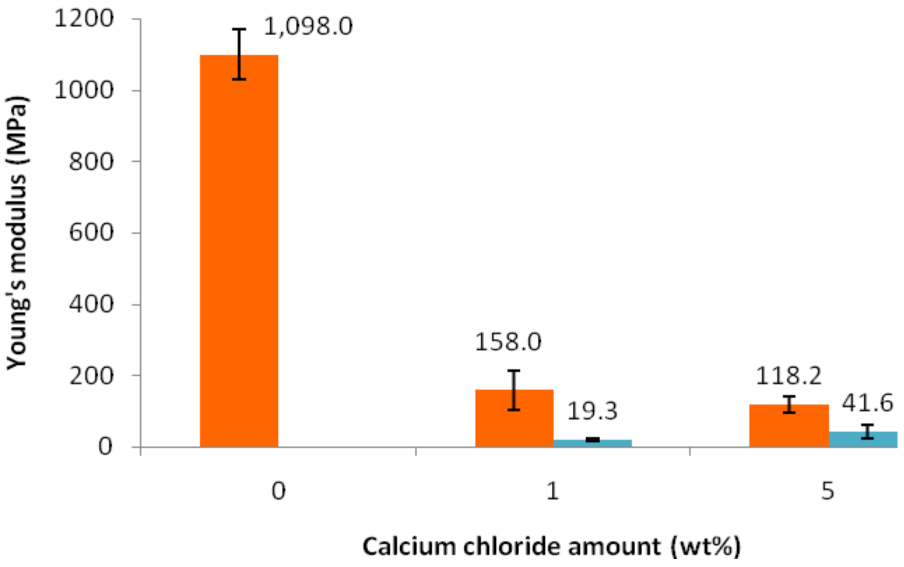


Figure 4.18: The effect of homogenous mixing with $CaCl_2$ and glycerol of 0 wt% (🟥) and 10 wt% (🟦) on the Young’s modulus of HP

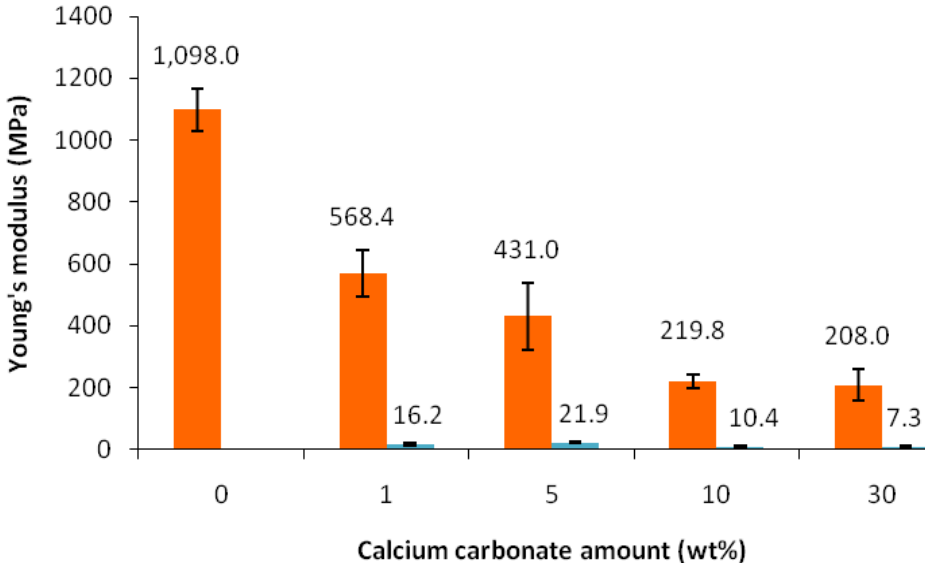


Figure 4.19: The effect of homogenous mixing with $CaCO_3$ and glycerol of 0 wt% (🟥) and 10 wt% (🟦) on the Young’s modulus of HP

4.2.10 Effect of Glycerol Post Treatment

4.2.10.1 Surface Treatment with Glycerol

Different amount of glycerol solution was used to treat the surface of HP film. Figure 4.12 shows that treatment with 10 wt% of glycerol gave higher elongation at break compared to 5 wt% of the plasticiser. However, post treatment with glycerol generally did not improve the tensile strength and Young's modulus of the films. This might be due to the presence of plasticiser in the treatment process. Glycerol molecules intersperse between the polymer chains, causes the chains to slip apart and reduce the rigidity of the structure, thus decreasing strength and increasing flexibility of the films (Olivas et al., 2008).

4.2.10.2 Homogenous Mixing with Glycerol

HP emulsion containing $CaCl_2.2H_2O$ or $CaCO_3$ was added with different amount of glycerol solution. Films treated with 10 wt% of glycerol and either $CaCl_2$ and $CaCO_3$ solution showed better elongation at break compared to those treated without glycerol (Figure 4.16 and 4.17). This may be attributed to the change of chemical interactions between polymer and glycerol (Avella et al., 2007). Plasticiser can interpose itself between the polymer chains and decrease the forces holding the chains together (Guerrero and de la Caba, 2010), thus making the film less likely to break and more flexible (Olivas et al., 2008).

4.3 Solubility of HP and HPCC Films in Different Solvents

Films of HP with 5 wt% of *N*-MBA and HPCC with 5 wt% of $CaCO_3$ were subjected to solubility with various solvent at 25 ^{o}C and the results are tabulated in Tables 4.9. Both HP and HPCC disintegrated into very fine pieces during immersion in water, which made it impossible to measure their solubility in water. Films made of sodium alginate are water-soluble. Water-insoluble films can be prepared by treating the water-soluble alginate film with a di- or trivalent cation such as Ca^{2+} (McHugh, 1987). However, HPCC film has poor water resistance although crosslinked with 5 wt% of $CaCO_3$. This might be due to insufficient amount of Ca^{2+}. Rhim (2004) reported that in the effort to form water insoluble alginate films by immersing it in $CaCl_2$ solution, it was found not sufficient to desolubilise the alginate films.

Generally, HP had slightly higher solubility percentage, which was in the range of 0.6 – 1.0%, compared to HPCC which was below 0.5% (Table 4.9). This might be due to the stronger ionic crosslinking bond between Ca^{2+} and alginate (Rhim, 2004) in HPCC compared to covalent crosslinking bond between *N*-MBA and polyacrylamide (Plantenga, 2007) or poly(butyl acrylate) in HP.

Although, theoretically, crosslinked materials cannot dissolve in most solvents (Stevens, 1999), it was observed that there are still less than 1% of HP and HPCC dissolved in the solvents tested. Solubilised materials could come from the entrapped or unused monomer or sodium alginate which is not crosslinked into the polymer network. According to Pongjanyakul and Puttipipatkhachorn (2008), erosion of the sodium alginate-magnesium aluminium silicate films took place because of the dissolution of some sodium alginate on the surface of the films.

Table 4.9: Solubility percentage of HP with 5 wt% of *N*-MBA and HPCC with 5 wt% of $CaCO_3$

Solvent	Solubility (%)	
	HP	**HPCC**
Water	-	-
Acetonitrile	1.0	0.2
Dimethylformamide	0.6	0.4
Chloroform	0.6	0
Toluene	0.9	0.2

4.4 Swelling of HP and HPCC Films in Different Solvents

Swelling analysis of HP (5 wt% of *N*-MBA) and HPCC (5 wt% of $CaCO_3$) films in various solvents were also done at 25 ^{o}C. As both HP and HPCC break into very fine pieces after soaked in water, their swelling in water is not measured.

There were higher swelling percentage of both HP and HPCC in less polar solvent (chloroform and toluene) than in more polar solvent (acetonitrile and dimethylformamide) (Tables 4.10). In the present of a solvent, a crosslinked polymer swells as solvent molecules penetrate the network. The degree of swelling depends on the affinity of polymer and solvent for one another (Stevens, 1999). Therefore, it appeared that HP and HPCC had higher affinity for non polar solvents.

Table 4.10: Swelling percentage of HP with 5 wt% of *N*-MBA and HPCC with 5 wt% of $CaCO_3$

Solvent	Swelling (%)	
	HP	HPCC
Water	-	-
Acetonitrile	2.3	3.9
Dimethylformamide	3.6	9.3
Chloroform	12.0	9.6
Toluene	9.4	10.8

4.5 Fourier Transform Infrared Spectra (FTIR) Analysis

The FTIR spectrum of the ungrafted sodium alginate (Figure 4.20) shows band at 3450 cm^{-1}, peaks at 2935 cm^{-1}, 1632 cm^{-1}, 1419 cm^{-1} and 1029 cm^{-1} that are attributed respectively to O–H stretch, aliphatic CH, COO^- (asymmetric), COO^- (symmetric) stretching vibration of free carboxyl group of sodium alginate (Pathak et al., 2010) and carbonyl stretch C-O-C of ether, which are characteristics of polysaccharide (Isiklan et al., 2010). The unprocessed sodium alginate had also a broad peak at 650 cm^{-1}, as described by Ashikin et al. (2010).

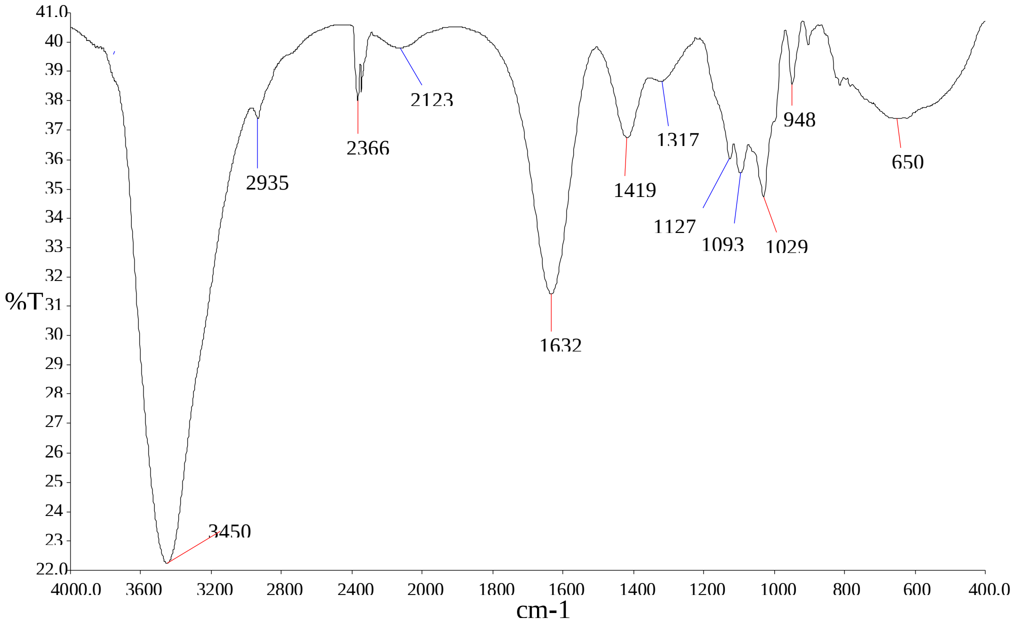


Figure 4.20: Infrared spectrum of sodium alginate

The IR spectum of HP (Figure 4.21) shows broad peak around 3367 cm^{-1} and a sharp peak at 2959 cm^{-1} which indicated that the O-H of carboxylic acid stretch overlaps the N–H stretching of primary amides and aliphatic C-H. The peak at 1657 cm^{-1} is for C=O of primary amides stretching and the peak at 1416 cm^{-1} of C-N bend shows the presence of the $CONH_2$ group in the hybrid polymer, which indicates the grafting of acrylamide on alginate. The appearance of the peak at 1735 cm^{-1} indicates C=O stretch ester group of butyl acrylate, which confirmed the grafting of the monomer (Qin et al., 2011). The carbonyl stretch of C-O-C of ether at 1033 cm^{-1} characterises sodium alginate. Therefore, it was confirmed that both butyl acrylate and acrylamide have been grafted onto sodium alginate. This is in good agreement with the results reported in the studies of Lanthong et al. (2006) and Isiklan et al. (2010).

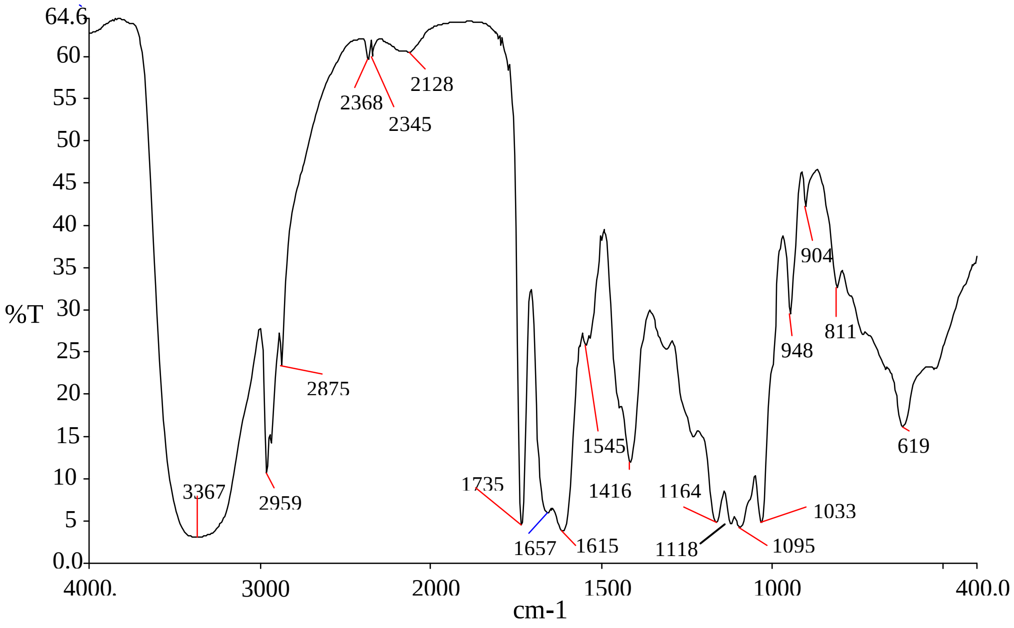


Figure 4.21: **Infrared spectrum of HP**

Both sodium alginate and cellulose fibre are carbohydrate polymers with a lot of identical groups. FTIR peak of bamboo leaf fibre at 3421 cm^{-1}, 2919 cm^{-1} and 1061 cm^{-1} (Figure 4.22) are ascribed to the aliphatic C-H, O–H and C-O moiety of cellulose. On the other hand, FTIR spectrum of HPFC (Figure 4.23) shows a broad peak at 3385 cm^{-1} which is attributed to the O-H group of cellulose and sodium alginate. There are also peaks at 1612 cm^{-1} and 1032 cm^{-1} that represent C-O overlapping N-H of CONH$_2$ group and carbonyl stretch C-O-C of ether. The existence of the peak at 1734 cm^{-1} of C-O group and bend at 1414 cm^{-1} of C-N group (Figure 4.23) suggest that both butyl acrylate and acrylamide monomers have been successfully grafted onto sodium alginate in the HPFC.

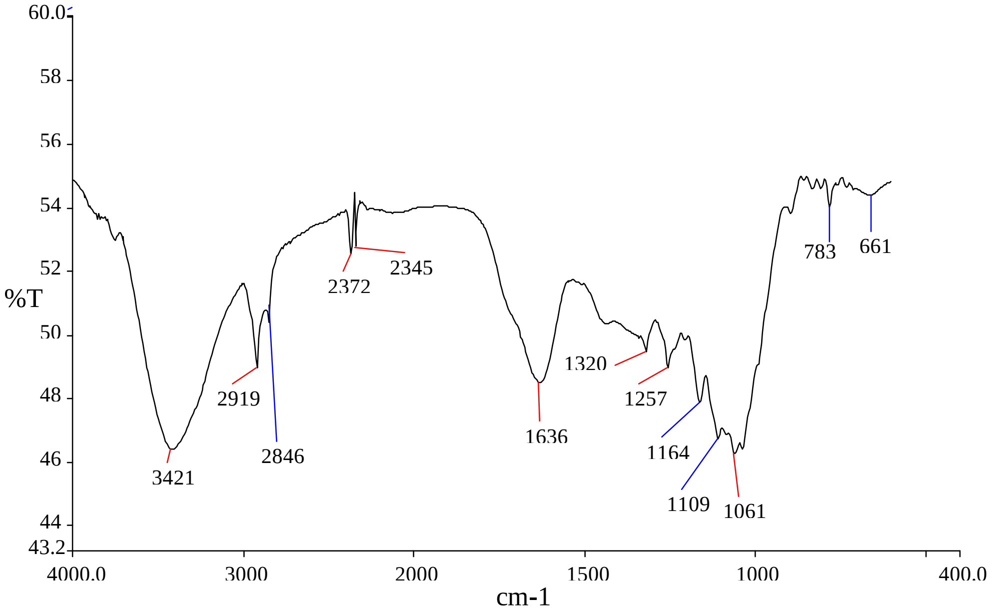


Figure 4.22: Infrared spectrum of bamboo leaf fibre

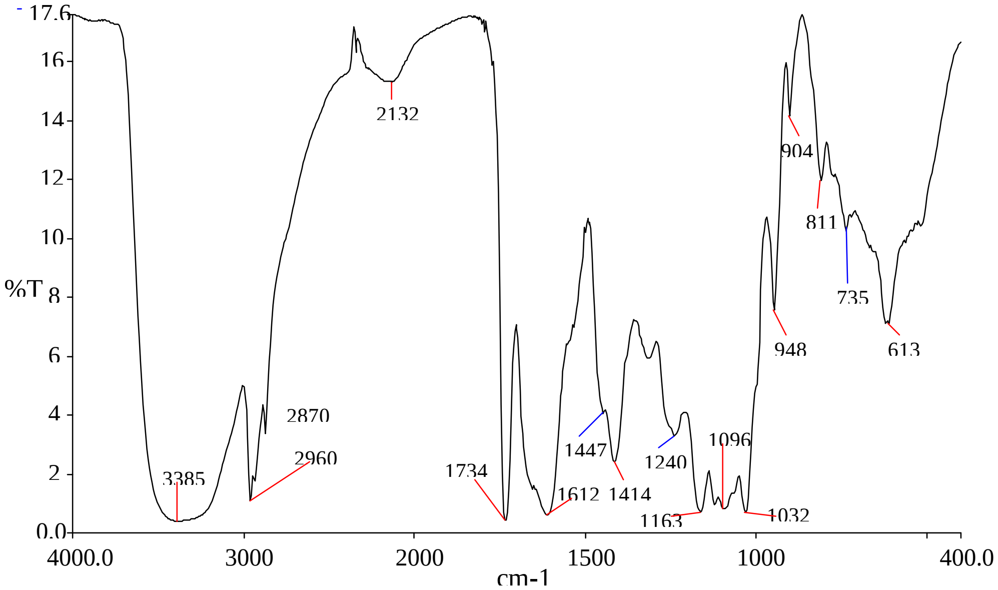


Figure 4.23: Infrared spectrum of HPFC

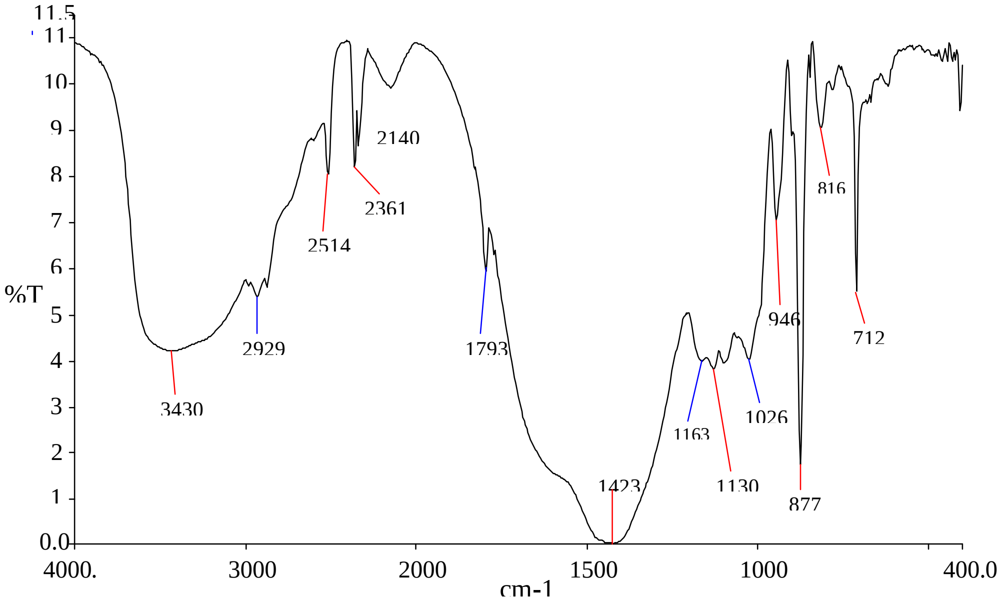


Figure 4.24: Infrared spectrum of HPCC

The infrared spectrum of HPCC (Figure 4.24) shows a strong band at 3430 cm^{-1} which is of the O-H stretch, a small peak at 2929 cm^{-1} that represents aliphatic C-H and another band at 1026 cm^{-1} of the carbonyl stretch C-O-C of ether. Strong absorption peaks at 1423 cm^{-1}, sharp peaks at 1793 cm^{-1}, 877 cm^{-1}, and 712 cm^{-1}, are attributed to the vibration of C=O double bond in the carbonate ion of $CaCO_3$ (Xie et al., 2010a). The interaction between $CaCO_3$ and the hybrid polymer is indicated by the overlapping peaks of CONH group in acrylamide and CO group in butyl acrylate. Thus, individual peaks of C-N bend in acrylamide and C-O stretch in butyl acrylate that should appear around the region of 1415 cm^{-1} and 1735 cm^{-1}, respectively, are not shown in the spectrum (Figure 4.24).

4.6 Thermogravimetric Analysis (TGA)

Thermal stability of the HP and composites were characterised using TGA. The weight loss of the different components of HP (with 5 wt% of *N*-MBA), HPFC (with 5 wt% of fibre) and fibre were determined by thermogravimetric analysis under nitrogen at a heating rate of 10 ^{o}C/min, and in the heating range of 30 to 600 ^{o}C. On the other hand, HPCC (with 5 wt% of $CaCO_3$) was scanned from 30 to 900 ^{o}C at the same heating rate under nitrogen air flow. The thermal stability of graft copolymer can be compared at the onset temperature of decomposition and the percentage of weight loss for different stages of the decomposition (Lanthong et al., 2006). It is suggested that in the initial stage of the thermal diagram of all HP and composites analyses, when the temperature was between ambient temperature and about 100 ^{o}C, the weight loss observed is a result of the elimination of water.

In the thermogravimetric analysis of HP with 5 wt% of *N*-MBA (Figure 4.25), severe weight loss (~26%) between 192 – 292 ^{o}C was attributed to depolymerisation of sodium alginate (Isiklan et al., 2010). Weight loss in the range of 291 – 418 ^{o}C might be due to the degradation of butyl acrylate. The last stage of weight loss in the range of 418 – 484 ^{o}C was possibly due to the degradation of acrylamide portion (Lanthong et al., 2006). Above 484 ^{o}C, a slower and gradual rate of weight loss continued and less than 45% of residue remained at 600 ^{o}C.

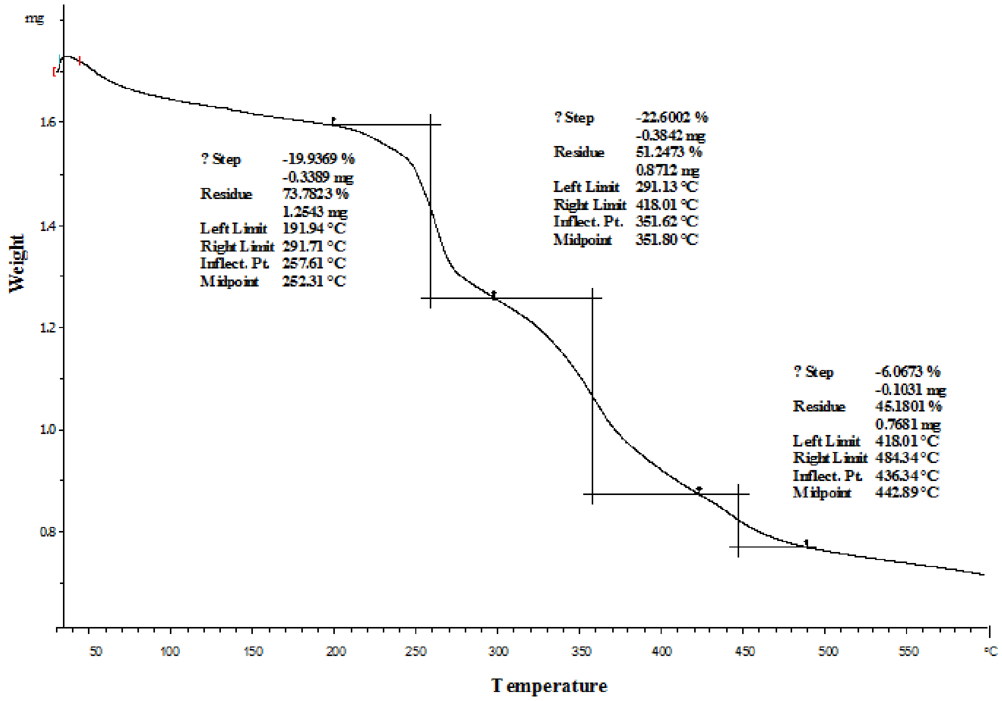


Figure 4.25: Thermogram of HP

The thermogram of HP shows three decomposition stages while the thermogram of HPCC (with 5 wt% of $CaCO_3$) shows four decomposition stages. The fourth decomposition stage of HPCC (Figure 4.26) reflects the decomposition process of calcium carbonate to calcium oxide, as described by Raz et al. (2002). HP had a lower overall maximum decomposition temperature (500 ^{o}C) than HPCC (820 ^{o}C). Stanmore and Gilot (2005) stated that calcination of $CaCO_3$ favours high temperature since it is an endothermic reaction.

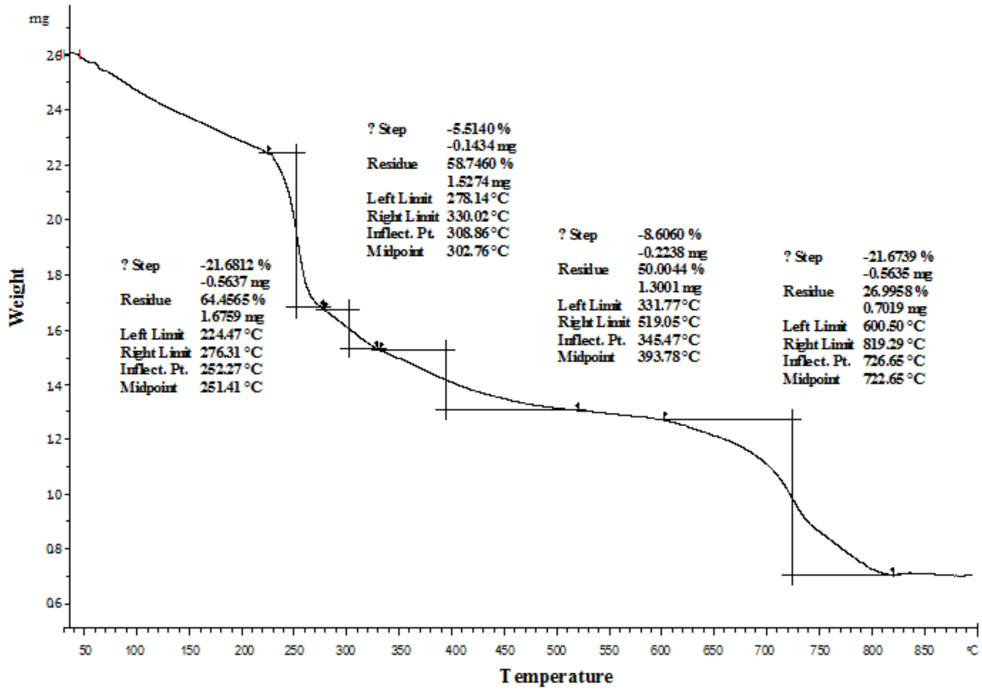


Figure 4.26: Thermogram of HPCC

Jin and Park (2008) found that thermal stability of rubber composite was significantly enhanced by the addition of nano-$CaCO_3$ as the initial decomposition temperature of $CaCO_3$-rubber composite was higher than the rubber system. Pathak et al. (2010) mentioned that the complex formation nature between metal ion and functional group on the alginate surface was complicated and thus thermal degradation behavior of metal alginates is not clear.

It is noticed that HP had higher residue percentage (45%) than HPFC (34%) at about 480 ^{o}C. This could be due to the fact that the presence of natural fibre that provided more burning material to the composite and thus promoted combustibility of the composite.

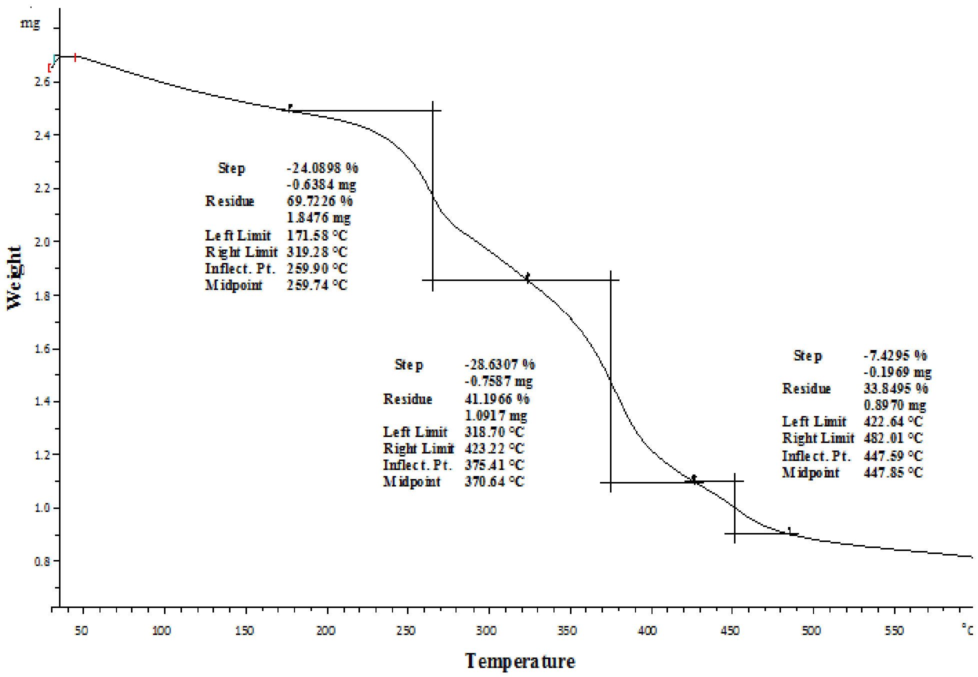


Figure 4.27: Thermogram of HPFC

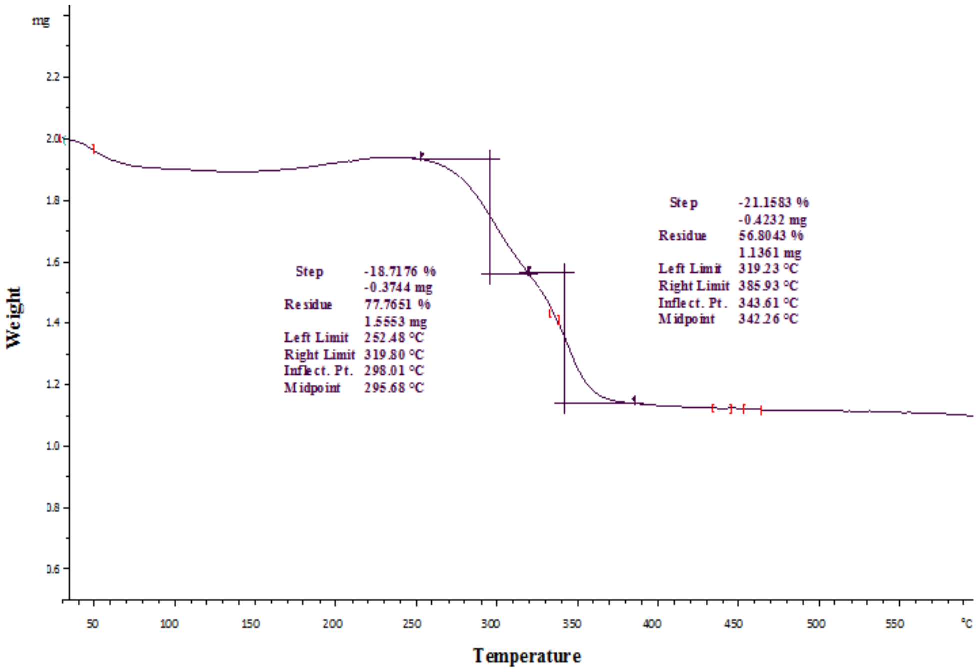


Figure 4.28: Thermogram of bamboo leaf fibre

By comparing the thermograms between HPFC (Figure 4.27) and fibre alone (Figure 4.28), HPFC had significantly higher decomposition temperature than that of the fibre alone. HPFC decomposed at around 480 °C, whereas fibre alone decomposed at around 385 °C, although the former had lesser residue after decomposition. The better thermal resistance of grafted composites were due to the incorporation of covalent bonds through cross-linking and reinforced graft copolymers (Kaith et al., 2010). Wan et al. (2011) stated that the maximum decomposition temperature of bamboo cellulose-graft-poly(methyl methacrylate) composite were higher than those of bamboo cellulose. This is possibly because carbonisation in composite (conversion of an organic substance into carbon or a carbon-containing residue) was lesser than that of bamboo cellulose.

4.7 Scanning Electron Microscopy (SEM)

The scanning electron micrographs of the surface of HP (with 5 wt% of *N*-MBA), HPFC (with 5 wt% fibre) and HPCC (with 5 wt% of $CaCO_3$) films are shown in Figures 4.29, 4.30 and 4.31 respectively. By comparing the SEM images of HP (Figure 4.29) and HPFC (Figure 4.30) film, it was found that the addition of fibre changed the morphology of HP. As seen in the HPFC images, there are white spots around the amorphous zone that indicate the present of fibres in the polymer matrix. From the images, it is clear that the fibres were not well dispersed and only appeared in certain spots of the matrix (which is marked by a circle in Figure 4.30). This result in poor stress distribution and the incorporation of fibre failed to give reinforcing effect (Mamoor et al., 2009). Alemdar and Sain (2008) observed that nanofibres of wheat straw were well dispersed in the thermoplastic starch polymer-wheat straw fibre composite that had high mechanical properties. Besides, the appearance of crack (marked by a square in Figure 4.30) might have also contributed to the poor tensile strength of HPFC.

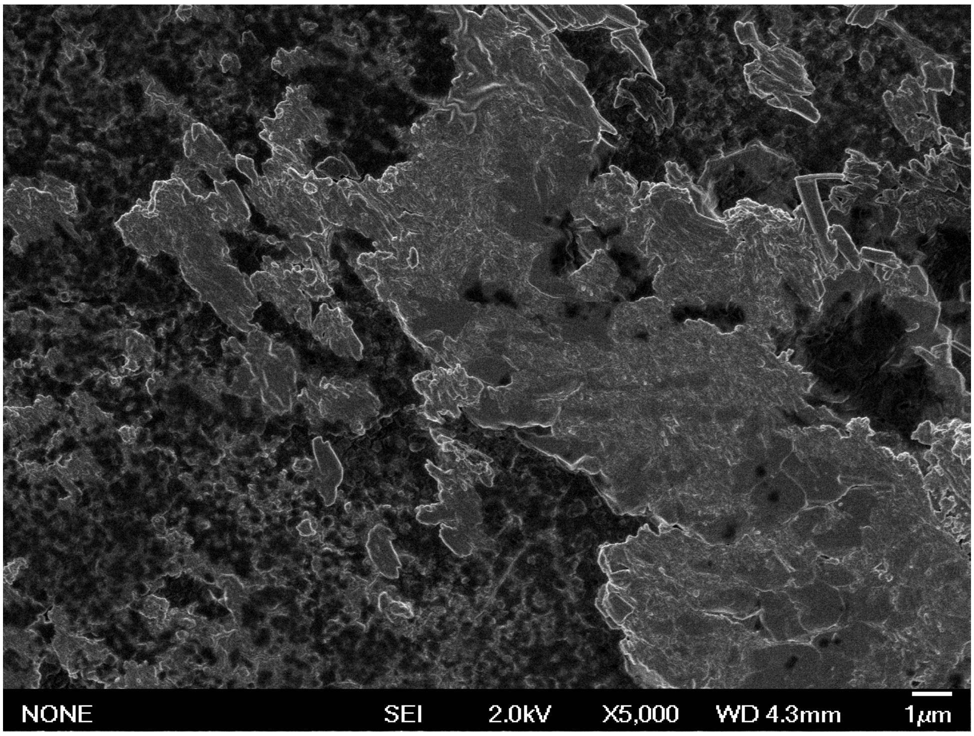


Figure 4.29: SEM images of HP film surface

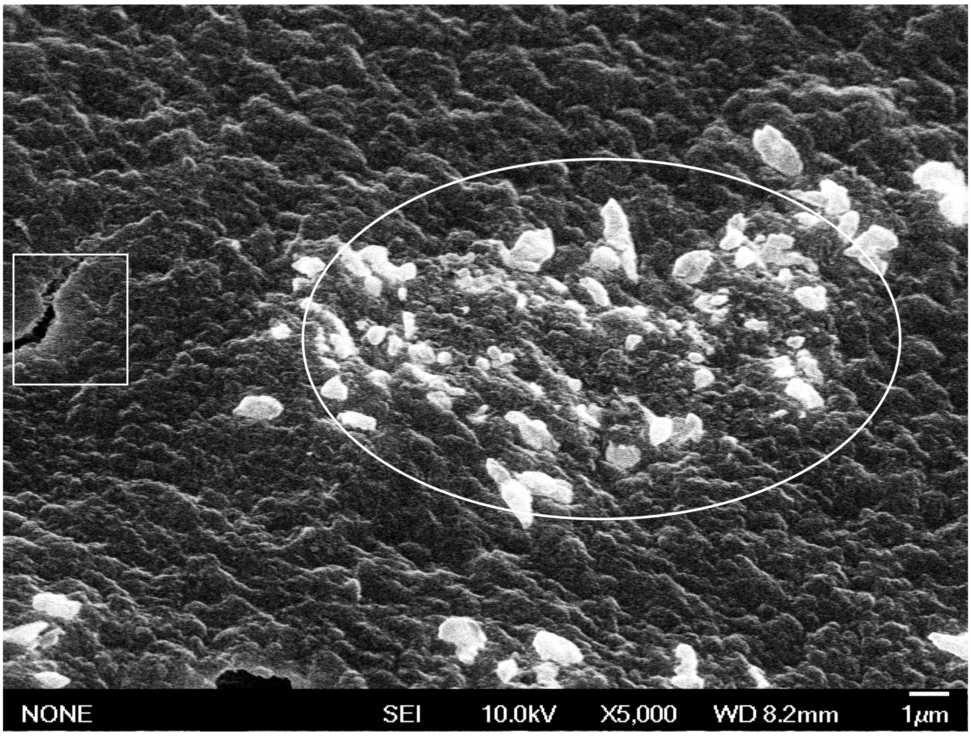


Figure 4.30: SEM images of HPFC film surface

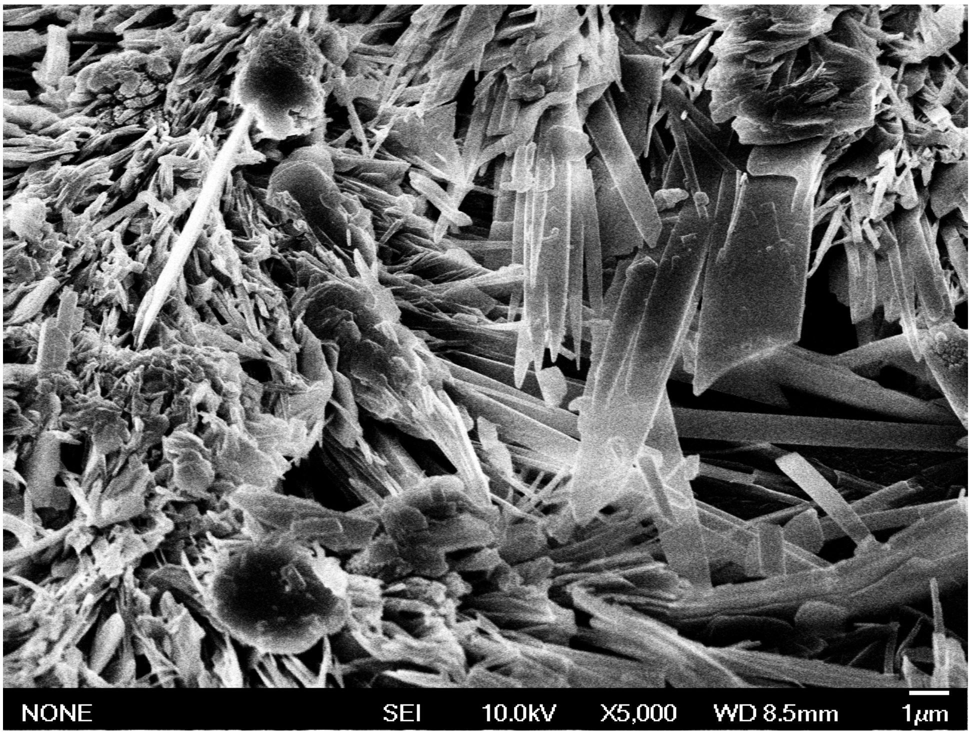


Figure 4.31: SEM images of HPCC film surface

It was seen that there are more crystalline structures in HPCC (Figure 4.31) than HP (Figure 4.29) and HPFC (Figure 4.30). These sharp rod-shaped crystalline structures are believed to be calcium carbonate crystals (Quantum Micronet, 2011). High crystallinity might have contributed to the higher tensile strength of the HPCC compared to HP and HPFC. Alginate has been used as addictives to grow calcium carbonate crystals for its high affinity for Ca^{2+} ion (Matahwa et al., 2008).

CHAPTER 5

CONCLUSIONS

Acrylamide and butyl acrylate were successfully grafted onto gelatinised alginate using potassium persulfate and sodium formaldehyde sulfoxylate as redox initiator pair in the presence of crosslinking agent, *N*-MBA to form HP, and with the addition of $CaCO_3$ to synthesis HPCC. Bamboo leaf fibre was incorporated into HP to form HPFC.

Upon investigation, it was found that varying the reaction conditions and the ingredient composition could result in composites with different mechanical properties. HPFC was found to have lower tensile strength, Young's modulus and elongation at break than HP and HPCC, probably due to the poor compatibility between fibre and the polymer matrix. For the composites, HPCC prepared with monomer-sodium alginate ratio of 1: 0.24, 5 wt% of $CaCO_3$, at the reaction and drying temperatures of 50 ^{o}C and stirring speed of 1000 rpm showed the highest tensile strength of 38 MPa at pH 8. Both HP and HPCC disintegrated in water but have very low swelling and solubility in solvents such as acetonitrile, dimethylformamide, chloroform and toluene.

The obtained results of FTIR analysis proved that the monomers were grafted onto sodium alginate in the presence of crosslinking agent to form the polymer and composites. According to the TGA results, HPCC showed better thermal stability than HPFC and HP because of the high calcination temperature of $CaCO_3$. It was observed that HPFC had the lowest residue percentage compared to HP and HPCC due to the presence of natural fibre in HPFC that could promote the combustibility of the composite. SEM pictures displayed that the surface of HPCC film had calcium carbonate crystal region. From the HPFC images, bamboo leaves fibres were identified as white spots and only sparsely distributed in the film.

For further studies, biocomposite film could be prepared with the combination of different natural fibrous fillers such as coconut and banana leaf fibre, and particulate fillers, such as carbon black and ground rice hulls. Besides, there should be more research on the use of different type of natural polymers such as gelatine and soy protein to make biocomposite film by graft polymerisation method.

Other properties such as tear resistance, heat seal and optical characteristics of such composites should be evaluated to establish its potential use as biocomposite in different applications. In addition, the ability of the composites to biodegrade in different disposal conditions should be determined; as such information is important to assess its prospect as green composite in the environmental aspect. By doing so, more data would be obtained to explore the possibilities of combining various types of natural polymer and fillers to form composites with different properties that are not found in conventional polymeric materials.

REFERENCES

Agamuthu, P., Faizura, P.N., (2005). Biodegradability of degradable plastic waste. *Waste Management & Research,* 23, 95–100.

Ahmad, F.N., Jaafar, M., Palaniandy, S., Azizli, K.A.M., (2008). Effect of particle shape of silica mineral on the properties of epoxy composites. *Composites Science and Technology,* 68, 346–353.

Ahmad, S.R., Husseinsyah, S., Kamarudin Hussin, K., (2011). The Effects of Chemical Modifiers on the Thermal Properties of Calcium Carbonate Filled Polypropylene/Ethylene Propylene Diene Terpolymer Composites. *Pertanika J. Sci. & Technol.,* 19, 153–159.

Alemdar, A., Sain, M., (2008). Biocomposites from wheat straw nanofibers: Morphology, thermal and mechanical properties. *Composites Science and Technology,* 68, 557–565.

Ashikin, W.H.N.S, Wong, T.W., Law, C.L., (2010). Plasticity of hot air-dried mannuronate- and guluronate-rich alginate films. *Carbohydrate Polymers,* 81, 104–113.

Avella, M., Pace, E.D., Immirzi, B., Impallomeni, G., Malinconico, M., Santagata, G., (2007). Addition of glycerol plasticizer to seaweeds derived alginates: Influence of microstructure on chemical–physical properties. *Carbohydrate Polymers,* 69, 503–511.

Avella, M., Vlieger, J.J.D., Errico, M.E., Fischer, S., Vacca, P., Volpe, M.G., (2005). Biodegradable starch/clay nanocomposite films for food packaging applications. *Food Chemistry,* 93, 467–474.

Averous, L. (2012). *Bioplastic*. URL: http://www.biodeg.net/bioplastic.html. Accessed on 12th February 2012.

Barbosa Jr., V., Ramires, E.C., Razera, I.A.T., Frollini, E., (2010). Biobased composites from tannin–phenolicpolymers reinforced with coir fibers. *Industrial Crops and Products*, 32, 305–312.

Bakare, I.O., Okieimen, F.E., Pavithran, C., Abdul Khalil, H.P.S., Brahmakumar, M., (2010). Mechanical and thermal properties of sisal fiber-reinforced rubber seed oil-based polyurethane composites. *Materials and Design,* 31, 4274–4280.

Behari, K., Pandey, R., Kumar, R., Taunk, K., (2001). Graft compolymerization of acrylamide onto xanthan gum. *Carbohydrate Polymers,* 46, 185-189.

Bhattacharya, A., Misra, B.N., (2004). Grafting: a versatile means to modify polymers techniques, factors and applications. *Progress in Polymer Science,* 29, 767–814.

Bilck, A.P., Grossmann, M.V.E., Yamashita, F., (2010). Biodegradable mulch films for strawberry production. *Polymer Testing,* 29, 471–476.

Brydson, J.A., (1999). Relation of structure to thermal and mechanical properties. In: *Plastics Material*. 7th Edition. (pp 59–75). Oxford: Butterworth Heinemann.

Bu, H., Kjøniksen, A., Nystro¨m, B., (2005). Effects of pH on dynamics and rheology during association and gelation via the Ugi reaction of aqueous alginate. *European Polymer Journal,* 41, 1708–1717.

Cai, Y., Fan, S., Liu, H., Zhang, L., Cheng, L., Jiang, J., Dong, B., (2010). Mechanical properties of a 3D needled C/SiC composite with graphite filler. *Materials Science and Engineering A*, 527, 539–543.

Carneiro-da-Cunha, M.G., Cerqueirab, M.A., Souzab, B.W.S., Carvalhoc, S., Quintasb, M.A.C., Teixeirab, J.A., Vicente, A.A., (2010). Physical and thermal properties of a chitosan/alginate nanolayered PET film. *Carbohydrate Polymers,* 82, 153-159.

Chee, S.Y., Wong, P.K., Wong, C.L., (2011). Extraction and characterisation of alginate from brown seaweeds (Fucales, Phaeophyceae) collected from Port Dickson, Peninsular Malaysia. *Journal of Applied Phycology*, 23, 191–196.

Choi, Y., Lee, W., (2010). Effects of agitation in emulsion polymerization of vinyl acetate, ethylene, and N-methylol acrylamide. *Journal of Industrial and Engineering Chemistry,* 16, 431–436.

Cutter, C.N., (2006). Opportunities for bio-based packaging technologies to improve the quality and safety of fresh and further processed muscle foods. *Meat Science*, 74, 131–142.

Dahou, W., Ghemati, D., Oudia, A., Aliouche, D., (2010). Preparation and biological characterization of cellulose graft copolymers. *Biochemical Engineering Journal*, 48, 187–194.

Da Silva, M.A., Bierhalz, A.C.K., Kieckbusch, T.G., (2009). Alginate and pectin composite films crosslinked with Ca^{2+} ions: Effect of the plasticizer concentration. *Carbohydrate Polymers,* 77, 736–742.

De Carvalho, A.J.F., Curvelo, A.A.S., Agnelli, J.A.M., (2001). A first insight on composites of thermoplastic starch and kaolin. *Carbohydrate Polymers*, 45, 189–194.

Denavi, G., Tapia-Blácido, D.R., Añón, M.C., Sobral, P.J.A., Mauri, A.N., Menegalli, F.C., (2009). Effects of drying conditions on some physical properties of soy protein films. *Journal of Food Engineering,* 90, 341–349.

Draget, K.I., Taylor, C., (2011). Chemical, physical and biological properties of alginates and their biomedical implications. *Food Hydrocolloids*, 25, 251-256.

Emmambux, M.N., Iannace, S., and Stading, M., (2003, April). *Cereal biopolymer films, coatings and other industrial products*. Paper presented at the Afripro Workshop on Sorghum and Millet Proteins, Pretoria, South Africa.

Fang, J., Fowler, P., (2003). The use of starch and its derivatives as biopolymer sources of packaging materials. *Food Agricultural Environment,* 1, 82–84.

Gao, Y., Liu, L., Zhang, Z., (2009). Mechanical performance of nano-$CaCO_3$ filled polystyrene composites. *Acta Mechanica Solida Sinica*, 22, 555-562.

Ghosh, P., Ganguly, P.K., (1994). Graft copolymerization of methyl methacrylate on jute using the aqueous IO_4^- - Cu^{2+} combination as the initiator system and evaluation of the graft copolymers. *Polymer,* 35, 383-390.

Graupner, N., Herrmann, A.S., Müssig. J., (2010). Natural and man-made cellulose fibre-reinforced poly(lactic acid) (PLA) composites: An overview about mechanical characteristics and application areas. *Composites*: *Part A,* 40, 810–821.

Guerrero, P., de la Caba, K., (2010). Thermal and mechanical properties of soy protein films processed at different pH by compression. *Journal of Food Engineering,* 100, 261–269.

Hamdani, S., Longuet, C., Lopez-Cuesta, J., Ganachaud, F., (2010). Calcium and aluminium-based fillers as flame-retardant additives in silicone matrices. I. Blend preparation and thermal properties. *Polymer Degradation and Stability,* 95, 1911–1919.

Harding, K.G., Dennis, J.S., Blottnitz, H.v, Harrison, S.T.L., (2007). Environmental analysis of plastic production processes: Comparing petroleum-based polypropylene and polyethylene with biologically-based poly-β-hydroxybutyric acid using life cycle analysis. *Journal of Biotechnology,* 130, 57–66.

Hartikainen, J., Hine, P., Szabo´, J.S., Lindner, M., Harmia, T., Duckett, R.A., Friedrich, K., (2005). Polypropylene hybrid composites reinforced with long glass fibres and particulate filler. *Composites Science and Technology,* 65, 257–267.

Herrera-Franco, P.J., Valadez-Gonzalez, A., (2005). A study of the mechanical properties of short natural-fiber reinforced composites. *Composites: Part B,* 36, 597–608.

Huang, X., Netravali, A., (2009). Biodegradable green composites made using bamboo micro/nano-fibrils and chemically modified soy protein resin. *Composites Science and Technology,* 69, 1009–1015.

Ibrahim, M.I., Dufresne, A., El-Zawawya, W.K., Agblevor, F.A., (2010). Banana fibers and microfibrils as lignocellulosic reinforcements in polymer composites. *Carbohydrate Polymers,* 81, 811–819.

Interplast, (2007). *Biopolymers: market potential and research challenges.* URL: http://www.inter-plast.info/LinkClick.aspx?fileticket=5coYZ5aamUw%3D&tabid=74&language=it-IT. Accessed on 1st April 2011.

Işıklan, N., Kursun, F., Inal, M., (2010). Graft copolymerization of itaconic acid onto sodium alginate using benzoyl peroxide. *Carbohydrate Polymers,* 79, 665–672.

Jiao, W., Liu, Y., Qi, G., (2009). Studies on mechanical properties of epoxy composites filled with the grafted particles PGMA/Al_2O_3. *Composites Science and Technology*, 69, 391–395.

Jin, F.L., Park, S.J., (2008). Thermo-mechanical behaviors of butadiene rubber reinforced with nano-sized calcium carbonate. *Materials Science and Engineering A*, 478, 406–408.

John, M.J., Thomas, S., (2008). Biofibres and biocomposites. *Carbohydrate Polymers*, 71, 343–364.

Kaith, B.S., Jindal, R., Jana, A.K., Maiti, M., (2010). Development of corn starch based green composites reinforced with *Saccharum spontaneum L* fiber and graft copolymers – Evaluation of thermal, physico-chemical and mechanical properties. *Bioresource Technology,* 101, 6843–6851.

Kaewtatip, K., Tanrattanakul, V., (2008). Preparation of cassava starch grafted with polystyrene by suspension polymerization. *Carbohydrate Polymers*, 73, 647–655.

Katz, H.S., (1998). Particulate Filler. In: Peters, S.T. (Ed.), *Handbook of Composites*. 2nd Edition. (pp 242 – 253). London: Chapman and Hall.

Kemal, I., Whittle, A., Burford, R., Vodenitcharova, T., Hoffman, M., (2009). Toughening of unmodified polyvinylchloride through the addition of nanoparticulate calcium carbonate. *Polymer,* 50, 4066–4079.

Kim, M., (2003). Evaluation of degradability of hydroxypropylated potato starch/polyethylene blend films. *Carbohydrate Polymers*, 54, 173-181.

Kim, S.J., Moon, J.B., Kim, G.H., Ha, C.S., (2008). Mechanical properties of polypropylene/natural fiber composites: Comparison of wood fiber and cotton fiber. *Polymer Testing*, 27, 801-806.

Kinoshita, H., Kaizu, K., Fukuda, M., Tokunaga, H., Koga, K., Ikeda, K., (2009). Development of green composite consists of woodchips, bamboo fibers and biodegradable adhesive. *Composites: Part B,* 40, 607–612.

Lam, T.D., Hoang, T.V., Quang, D.T., Kim, J.S., (2009). Effect of nanosized and surface-modified precipitated calcium carbonate on properties of $CaCO_3$/polypropylene nanocomposites. *Materials Science and Engineering A*, 501, 87–93.

Lanthong, P., Nuisin, R., Kiatkamjornwong, S., (2006). Graft copolymerization, characterization, and degradation of cassava starch-g-acrylamide/itaconic acid superabsorbents. *Carbohydrate Polymers*, 66, 229–245.

Laurienzo, P., Malinconico, M., Motta, A., Vicinanza, A., (2005). Synthesis and characterization of a novel alginate–poly(ethylene glycol) graft copolymer. *Carbohydrate Polymers*, 62, 274–282.

Lazzeri, A., Zebarjad, S.M., Pracella, M., Cavalier, K., Rosa, R., (2005). Filler toughening of plastics. Part 1—The effect of surface interactions on physico-mechanical properties and rheological behaviour of ultrafine CaCO3/HDPE nanocomposites. *Polymer,* 46, 827–844.

Li, G., Zhang, C., Li, Y., Peng, H., Chen, K., (2010). Rapid polymerization initiated by redox initiator for the synthesis of polyaniline nanofibers. *Polymer,* 51, 1934–1939.

Liu, D., Zhong, T., Chang, P.R., Li, K., Wu, Q., (2010). Starch composites reinforced by bamboo cellulosic crystals. *Bioresource Technology,* 101, 2529–2536.

Lodha, P., Netravali, A. N., (2005a). Characterization of stearic acid modified soy protein isolate resin and ramie fiber reinforced ‘green’ composites. *Composites Science and Technology,* 65, 1211–1225.

Lodha, P., Netravali, A. N., (2005b). Thermal and mechanical properties of environment-friendly ‘green’ plastics from stearic acid modified-soy protein isolate. *Industrial Crops and Products,* 21, 49–64.

Madugu, L.A., Abdulwahab, M., Aigbodion, V.S., (2009). Effect of iron fillings on the properties and microstructure of cast fiber–polyester/iron filings particulate composite. *Journal of Alloys and Compounds*, 476, 807–811.

Mamoor, G.M., Qamar, N., Mehmood, U., Kamal, M.S., (2009). Effect of short glass fiber on mechanical and rheological properties of PMMA/SBR vulcanisate. *Chemical Engineering Research Bulletin,* 13, 51-54.

Matahwa, H., Ramiah, V., Sanderson, R.D., (2008). Calcium carbonate crystallization in the presence of modified polysaccharides and linear polymeric additives. *Journal of Crystal Growth,* 310, 4561–4569.

Ma, X., Yua, J., Kennedy, J.F (2005). Studies on the properties of natural fibers-reinforced thermoplastic starch composites. *Carbohydrate Polymers,* 62, 19–24.

McHugh, D.J., (1987). *Production, properties and uses of alginates.* URL: http://www.fao.org/docrep/X5822E/x5822e04.htm#chapter%202%20%20%20production,%20properties%20and%20uses%20of%20alginates. Accessed on 9th November 2010.

Mirmohseni, A., Zavareh, S., (2010). Preparation and characterization of an epoxy nanocomposite toughened by a combination of thermoplastic, layered and particulate nano-fillers. *Materials and Design*, 31, 2699–2706.

Mohee, R., Unmar, G.D., Mudhoo, A., Khadoo, P., (2008). Biodegradability of biodegradable/degradable plastic materials under aerobic and anaerobic conditions. *Waste Management*, 28, 1624–1629.

Nachwachsende-rohstoffe.de, (2007). *Generation of a new biopolymer database*. URL: http://www.m-base.de/main/fileadmin/mbase/main/documents/Biopolymerdatenbank_e.pdf. Accessed on 30th March 2010.

Nayak, S.K., Mohanty, S., Samal, S.K., (2009). Influence of short bamboo/glass fiber on the thermal, dynamic mechanical and rheological properties of polypropylene hybrid composites. *Materials Science and Engineering A*, 523, 32–38.

Nishino, T., Matsuda, I., Hirao, K., (2004). All-Cellulose Composite. *Macromolecules,* 37, 7683-7687.

Olivas, G.I., Barbosa-Canovas, G.V., (2008). Alginate–calcium films: Water vapor permeability and mechanical properties as affected by plasticizer and relative humidity. *LWT,* 41, 359–366.

Oprea, S., Dodita, T., (2001). Influence of agitation during emulsion polymerization of acrylic–styrene latexes on end product properties. *Progress in Organic Coatings,* 42, 194–201.

Pathak, T.S., Yun, J.H., Lee, J., Paeng, K.J., (2010). Effect of calcium ion (cross-linker) concentration on porosity, surface morphology and thermal behavior of calcium alginates prepared from algae (*Undaria pinnatifida*). *Carbohydrate Polymers*, 81, 633–639.

Plantenga, T.L., (2007). *Design of a fixture and method for direct measurement of the shear modulus of thin, soft polyacrylamide substrates*. URL: http://www.mate.tue.nl/mate/pdfs/8835.pdf. Accessed on 19th April 2011.

Pongjanyakul, T., Priprem, A., Puttipipatkhachorn, S., (2005). Investigation of novel alginate-magnesium aluminum silicate microcomposite films for modified-release tablets. *Journal of Controlled Release*. 107, 343–356.

Pongjanyakul, T., Puttipipatkhachorn, S., (2008). Alginate–magnesium aluminum silicate composite films: Effect of film thickness on physical characteristics and permeability. *International Journal of Pharmaceutics,* 346, 1–9.

Prachayawarakorn, J., Sangnitidej, P., Boonpasith, P., (2010). Properties of thermoplastic rice starch composites reinforced by cotton fiber or low-density polyethylene. *Carbohydrate Polymers,* 81, 425–433.

Pulat, M., & Babayigit, D., (2001). Surface modification of PU membranes by graft copolymerization with acrylamide and itaconic acid monomers. *Polymer Testing,* 20, 209–216.

Qin, L., Qiu, J., Liu, M., Ding, S., Shao, L., Lu, S., Zhang, G., Zhao, Y., Fu, X., (2011). Mechanical and thermal properties of poly(lactic acid) composites with rice straw fiber modified by poly(butyl acrylate). *Chemical Engineering Journal*, 166, 772–778.

Quantum Micronet (2011). *Quantum Micronet. SEM-EDAX-Optical Microscopy.* URL: http://www.quantummicromet.co.uk/microimages.html. Accessed on 20th August 2011.

Rai, U.S., Singh, R.K., (2003). Synthesis and mechanical characterization of polymer-matrix composites containing calcium carbonate/white cement filler. *Materials Letters,* 58, 235– 240.

Rao, K.M.M., Rao, K.M., (2007). Extraction and tensile properties of natural fibers: Vakka, date and bamboo. *Composite Structures,* 77, 288–295.

Ratnayake, W.S., Jackson, D.S., (2009). Starch gelatinization. *Advanced Food Nutrition Research,* 55, 221-268.

Raz, S., Testeniere, O., Hecker, A., Steve Weiner, S., Gilles Luquet, G., (2002). Stable Amorphous Calcium Carbonate Is the Main Component of the Calcium Storage Structures of the Crustacean Orchestia cavimana. *Biol. Bull.*, 203, 269–274.

Rhim, J., (2004). Physical and mechanical properties of water resistant sodium alginate films. *Lebensmittel-Wissenschaft und-Technologie*, 37, 323–330.

Rhim, J., Ng, P.K.W., (2007). Natural Biopolymer-Based Nanocomposite Films for Packaging Applications. *Critical Reviews in Food Science and Nutrition*, 47, 411–433.

Rong, M.Z., Zhang, M.Q., Shi, G., Ji, Q.L., Wetzel, B., Friedrich, K., (2003). Graft polymerization onto inorganic nanoparticles and its effect on tribological performance improvement of polymer composites. *Tribology International*, 36, 697–707

Sahebian, S., (2007). Effect of Nano-sized Calcium Carbonate on Creep Behavior of Medium Density Polyethylene. M.Sc Thesis, University of Mashhad, Ferdowsi.

Sahebian, S., Zebarjada, S.M., Khakia, J.V., Sajjadi, S.A., (2009). The effect of nano-sized calcium carbonate on thermodynamic parameters of HDPE. *Journal of Materials Processing Technology*, 209, 1310–1317.

Said, N., (2010). *The Importance of Starch Gelatinization*. URL: http://www.insta-pro.com/pdfs/Starch-Gelatinization.pdf. Accessed on 13th January 2010.

Sanchez-Garcia, M.D., Gimenez, E., Lagaron, J.M., (2008). Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. *Carbohydrate Polymers*, 71, 235–244.

Satyanarayana, K.G., Arizaga, G.G.C., Wypych, F., (2009). Biodegradable composites based on lignocellulosic fibers—An overview. *Progress in Polymer Science,* 34, 982–1021.

Scott, G., Wiles, D.M., (2002). Degradable hydrocarbon polymers in waste and litter control. In: Scott, G. (Ed.), *Degradable polymers: Principles and Applications*. 2nd Edition. (pp 449 – 479). Netherlands: Kluwer Academic Publishers.

Shah, A.A., Hasan, F., Hameed, A., Ahmed, S., (2008). Biological degradation of plastics: A comprehensive review. *Biotechnology Advances*, 26, 246–265.

Shiwanov, E., (2008). *The Green Glossary*. URL: http://www.insideoutdoor.com/documents/GreenGlossary8-08.pdf. Accessed on 12th November 2010.

Shui, M., (2003). Polymer surface modification and characterization of particulate calcium carbonate fillers. *Applied Surface Science,* 220, 359–366.

Šimkovic, I., (2008). What could be greener than composites made from polysaccharides? *Carbohydrate Polymers,* 74, 759–762.

Siracusa, V., Rocculi, P.,, Romani, S., Rosa, M.D., (2008). Biodegradable polymers for food packaging: A review. *Trends in Food Science & Technology*, 19, 634–643.

Stanmore, B. R., Gilot, P. (2005). Review: Calcination and carbonatoin of limestone during thermal cycling for CO_2 sequestration. *Fuel Processing Technology*, 86, 1707-1743.

Stevens, M.P., (1999). *Polymer chemistry: An introduction.* 3rd Edition. New York: Oxford University Press.

Suresha, B., Kumar, B.N.R., Venkataramareddy, M., Jayaraju, T., (2010). Role of micro/nano fillers on mechanical and tribological properties of polyamide66/polypropylene composites. *Materials and Design,* 31, 1993–2000

The Plastics Portal (2010). *Plastics – the facts 2010. An analysis of European plastics production, demand and recovery for 2009.* URL: http://www.plasticseurope.org/documents/document/20101028135906-final_plasticsthefacts_26102010_lr.pdf. Accessed on 19th November 2010.

Thwe, M.M., Liao, K., (2003). Durability of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Composites Science and Technology,* 63, 375–387.

Wang, K., Wu, J., Ye, L., Zeng, H., (2003). Mechanical properties and toughening mechanisms of polypropylene/barium sulfate composites. *Composites: Part A,* 34, 1199–1205.

Wang, L., Auty, M.A.E., Kerry, J.P., (2010). Physical assessment of composite biodegradable films manufactured using whey protein isolate, gelatin and sodium alginate. *Journal of Food Engineering,* 96, 199–207.

Wan, Z., Xiong, Z., Ren, H., Huang, Y., Liu, H., Xiong, H., Wu, Y., Han, J., (2011). Graft copolymerization of methyl methacrylate onto bamboo cellulose under microwave irradiation. *Carbohydrate Polymers,* 83, 264–269.

Wong, K.J., Zahi, S., Low, K.O., Lim, C.C., (2010). Fracture characterisation of short bamboo fibre reinforced polyester composites. *Materials and Design,* 31, 4147–4154.

Xie, M., Olderøy, M., Andreassen, J., Selbach, S.M., Strand, B.L., Sikorski, P., (2010a). Alginate-controlled formation of nanoscale calcium carbonate and hydroxyapatite mineral phase within hydrogel networks. *Acta Biomaterialia,* 6, 3665–3675.

Xie, Y., Hill, C.A.S, Xiao, Z., Militz, H., Mai, C., (2010b). Silane coupling agents used for natural fiber/polymer composites: A review. *Composites: Part A,* 41, 806–819.

Xu, Y.X., Kim, K.M., Hannaa, M.A., Nag, D., (2005). Chitosan–starch composite film: preparation and characterization. *Industrial Crops and Products,* 21, 185–192.

Yue, P., Rayas-Duarte, P., and Elias, E., (1999). Effect of Drying Temperature on Physicochemical Properties of Starch Isolated from Pasta. *Cereal Chemistry,* 76, 541–547.

Zhang, M.Q., Rong, M.Z., Lu, X., (2005). Fully biodegradable natural fiber composites from renewable resources: All-plant fiber composites. *Composites Science and Technology*, 65, 2514–2525.

Zuiderduin, W.C.J., Westzaan, C., Hue´tink, J., Gaymans, R.J., (2003). Toughening of polypropylene with calcium carbonate particles. *Polymer,* 44, 261–275.

Appendix A

Determination on mechanical properties of HP grafted with different monomer-sodium alginate ratio

Monomer -sodium alginate ratio	Tensile strength (MPa)				Standard Deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1 : 0.16	2.4588	2.0566	2.0566	2.1907	0.2322
1 : 0.24	18.5318	15.1184	19.4660	17.7054	2.2886
1 : 0.49	7.3486	6.2984	8.4419	7.3630	1.0718
1 : 0.73	11.5027	15.4405	15.0948	14.0127	2.1806

Monomer -sodium alginate ratio	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1 : 0.16	15.17	10.55	17.76	14.49	3.65
1 : 0.24	5.68	5.13	12.63	7.82	4.18
1 : 0.49	39.04	42.04	60.80	47.29	11.79
1 : 0.73	17.75	26.74	44.62	29.70	13.68

*Initial distance between grips = 20 mm

Monomer -sodium alginate ratio	Young’s modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1 : 0.16	43.9395	45.7855	40.6394	43.4548	2.6071
1 : 0.24	844.3398	717.1436	540.8598	700.7811	152.4002
1 : 0.49	36.6296	27.8731	20.1461	28.2163	8.2471
1 : 0.73	221.7848	236.4092	118.5998	192.2646	64.2133

Appendix B

Determination on mechanical properties of HPCC prepared with water (W) added to sodium alginate (SA) powder during gelatinisation (W + SA)

$CaCO_3$ (wt%)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1	18.4375	15.2999	14.4302	16.0559	2.1079
2	13.6256	11.8269	13.5662	13.0062	1.0218
3	12.5539	18.9085	13.2272	14.8965	3.4907
4	18.8752	11.5931	12.6115	14.3600	3.9434
5	21.9894	21.8217	21.7930	21.8680	0.1061
10	18.9131	19.5471	18.8391	19.0998	0.3892

$CaCO_3$ (wt%)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1	7,68	5.36	4.40	5.81	1.69
2	7.77	6.00	6.72	6.83	0.89
3	7.10	11.66	10.71	9.82	2.41
4	11.76	7.14	12.30	10.40	2.84
5	10.51	7.14	6.16	7.93	2.28
10	6.86	8.67	5.29	6.94	1.69

*Initial distance between grips = 20 mm

$CaCO_3$ (wt%)	**Young's modulus (MPa)**				**Standard deviation**
	Replicate 1	**Replicate 2**	**Replicate 3**	**Average**	
1	733.8543	666.2432	624.5479	674.8818	55.1629
2	151.7972	209.1356	257.8153	206.2494	53.0679
3	484.0887	247.2891	394.2279	375.2019	119.5408
4	157.9587	413.0523	351.7964	307.6024	133.1654
5	678.4670	792.4124	820.4345	763.7713	75.1926
10	595.5190	612.5828	707.8537	638.6518	60.5348

Appendix C

Determination on mechanical properties of HPCC prepared with sodium alginate (SA) powder added into water (W) during gelatinisation (SA + W)

$CaCO_3$ (wt%)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1	20.8404	23.9780	21.7747	22.1977	1.6110
2	35.2996	30.1256	28.6769	31.3673	3.4816
3	32.7373	33.6080	29.2195	31.8549	2.3235
4	31.2954	33.2784	34.5680	33.0473	1.6485
5	36.7481	33.2423	28.7546	32.9150	4.0068
10	23.8353	23.4119	29.8538	25.7004	3.6032

$CaCO_3$ (wt%)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1	30.25	42.35	32.98	35.19	6.34
2	18.50	12.92	12.15	14.52	3.46
3	17.15	23.15	29.88	23.39	6.37
4	25.25	27.07	26.55	26.29	0.94
5	21.54	20.65	22.38	21.52	0.87
10	10.95	13.01	20.17	14.71	4.84

*Initial distance between grips = 20 mm

$CaCO_3$ (wt%)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1	243.2714	173.9466	222.7449	213.3210	35.6102
2	731.4511	632.6192	614.8509	659.6404	62.8212
3	591.2185	554.8995	342.6611	496.2597	134.2541
4	364.1344	429.8842	452.8705	415.6297	46.0534
5	628.1022	598.9403	511.0547	579.3657	60.9295
10	706.9626	677.4592	491.7692	625.3970	116.6615

Appendix D

Determination on mechanical properties of HP processed with different reaction time

Reaction time (minutes)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
30	11.2354	9.6356	11.5709	10.8139	1.0342
90	18.5318	15.1184	19.4660	17.7054	2.2886

Reaction time (minutes)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
30	17.88	20.71	23.36	20.65	2.74
90	5.68	5.13	12.63	7.82	4.18

*Initial distance between grips = 20 mm

Reaction time (minutes)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
30	273.9829	219.9706	212.3068	235.42	33.6155
90	844.3398	717.1436	540.8598	700.78	152.4002

Appendix E

Determination on mechanical properties of HP processed with different reaction temperature and dried at 27 °C.

Reaction temperature (°C)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
50	6.9876	11.9369	10.3488	9.7578	2.5270
60	1.2014	1.9291	0.8872	1.3393	0.5344
70	9.4409	7.9060	6.9421	8.0963	1.2602
80	4.2343	6.5442	5.1659	5.3148	1.1621

Reaction temperature (°C)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
50	13.69	12.86	6.83	11.13	3.75
60	3.90	10.36	5.76	6.67	3.32
70	12.08	13.28	12.52	12.62	0.61
80	10.59	9.38	12.58	10.85	1.62

Reaction temperature (°C)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
50	298.0768	295.2521	331.9034	308.4108	20.3942
60	168.6821	207.8683	148.0275	174.8593	30.3949
70	210.1761	182.0562	141.6261	177.9528	34.4587
80	163.5904	218.1156	107.5311	163.0790	55.2941

Appendix F

Determination on mechanical properties of HP processed with different reaction temperature and dried at 50 °C.

Reaction temperature (°C)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
50	24.5291	19.0950	17.9814	20.5352	3.5034
60	8.5563	14.5079	19.1801	14.0814	5.3247
70	11.5502	9.2777	13.9231	11.5837	2.3229
80	4.2288	4.5371	5.0637	4.6099	0.4222

Reaction temperature (°C)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
50	7.38	7.36	6.92	7.22	0.26
60	4.20	10.19	10.51	8.30	3.56
70	6.25	4.85	5.69	5.60	0.71
80	5.18	6.17	9.35	6.90	2.18

*Initial distance between grips = 20 mm

Reaction temperature (°C)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
50	1003.8167	991.4748	797.2223	930.8379	115.8790
60	371.9735	368.2551	315.5483	351.9256	31.5585
70	585.7141	456.4387	466.6221	502.9250	71.8780
80	152.4868	178.8792	185.3326	172.2329	17.4023

Appendix G

Determination on mechanical properties of HP prepared at different stirring speed.

Stirring speed (rpm)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
300 rpm	4.2236	3.9523	5.1749	4.4503	0.6420
400 rpm	2.6606	1.9420	2.5191	2.3739	0.3807
600 rpm	2.5729	2.1333	3.6472	2.7844	0.7788
800 rpm	3.8501	4.0760	6.3072	4.7444	1.3581
1000 rpm	22.6574	23.1671	21.9716	22.5987	0.5999
1200 rpm	24.5291	19.0951	17.9814	20.5352	3.5034
1400 rpm	6.0576	8.7552	10.3035	8.3721	2.1487

Stirring speed (rpm)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
300 rpm	5.68	5.13	12.63	7.82	4.18
400 rpm	51.50	23.96	34.08	36.51	13.93
600 rpm	11.97	10.52	21.27	14.59	5.83
800 rpm	17.66	16.49	27.09	20.41	5.81
1000 rpm	19.22	16.37	18.20	17.93	1.44
1200 rpm	9.81	7.42	8.69	8.64	1.19
1400 rpm	9.55	13.93	9.35	10.94	2.59

*Initial distance between grips = 20 mm

Stirring speed (rpm)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
300 rpm	435.6600	717.1436	540.8598	564.5545	142.2299
400 rpm	8.7040	18.1651	15.5257	14.1316	4.8822
600 rpm	60.0815	64.6740	74.3127	66.3561	7.2632
800 rpm	95.2600	70.4025	81.9545	82.5390	12.4391
1000 rpm	1040.9407	1176.5864	1076.5822	1098.0364	70.3218
1200 rpm	1003.8167	991.4748	797.2223	930.8379	115.8790
1400 rpm	183.7560	231.6090	446.3165	287.2272	139.8375

Appendix H

Determination on mechanical properties of HPFC incorporated with different fibre amount.

Fibre amount (wt%)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0	22.6574	23.1670	21.9716	22.5987	0.5999
5	3.2719	4.1159	3.6276	3.6718	0.4237
10	2.4834	2.0787	2.5840	2.3820	0.2675
15	3.2007	2.4381	2.2595	2.6328	0.4999
20	2.8861	2.7976	3.1514	2.9450	0.1841

Fibre amount (wt%)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0	19.22	16.37	18.20	17.93	1.44
5	9.52	8.09	12.28	9.96	2.13
10	9.49	11.70	11.97	11.05	1.36
15	10.98	5.62	6.80	7.80	2.82
20	8.06	7.17	6.48	7.23	0.79

*Initial distance between grips = 20 mm

Fibre amount (wt%)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0	1040.9407	1176.5864	1076.5822	1098.0364	70.3218
5	93.1382	116.6666	126.4428	112.0825	17.1189
10	104.8543	46.0255	61.9809	70.9536	30.4235
15	80.2863	92.8811	81.7716	84.9797	6.8830
20	103.1718	117.0716	130.0562	116.7665	13.4448

Appendix I

Determination on mechanical properties of HPFC incorporated with different fibre size.

Fibre size (µm)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
100	7.5890	7.5183	9.4024	8.1699	1.0680
150	8.3094	9.5276	8.7008	8.8459	0.6219
300	10.1436	10.7211	9.3635	10.0761	0.6814
>300	3.2719	4.1159	3.6276	3.6718	0.4237

Fibre size (µm)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
100	7.81	9.40	8.43	8.55	0.80
150	5.97	6.92	6.95	6.61	0.56
300	6.93	6.76	6.93	6.88	0.10
>300	9.52	8.09	12.28	9.96	2.13

*Initial distance between grips = 20 mm

Fibre size (µm)	Young’s modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
100	210.2391	206.1617	348.7772	255.0594	81.1877
150	339.1046	338.7494	310.1509	329.3350	16.6148
300	405.8542	424.5104	395.0923	408.4856	14.8846
>300	93.1382	116.6666	126.4428	112.0825	17.1189

Appendix J

Determination on mechanical properties of HPFC incorporated with fibre by in-situ addition method

Fibre amount (wt%)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0	22.6574	23.1670	21.9716	22.5987	0.5999
5	7.3776	9.1509	9.4519	8.6601	1.1208
10	6.1728	5.5922	5.8493	5.8715	0.2909
15	5.8055	5.9823	5.3853	5.7244	0.3066
20	4.5158	3.9363	5.6300	4.6940	0.8608

Fibre amount (wt%)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0	19.22	16.37	18.20	17.93	1.44
5	5.23	5.42	6.50	5.72	0.68
10	4.71	4.46	4.41	4.53	0.16
15	8.42	8.89	9.56	8.96	0.57
20	4.25	4.15	4.66	4.35	0.27

*Initial distance between grips = 20 mm

Fibre amount (wt%)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0	1040.9407	1176.5864	1076.5822	1098.0364	70.3218
5	313.2649	370.2254	312.7556	332.0820	33.0341
10	333.1093	289.9308	335.8832	319.6411	25.7672
15	236.1875	218.5706	195.1402	216.6328	20.5922
20	322.8130	313.6995	322.6866	319.7330	5.2256

Appendix K

Determination on mechanical properties of HPFC incorporated with fibre by post addition method

Fibre amount (wt%)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0	22.6574	23.1670	21.9716	22.5987	0.5999
5	10.1436	10.7211	8.1981	9.6876	1.3219
10	7.9065	7.4662	7.3175	7.5634	0.3063
15	7.4158	7.2179	7.6204	7.4180	0.2012
20	5.9623	5.7496	5.7946	5.8355	0.1121

Fibre amount (wt%)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0	19.22	16.37	18.20	17.93	1.44
5	6.93	6.76	5.47	6.39	0.80
10	5.48	5.89	4.99	5.45	0.45
15	4.45	4.40	4.65	4.50	0.13
20	4.39	4.15	3.27	3.94	0.59

*Initial distance between grips = 20 mm

Fibre amount (wt%)	Young’s modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0	1040.9407	1176.5864	1076.5822	1098.0364	70.3218
5	405.8542	424.5104	460.6931	430.3526	27.8823
10	467.2427	407.4405	389.8538	421.5123	40.5681
15	479.7800	459.1874	450.8132	463.2602	14.9067
20	419.3953	416.5041	447.4699	427.7897	17.1047

Appendix L

Determination on mechanical properties of HP incorporated with 1 wt% of different type of crosslinker

Type of crosslinker (1wt%)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
N-MBA	11.1796	9.5584	10.3318	10.3566	0.8109
$CaCO_3$	20.8404	23.9782	21.7747	22.1977	1.6110
$CaCl_2$	11.5047	9.1189	8.30706	9.6435	1.6621

Type of crosslinker (1wt%)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
N-MBA	28.18	19.22	15.15	20.85	6.67
$CaCO_3$	7.68	5.36	4.40	5.81	1.69
$CaCl_2$	20.32	25.28	25.46	23.69	2.92

*Initial distance between grips = 20 mm

Type of crosslinker (1wt%)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
N-MBA	99.2563	254.9240	177.5742	177.2515	77.8343
$CaCO_3$	733.8543	666.2432	624.5479	674.8818	55.1629
$CaCl_2$	236.8466	156.4158	147.1465	180.1363	49.3307

Appendix M

Determination on mechanical properties of HP incorporated with different amount of *N*-MBA

N-MBA (wt%)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1	11.1796	9.5584	10.3318	10.3566	0.8109
2	11.2115	14.0161	11.0489	12.0922	1.6681
3	10.8128	9.7137	9.1785	9.9016	0.8332
4	15.8835	13.2746	12.8650	14.0077	1.6373
5	22.6574	23.1672	21.9716	22.5987	0.5999
10	13.4610	13.1958	13.2222	13.2930	0.1461

N-MBA (wt%)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1	28.18	19.22	15.15	20.85	6.67
2	13.55	53.08	51.30	39.31	22.33
3	20.56	21.03	18.95	20.18	1.09
4	13.92	8.80	19.53	13.87	5.39
5	19.22	16.37	18.20	17.93	1.44
10	16.10	8.78	13.00	12.63	3.67

*Initial distance between grips = 20 mm

***N*-MBA (wt%)**	**Young's modulus (MPa)**				**Standard deviation**
	Replicate 1	**Replicate 2**	**Replicate 3**	**Average**	
1	99.2563	254.9240	177.5742	177.2515	77.8343
2	364.8563	78.0136	75.5541	172.8080	166.3233
3	211.8334	209.3538	202.0313	207.7395	5.0965
4	405.8581	587.4236	298.7201	430.6673	145.9419
5	1040.9407	1176.5864	1076.5822	1098.0364	70.3218
10	285.7723	378.1039	315.9526	326.6096	47.0793

Appendix N

Determination on mechanical properties of HPCC incorporated with different amount of $CaCO_3$

$CaCO_3$ (wt%)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1	20.8404	23.9783	21.7747	22.1977	1.6110
2	30.4222	32.3866	30.2033	31.0040	1.2023
3	31.4415	34.2188	29.6755	31.7786	2.2903
4	34.2424	31.8366	32.2201	32.7664	1.2926
5	36.7481	33.2423	28.7546	32.9150	4.0068
10	26.7192	25.3319	26.1994	26.0835	0.7009

$CaCO_3$ (wt%)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1	7.68	5.36	4.40	5.81	1.69
2	7.77	6.00	6.72	6.83	0.89
3	7.10	11.66	10.71	9.82	2.41
4	11.76	7.14	12.30	10.40	2.84
5	10.51	7.14	6.16	7.93	2.28
10	6.86	8.67	5.29	6.94	1.69

*Initial distance between grips = 20 mm

$CaCO_3$ (wt%)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
1	733.8543	666.2432	624.5479	674.8818	55.1629
2	501.9753	519.1225	581.1777	534.0918	41.6691
3	484.0887	394.2279	433.5614	437.2927	45.0465
4	413.0523	351.7964	380.0165	381.6217	30.6595
5	792.4124	678.4670	820.4345	763.7713	75.1926
10	595.5190	612.5828	707.8537	638.6518	60.5348

Appendix O

Determination on mechanical properties of HPCC adjusted to different pH

PH	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
7	36.7481	33.2423	28.7546	32.9150	4.0068
8	36.8675	36.1323	39.9521	37.6506	2.0267
10	31.4223	34.3610	32.4488	32.7441	1.4914
12	16.8944	16.6849	14.5552	16.0448	1.2943

PH	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
7	10.51	7.14	6.16	7.93	2.28
8	6.73	9.40	12.84	9.66	3.06
10	9.57	10.12	10.26	9.98	0.36
12	14.38	11.91	12.13	12.81	1.37

*Initial distance between grips = 20 mm

PH	Young’s modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
7	792.4124	678.4670	820.4345	763.7713	75.1926
8	478.8012	420.6877	444.5429	448.0106	29.2115
10	751.8669	790.1535	734.5689	758.8631	28.4451
12	61.3705	69.0697	104.2803	78.2401	22.8776

Appendix P

Determination on mechanical properties of HP surface treated with $CaCl_2$ and glycerol

$CaCl_2$: Glycerol amount (% of polymer total solid)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0 : 0	22.6574	23.1670	21.9716	22.5987	0.5999
1 : 5	14.2824	11.6370	16.5995	14.1730	2.4831
1 : 10	7.7491	7.4250	10.2203	8.4648	1.5290
3 : 5	13.2177	8.0280	14.2602	11.8353	3.3382
3 : 10	9.2269	10.3331	11.8595	10.4732	1.3219
5 : 5	18.4394	29.7063	26.0559	24.7339	5.7486
5 : 10	14.4311	14.9926	10.2921	13.2386	2.5671
10 : 5	17.3625	22.2408	15.8528	18.4854	3.3387
10 : 10	11.9304	18.4134	14.5673	14.9704	3.2603

$CaCl_2$: Glycerol amount (% of polymer total solid)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0 : 0	19.22	16.37	18.20	17.93	1.44
1 : 5	12.03	12.47	16.88	13.79	2.68
1 : 10	24.43	19.25	19.02	20.90	3.06
3 : 5	5.55	14.62	21.08	13.75	7.80
3 : 10	18.46	18.48	14.29	17.08	2.42
5 : 5	9.77	12.71	5.72	9.40	3.51
5 : 10	17.68	20.70	19.96	19.45	1.57
10 : 5	2.97	5.79	9.19	5.98	3.12
10 : 10	12.43	17.22	5.64	11.76	5.82

*Initial distance between grips = 20 mm

$CaCl_2$: Glycerol amount (% of polymer total solid)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0 : 0	1040.9407	1176.5864	1076.5822	1098.0364	70.3218
1 : 5	328.5782	340.2938	223.8177	297.5632	64.1335
1 : 10	150.8842	137.8966	163.4263	150.7357	12.7655
3 : 5	514.3399	262.8094	357.1719	378.1071	127.0653
3 : 10	115.0130	145.5639	323.8083	194.7951	112.7681
5 : 5	764.2533	659.3975	1112.5135	845.3881	237.2039
5 : 10	375.1490	299.7095	379.0956	351.3180	44.7378
10 : 5	637.6712	862.2256	471.7758	657.2242	195.9579
10 : 10	219.4808	301.1250	431.2514	317.2858	106.8063

Appendix Q

Determination on mechanical properties of HP treated by homogenous mixing with $CaCl_2$ and glycerol.

$CaCl_2$: Glycerol amount (% of polymer total solid)	**Tensile strength (MPa)**				**Standard deviation**
	Replicate 1	**Replicate 2**	**Replicate 3**	**Average**	
0 : 0	22.6574	23.1670	21.9716	22.5987	0.5999
1 : 0	6.9068	6.4870	9.1515	7.5151	1.4326
1 : 10	3.6551	4.2762	3.0193	3.6502	0.6285
5 : 0	2.9481	3.2024	3.0673	3.0726	0.1273
5 : 10	1.4452	1.3650	2.3800	1.7301	0.5643

$CaCl_2$: Glycerol amount (% of polymer total solid)	**Elongation at break (%)**				**Standard deviation**
	Replicate 1	**Replicate 2**	**Replicate 3**	**Average**	
0 : 0	19.22	16.37	18.20	17.93	1.44
1 : 0	34.59	24.17	38.28	32.35	7.32
1 : 10	36.97	54.07	26.02	39.02	14.14
5 : 0	6.78	8.52	11.01	8.77	2.12
5 : 10	15.50	11.41	12.47	13.13	2.12

*Initial distance between grips = 20 mm

$CaCl_2$: Glycerol amount (% of polymer TSC)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0 : 0	1040.9407	1176.5864	1076.5822	1098.0364	70.3218
1 : 0	219.4043	134.7574	119.9608	158.0408	53.6548
1 : 10	17.5530	15.2169	25.0930	19.2876	5.1615
5 : 0	109.5152	143.8030	101.3959	118.2380	22.5090
5 : 10	29.5945	32.3621	62.7556	41.5707	18.3987

Appendix R

Determination on mechanical properties of HP treated by homogenous mixing with $CaCO_3$ and glycerol

$CaCO_3$: Glycerol amount (% of polymer total solid)	Tensile strength (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0 : 0	22.6574	23.1670	21.9716	22.5987	0.5999
1 : 0	10.3541	15.3455	17.4003	14.3666	3.6237
1 : 10	2.3698	3.6265	3.8918	3.2961	0.8130
5 : 0	10.9468	10.7688	11.2344	10.9833	0.2349
5 : 10	2.31388	3.1541	2.4163	2.6281	0.4584
10 : 0	8.71821	8.0789	8.4403	8.4125	0.3205
10 : 10	2.45232	2.7561	2.3765	2.5283	0.2009
30 : 0	8.92049	7.8657	9.7381	8.8414	0.9387
30 : 10	2.01614	2.5262	2.02143	2.1879	0.2930

$CaCO_3$: Glycerol amount (% of polymer total solid)	Elongation at break (%)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0 : 0	19.22	16.37	18.20	17.93	1.44
1 : 0	6.60	25.40	7.55	13.18	10.59
1 : 10	58.63	43.27	36.55	46.15	11.32
5 : 0	5.64	5.40	7.38	6.14	1.09
5 : 10	22.21	24.81	22.68	23.23	1.38
10 : 0	10.52	13.01	12.37	11.97	1.29
10 : 10	30.27	39.07	35.41	34.92	4.42
30 : 0	10.86	7.42	12.25	10.18	2.48
30 : 10	47.48	82.15	41.63	57.09	21.90

*Initial distance between grips = 20 mm

$CaCO_3$: Glycerol amount (% of polymer total solid)	Young's modulus (MPa)				Standard deviation
	Replicate 1	Replicate 2	Replicate 3	Average	
0 : 0	1040.9407	1176.5864	1076.5822	1098.0364	70.3218
1 : 0	481.8213	602.7058	620.7245	568.4172	75.5335
1 : 10	11.4647	17.7129	19.3890	16.1888	4.1762
5 : 0	499.6112	486.6208	306.8388	431.0236	107.7431
5 : 10	20.7444	23.9671	20.9163	21.8759	1.8130
10 : 0	243.9194	199.0673	216.4083	219.7984	22.6174
10 : 10	11.9114	9.5021	9.6599	10.3578	1.3478
30 : 0	251.8837	151.1205	221.1212	208.0418	51.6392
30 : 10	7.0706	4.5895	10.2943	7.3181	2.8604

Appendix S

Determination on swelling and solubility of HP in different solvents

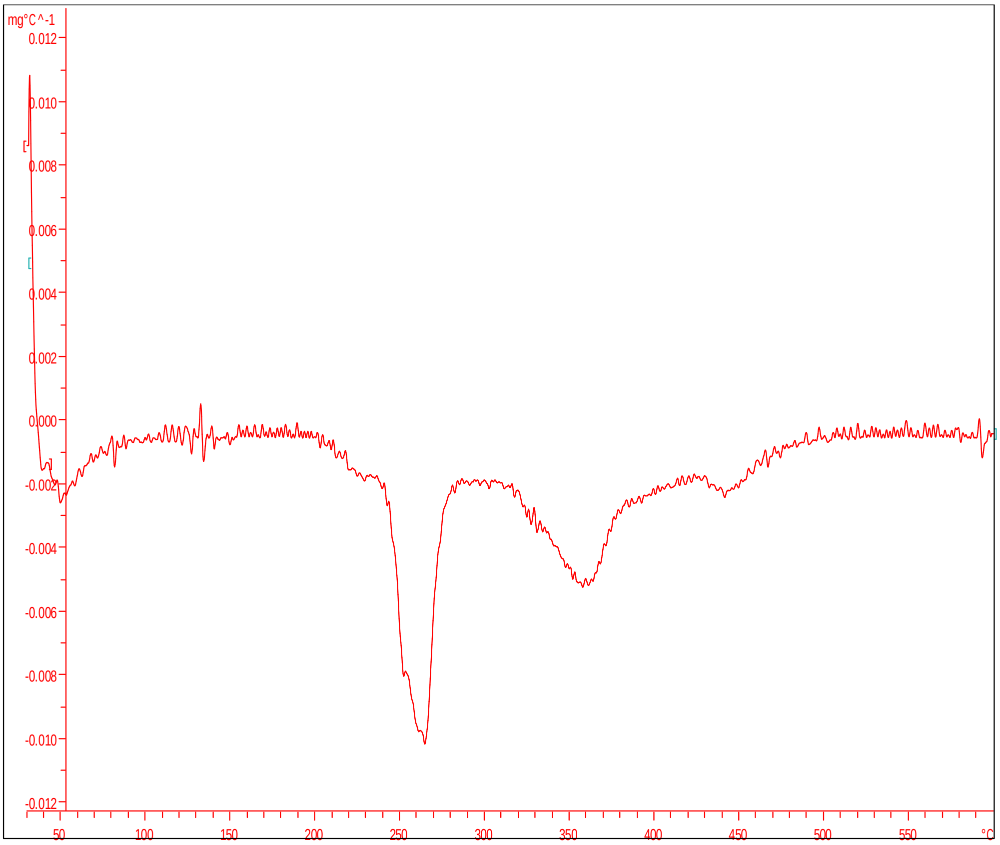
Solvent	**Original weight (g)**	**Wet weight (g)**	**Dry weight (g)**	**Swelling (%)**	**Solubility (%)**
Water	-	-	-	-	-
Acetonitrile	0.0520	0.0527	0.0515	2.33	0.96
Dimethylformamide	0.0533	0.0549	0.0530	3.58	0.56
Chloroform	0.0493	0.0549	0.0490	12.04	0.61
Toluene	0.0547	0.0593	0.0542	9.41	0.91

Appendix T

Determination on swelling and solubility of HPCC in different solvents

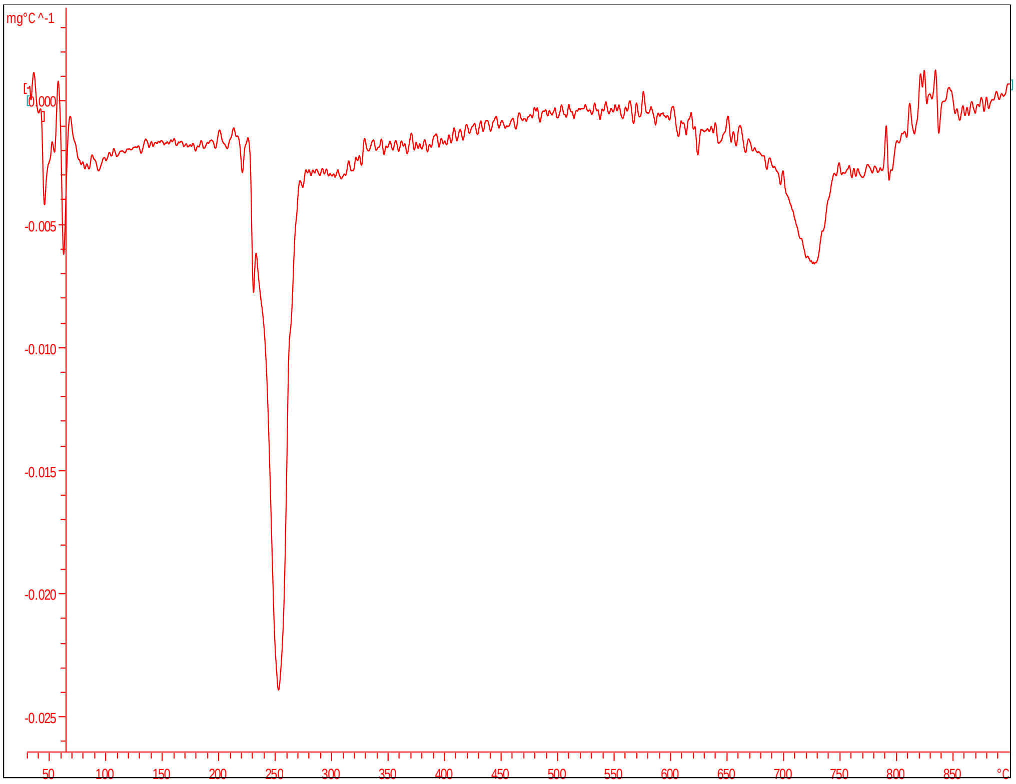
Solvent	Original weight (g)	Wet weight (g)	Dry weight (g)	Swelling (%)	Solubility (%)
Water	-	-	-	-	-
Acetonitrile	0.0441	0.0457	0.0440	3.86	0.23
Dimethylformamide	0.0487	0.0530	0.0485	9.28	0.41
Chloroform	0.0530	0.0581	0.0530	9.62	0.00
Toluene	0.0499	0.0552	0.0498	10.84	0.20

Appendix U



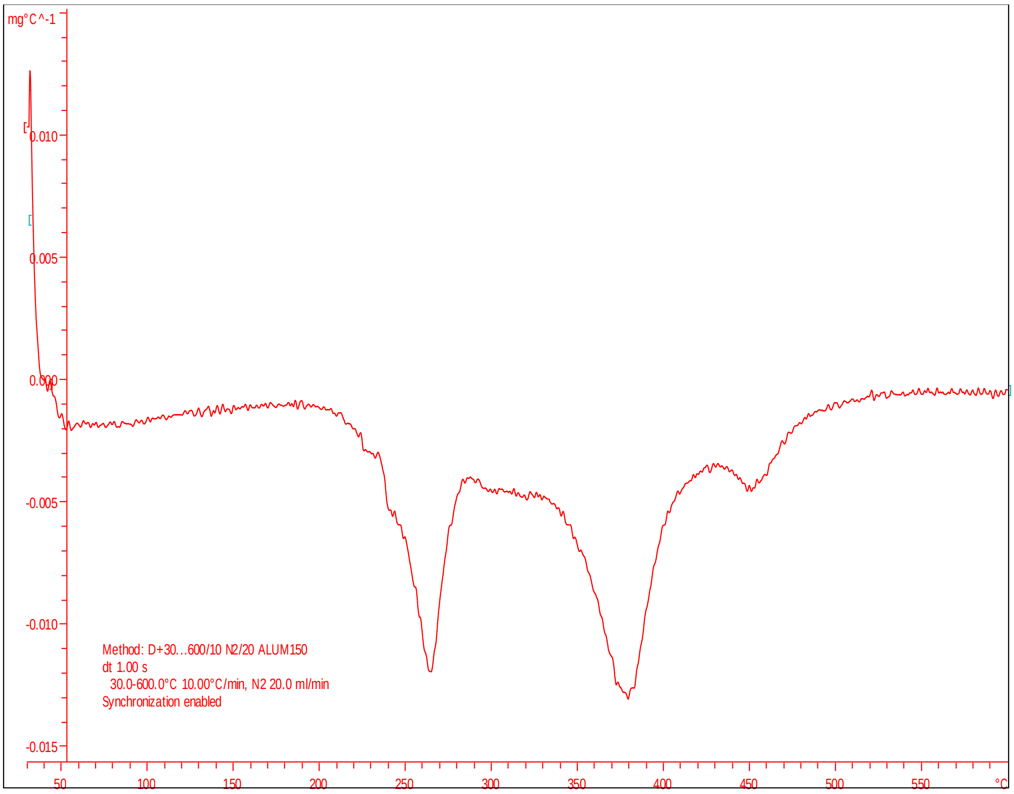
DTG thermogram of HP

Appendix V



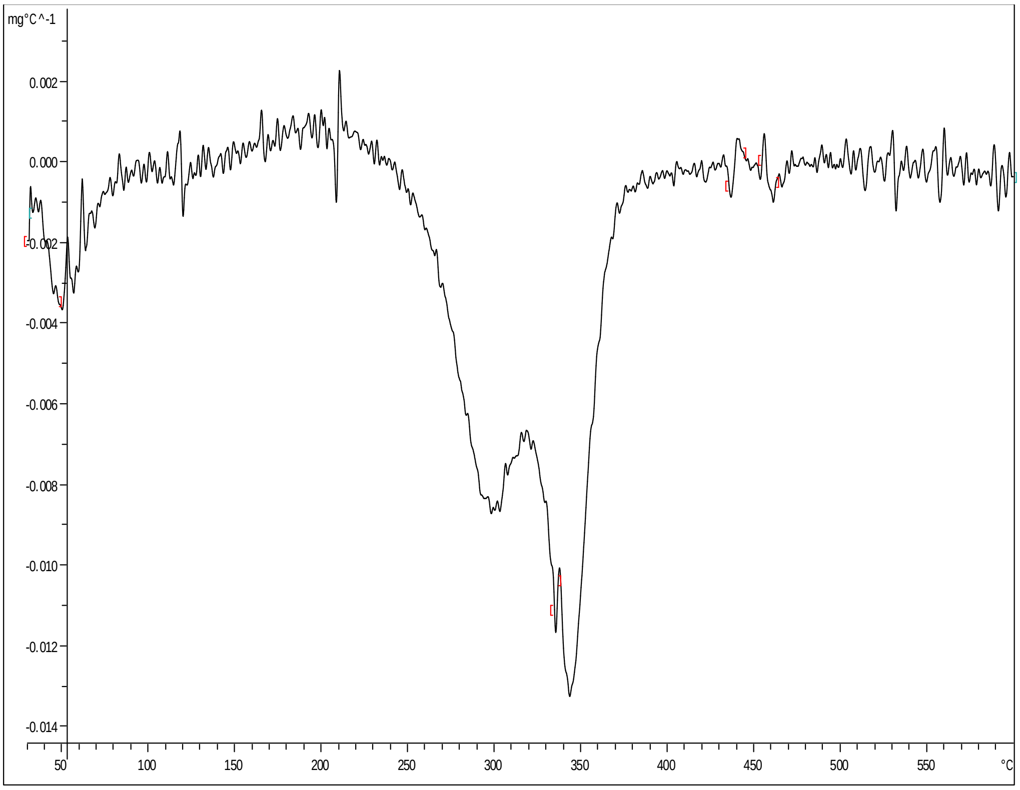
DTG thermogram of HPCC

Appendix W



DTG thermogram of HPFC

Appendix X



DTG thermogram of bamboo leaf fibre