CHAPTER ONE

INTRODUCTION

1.0 Introduction

Nowadays the amount of plastic waste increases every year and the exact time needed for its biodegradation is unknown. Plastic materials are widely used and since most of them are resistant to microbiological attack, there has been a continuous concern regarding the growing of plastic wastes in landfills (Kusaka *et al.*, 1998; Sadi *et al.*, 2010).

In general, natural polymers are produced by living organisms and are biodegradable, unlike most synthetic polymers (Prescott, 2006). It has controlled to growing interest in developing chemical and attracted an increasing biochemical processes to get and modify natural polymers. This further helps to develop their useful inherent properties for a wide range of applications in different fields, over the last few decades, mainly due to their richness, environmental concerns, and anticipated depletion of petroleum resources. There has been a marked growing interest in biodegradable materials for use in packaging, agriculture, medicine, and other areas (Kolybaba *et al.*, 2003).

Among natural polymers, poly(3-hydroxybutyric acid) (PHB) is one that is degraded by many microorganisms (bacteria, fungi and algae) in various environments (Edlund & Albertsson, 2002; Vroman & Tighzert, 2009). PHB occupies a special position due to its abundance. Poly(3-hydroxybutyrate) (PHB), a homopolymer of R(−)-3-hydroxybutyrate (3HB), storage material produced by a wide variety of bacteria under certain conditions. Intracellular PHB, which is accumulated in an amorphous state, is degraded by several hydrolases and the degraded products are used as a source of carbon and energy. When PHB-accumulating bacteria die, the PHB released into the environment is hydrolyzed by various microorganisms which secrete extracellular PHB deploymerases.(Kusaka *et al.*, 1998; Wang *et al.*, 2005). PHB is fully biodegradable polyester with optical activity, piezoelectricity and very good barrier properties.

Most synthetic polymers having molecular weights higher than about 1000 g/mol are resistant to microorganism attack. Exceptions are polymers having ester groups in the main chain, such as polyhydroxybutyrate (PHB), polycaprolactones (PCLO), polyvalerolactones (PVLO), poly(buthylene succinate) (PBS), poly(1,4-buthylene adipate) (PBA), polyglycolic acid (PGA), poly-L-lactic acid (PLLA), polyester-based urethanes (especially susceptible to fungi). Degradability in biopolymers is influenced by the chemical and physical microstructure of the polymer as well as the environmental conditions suitable for degradation to take place, like the conditions of soil and water.

The goals of this work were to improve PHB properties and natural biodegradable polyester and further diversify its applications; various modification strategies have been adopted. In order to improve mechanical properties and reduce the cost, blending of natural PHB with synthetic polymers was also performed. Miscibility studies of bacterial poly(3-hydroxybutyrate–co-3-hydroxyvalerate) with synthetic atactic (a-PHB) prepared by alkali metal alkoxide initiators are presented. To improve property of a biodegradable polymer, a lot of methods have been industrialized, such as random, grafting and blending. These methods develop both the biodegradation rate and the mechanical properties of the final products. Also mixing biopolymers or biodegradable polymers with each other can develop their intrinsic properties. PHB is a brittle polymer and to develop its mechanical properties it is mixed with other biodegradable materials (Smith, 2005).

PHB is a major composite in polyhydroxyalkanoates (PHA) which are intercellular polyester synthesized by bacteria. Although PHB is the best known and most used but for many applications close to the thermal degradation temperature, high melting point and the considerable brittleness of PHB are unfavorable properties. However, it has been the aim of this study to overcome these weaknesses by preparing blends of PHB

(Unger *et al.*, 2011). Poly(vinyl acetate) (PVAc) is a petroleum-derived polymer usually obtained by emulsion polymerization. It features excellent adhesion to various substrates (Pal & Gautam, 2013).

Recently, there has been a growing interest in developing natural polymeric materials with good film forming capacity for various applications. Biodegradable resources are used in packing, agriculture, medicine and other areas. Theoretically, PHB and PVAc affect the physiochemical properties of each other when they become miscible in a composite. A comprehensive study of structural, thermal, rheological and environmental properties of PHB/PVAc blends is carried out. The main reasons for its poor properties include low T_g and secondary crystallization formation which occurs during storage at ambient temperature. Polymer blending is considered to be one of the most effective methods for lowering the cost of production of these types of polymers, and in certain cases it improves processing and product quality.

First part of this research is to blend PHB, an expensive biodegradable semi-crystalline polymer and having a high amount of biodegradable aliphatic polyester with amorphous polymer, PVAc and to investigate the properties of the blends. Biodegradation studies of the blends were based on a standard burial soil test (Lim *et al.*, 2003; Mousavioun, 2011).

1.1 Problem of the Statement

PHB membranes have been found to lack chemical and mechanical stability. It has inherent favorable properties such as biodegradability, biocompatibility, non-toxicity, high melting degree, poor tensile strength and antimicrobial properties, it also has high brittleness and low flexibility. To overcome such disadvantages, PHB is modified by blending with PVAc.

The environmental influence of persistent plastic waste is raising general worldwide concern, and discarding methods are limited. Burning may generate toxic air pollution, satisfactory landfill sites were imperfect and recycling methods for commingled waste were expensive and often energy intensive. In addition, petroleum resources were determinate and were becoming limited. It will be important to find durable plastic substitutes, especially in short–term packaging and disposable applications.

Many studies have been made to improve the properties of PHB, but only a few of it focused on the blending PVAc/PHB films. Blending PHB with PVAc is an interesting approaches that can give friendly environmental polymers.

In this study, we propose another method to blend between PVAc with PHB to reduce the biodegradability of PHB. The blend component of (PVAc) could be transformed into degradable poly(vinyl alcohol) (PVA) by hydrolysis (Wada *et al.*, 2007). PHB has attracted much commercial interest as a biodegradable, plastic material because some of its physical properties are similar to those of polypropylene (PP), even though the two polymers have quite different chemical structures. PHB exhibits a high melting point of approximately 180 °C, with a high degree of crystallinity, and is rapidly biodegradable.

1.2 Objective of the study

The general objective of the present study is to prepare and characterize blending film made of PHB and PVAc with controlled biodegradability. The objective can be sub-divided into the following:

i. To prepare the blend film using different combinations of PHB and (PVAc)
ii. To characterize the obtained film
iii. To test biodegradability of the film in correlation with time

Some results of this research project were presented as posters at three national and international conferences, and accepted for publication in an international journal.

1.3 Scope of this study

The scope of the research covers the following stages:

i. Preparation of PHB and PVAc solution by dissolving the polymers in chloroform solvents.
ii. Casting the polymer blended into films in glass dishes by using solution blending to formulate combinations of the two polymers (PHB/PVAc) were 95/5, 90/10, 85/15, 80/20, 75/25, 70/30 and 65/35.
iii. The addition of a surfactant if needed (Methanol + n –Hexane).
iv. Investigation of chemical composition and determination of various properties of the blended films by FTIR.
v. Investigation of the morphological properties of the blended films using SEM.
vi. Analysis of the thermal stability of the blended films using TGA and DSC.
vii. Testing the biodegradability poly (PHB/PVAc) of the films using microbial and burial methods.

1.4 Organization of the thesis

This thesis is divided into five chapters: Introduction, Literature Review, Materials and Methods, Results and Discussion and Conclusions and Recommendation for future work as follows:

Chapter One is a general introduction that gives a brief idea about this work and describes the objectives of the research. Chapter Two, the previous literature related to PHB and its blends with poly(vinyl acetate).

Chapter Three, deals with materials and procedures for preparing blended solutions and films of the two polymers used in the current study. It also describes the equipment used to conduct the experimental research. Chapter Four includes the results of analyses of the two types of polymer blended solutions (PHB/PVAc). FTIR, FESEM, Thermal studies (TGA and DSC) and testing the biodegradability of the films were using burial method. The kinetics of thermal degradation of the blends are studied using thermogravimetric analysis (TGA). The biodegradability of PHB/PVAc blends is compared to that of PHB using the soil burial test. Chapter Five contains the conclusions and recommendation for future work of two blended films of PHB/PVAc. A list of references and appendices are included at the end of each chapter.

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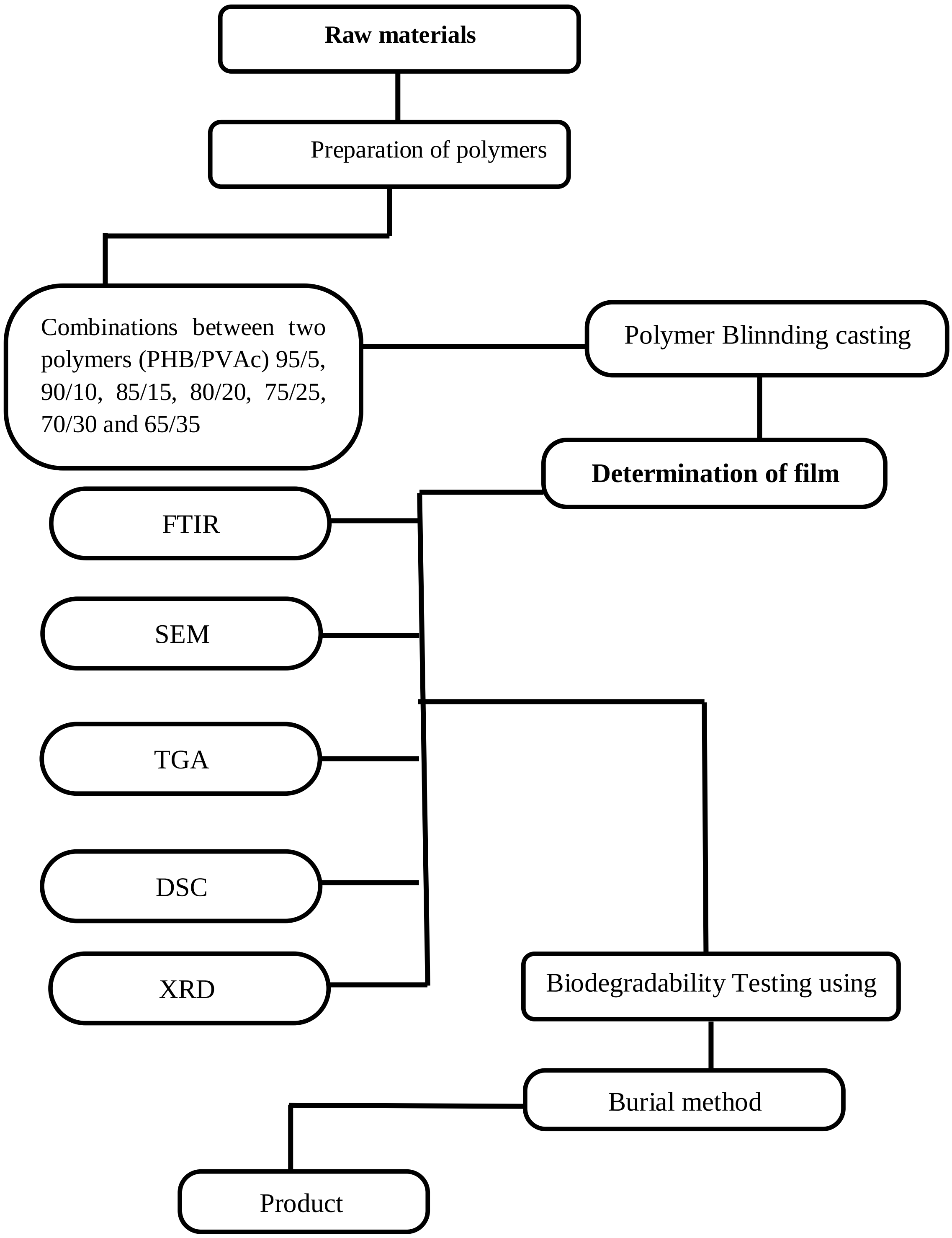

Figure 1.1: Schematic representation of the scope of this study.

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