PREPARATION AND CHARACTERIZATION OF BIODEGRADABLE POLYACRYLIC ACID BASED HYDROGEL FOR AGRICULTURAL APPLICATION

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To my beloved mother

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ABSTRACT

In this study, the influences of different plant natural fibres (PNF) on the properties of poly (acrylic acid) (PAA) based hydrogel were investigated. Polymer hydrogel composites (PHGCs) of poly (acrylic acid) grafted microfibre of cotton (CTN) and oil palm empty fruit bunch (OPEFB) were successfully prepared using solution polymerization technique. Surface methodology and central composite design (CCD) were used to optimize the best content of the initiator (APS), cross-linker (MBA), neutralizer (NaOH) and plant natural microfibres (CTN, OPEFB). The functional groups of PHGs were characterized using Fourier Transform Infrared (FTIR). The effects of CTN and OPEFB on swelling rate, re-swelling capability, thermal, mechanical, biodegradation properties were investigated. Morphological study of PHGs was carried out using Scanning Electron Microscopy (SEM). The effect of PHGs on soil holding capacity, urea leaching loss rate (ULLR) and red okra plant growth were evaluated. The average optimum content of APS, MBA, NaOH and natural fibre were 1.3-1.6, 0.15-0.16, 11.9-14.6 and 13.9-15 wt. % respectively. SEM images indicated that the polymer hydrogel grafted CTN fibre has bigger pore size than that of polymer hydrogel grafted OPEFB fibre and plain PHG. PHGs grafted natural fibres showed higher thermal stability, mechanical properties, biodegradation, swelling rate and re-swelling capability compared to plain polymer hydrogel. Polymer hydrogel grafted micro natural fibre of high cellulose content (CTN) has superior properties compared to that of grafted with microfibre of less cellulose content (OPEFB) and plain polymer hydrogel. Polymer hydrogel composites as soil conditioner and slow release system have positive effect on the holding capacity of sandy soil, ULLR and consequently on red okra plant growth.

ABSTRAK

Dalam kajian ini, pengaruh serat semulajadi tumbuhan (PNF) yang berbeza ke atas sifat-sifat poli (akrilik asid) (PAA) berasaskan hidrogel telah disiasat. Komposit-komposit hidrogel polimer (PHGCs) daripada poli (akrilik asid) tercangkuk berserat kapas gentian mikro dan tandan kosong kelapa sawit (OPEFB) telah berjaya disediakan dengan menggunakan teknik pempolimeran larutan. Kaedah permukaan dan rekabentuk komposit berpusat (CCD) telah digunakan untuk mengoptimumkan kandungan terbaik pemula (APS), pemaut silang (MBA), peneutral (NaOH) dan gentian-gentian mikro semulajadi tumbuhan (CTN, OPEFB). Kumpulan berfungsi PHGs telah dicirikan menggunakan Spektroskopi Infra Merah (FTIR). Kesan CTN dan OPEFB ke atas kadar pembengkakan, kebolehan membengkak semula, terma, mekanikal dan sifat-sifat biodegradasi telah dikaji. Kajian morfologi PHGs telah dijalankan menggunakan Mikroskopi Imbasan Elektron (SEM). Kesan PHGs ke atas kapasiti pegangan tanah, kadar kehilangan larut lesap urea (ULLR) dan pertumbuhan tanaman bendi merah telah dinilai. Kandungan purata optimum APS, MBA, NaOH dan serat semula jadi masing-masing adalah 1.3-1.6, 0.15-0.16, 11.9-14.6 dan 13.9-15 wt.%. Imej SEM menunjukkan bahawa polimer hydrogel tercangkuk gentian CTN mempunyai saiz liang yang lebih besar berbanding polimer hydrogel tercangkuk OPEFB dan PHG tulen. PHGs tercangkuk gentian-gentian semulajadi menunjukkan kestabilan terma, sifat-sifat mekanikal, biodegradasi dan kebolehan membengkak semula yang tinggi terhadap PHGs tulen. PHG tercangkuk gentian mikro semulajadi dengan kandungan selulosa tinggi (CTN) mempunyai sifat-sifat lebih baik berbanding dengan yang tercangkuk gentian mikro kandungan selulosa rendah (OPEFB) dan polimer hidrogel tulen. Komposit polimer hidrogel sebagai pelembap tanah dan sistem lepas perlahan mempunyai kesan positif ke atas kapasiti pegangan tanah berpasir, ULLR dan pertumbuhan tanaman bendi merah.

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LIST OF ABBREVIATIONS

AA	-	Acrylic Acid
AC	-	Absorption Capacity
Ag	-	Silver
APS	-	Ammonium Persulfate
Au	-	Gold
AUL	-	Absorption Under Load
C	-	Capacity
Cd^{+2}	-	Cadmium
CCD	-	Central Composite Design
CMC	-	Carboxymethycellulose
Cu^{+2}	-	Copper
CTN	-	Cotton
DON	-	Degree of Neutralization
FTIR	-	Fourier Transform Infrared
g	-	Grafted
GG	-	Guar Gum
Fe^{+3}	-	Iron
kC	-	Kappa-carrageenan
LCST	-	Low Critical Solution Temperature
LLR	-	Leaching Loss Rate
MMT	-	Montmorillonite
MBA	-	N,`N –Methylenebisacarylamide
MB	-	Methylene Blue
Mg	-	Magnesium
Na	-	Sodium
Na-AG	-	Sodium Alginate
PNIPAAm	-	Poly N-isopropyl Acrylamide

N_2	-	Nitrogen
NaOH	-	Sodium Hydroxide
OPEFB	-	Oil Palm Empty Fruit Bunch
PAA	-	Polyacrylic Acid
PAAm	-	Poly Acrylamide
PAN	-	Polyacrylonitril
PEO	-	Poly Ethylene Oxide
PVA	-	Poly (Vinyl Alcohol)
PHGs	-	Polymer Hydrogels
PHGCs	-	Polymer Hydrogel Composites
pKa	-	Acid Dissociated Constant
pKb	-	Base Dissociated Constant
PNaA	-	Polysodium Acrylate
PNF	-	Plant Natural Fibre
Refr.	-	Reference
S	-	Safranine
SAPC	-	Superabsorbent Polymer Composite
SAP	-	Superabsorbent Polymer
SEM	-	Scanning Electron Microscopy
SH	-	Sodium Humate
SR	-	Swelling Ratio
TGA	-	Thermogravimetric Analysis
U	-	Urea
UCST	-	Upper Critical Solution Temperature
ULLR	-	Urea Leaching Loss Rate
WAC	-	Water Absorbent Capacity
WS	-	White Straw
Wt %	-	Weight Percentage
M	-	Mass
MW	-	Molecular Weight
Pb^{+2}	-	Lead
V	-	Volume
W	-	Weight

LIST OF SYMBOLS

^oC	-	Celsius
µm	-	Micrometer
mm	-	Millimeter
min	-	Minute
mg	-	Milligram
h	-	Hour
S^*	-	Ionic strength of the Swollen Liquid
Y	-	Response

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Polymer hydrogels (PHGs) are visco-elastic, loosely cross-linked, hydrophilic, of flexible polymer, three dimensional networks chains with dissociated ionic functional groups, that can absorb large amount of water or other biological fluid in a short time [1-5]. PHGs have been abundantly used in disposable diaper industry for the past 35 years; their applications are still being expanded to many fields including agriculture, horticulture, sealing composites, artificial snow, drilling fluid additives, medicine for drug delivery system. Recently, the preparation of polymer hydrogels composites (PHGCs) received great attention because of their relatively low production cost and high water absorbency.

There is a wide range of organic and inorganic materials available for preparation of PHGCs such as kaolinite, montmorillonite (MMT), hectite, saponite , synthetic mica, used paper, oil palm empty fruit bunch (OPEFB) , and wheat straw (WS). Some of these materials are used in nanosize to prepare Nanocomposite of PHGs such as fabricated silver or zinc nanoparticles. PHGC materials find many new applications beyond those of PHG such as catalysis, optics, electronics, bio-medicals and quantum-sized domain applications. In addition, there are some potential applications of PHGC in water treatments which have already been described [6, 7].

Certain kinds of fertilizer normally used to enhance agricultural soil and plants growth. There are three main types of fertilizers that have been used in agriculture field which are soluble materials such as urea-formaldehyde, materials for deep placement such as urea super granules, and coated fertilizer [8]. The main issue that has to be considered during the use of these type of fertilizer is the leaching rate out of the soils structure which might lead to environmental pollution and low fertilization efficiency [9-13]. In addition, there are problems related with sandy soils such as high porosity, high irrigation water consumption, and low fertilizer retention [8, 14, 15].

Therefore, materials with ability to absorb high amount of water and release it for long period of time combined with dissolved fertilizer can be a possible solution for mentioned problems. The system that is needed to do above mentioned purpose should have special characteristics such as high absorption capacity, biodegradability, optimum mechanical properties, slow and control release, and cheap.

The main raw materials that are normally needed to synthesis PHGs are; polymer or monomers repeating unit, cross-linking agent, and initiator. Several polymerization methods have been used to synthesize and prepare PHGC such as solution polymerization or aqueous polymer solution [16], radiation polymerization [17] or photopolymerization [18, 19], suspension polymerization [20], reversible addition-fragmentation chain transfer (RAFT) polymerization [21], and free radical polymerization [14, 18, 22].

Previously, considerable number of studies have been conducted on using polymer hydrogels in agriculture application for control-release of fertilizers [8, 12, 23-25], reduce environmental pollution [9-13], reduce irrigation water consumption, improve fertilizer retention in soil [8, 14, 15], eliminates leaching of nutrients, increase soil aeration and diminishes soil density [5].

Recently, some studies have been conducted on using PAA hydrogels and PAA hydrogel composite as slow release system in agriculture. These studies showed very good fertilizer (nitrogen, phosphorus, potassium, urea) management and low leaching rate [8, 9, 15].

1.2 Problem Statement

There are some problems associated with fertilization process in agricultural fields particularly in sandy soil agricultural fields. Deep placement fertilizer such as urea is used worldwide in fertilization process. Urea leaching rate (ULR) considered as the main factor for fertilization efficiency. ULR is more pronounce in sandy soil due to its loose properties (high porosity and permeability). High ULR in sandy soil leads to environmental pollution and low fertilization efficiency. In addition, sandy soil agricultural fields are the most irrigation water consumption in contrast to other kind of soil which means, sandy soils have low water retention.

Biodegradation, mechanical properties and cost are the main challenges for using PHGs in agricultural application. It is well known that PHGs based synthetic polymer have high resistant to microorganisms (bacteria, enzyme and fungus) and that might lead to environment pollution due to high amount of these materials have to be added to the agricultural fields. Poor mechanical properties of swollen PHGs lead to high release rate of absorbed water under a slight pressure. Moreover, using PHGs in agricultural application added an extra cost on crops production [8, 15, 26, 27].

PHGs have to meet some characteristics to be suitable for agricultural application in irrigation and fertilization process. These characteristics include low production cost, high swelling capacity, slow release behaviors, high swelling rate, and biodegradable properties.

In order to reduce costs and improve the comprehensive water absorption, degradability, and mechanical properties of the PAA hydrogels, PHG composites were synthesized consisting AA monomer and micro powder of oil palm empty fruit bunch and natural cotton fibers.

1.3 Objectives of the Study

The main aim of this work is to prepare polymer hydrpgel composite based on polyacrylic acid and natural fibre and study the effect of using different natural fibre of different chemical content on polymer hydrogel properties. The objectives of this study are as follows:

i) To synthesize polymer hydrogel composite (PHGC) of poly acrylic acid (PAA) filled with microfiber of oil palm empty fruit bunch (OPEFB) and cotton (CTN) using solution polymerization technique.

ii) To determine the optimum content of the initiator (APS), cross-linker (MPA), neutralizer (NaOH) and microfibers of CTN and OPEFB that give the highest absorption capacity sample.

iii) To study the effect of CTN and OPEFB on mechanical properties (absorbing under load), biodegradation, thermal stability, swelling rate and re-swelling capability of PHGs.

iv) To evaluate the implementation of PHGC as soil conditioner and slow release system through soil holding capacity, urea leaching loss rate and the effect of PHGC on okra plant growth.

1.4 Scope of the Study

In order to achieve the objectives of the study the following scopes were used:

i) Preparation of Polymer hydrogel composites of PAA grafted OPEFB and CTN using free radical mechanism and solution polymerization technique.

ii) Optimizations of the main factors that affect absorption capacity using design of experiment software and central composite design methodology.

iii) Investigating the effect of buffer and saline solution on water absorption capacity and swelling properties.

iv) Examining the effect of natural fibreon swelling rate, biodegradability and thermal stability of polymer hydrogel.

v) Characterization of the functional groups and the internal networks structure of PHGs samples using FTIR and scanning electron microscopy (SEM) respectively.

vi) Studying the effect of PHGCs on soil holding capacity and urea leaching loss rate (ULLR) using sandy soil and vessel method.

vii) Evaluating the effect of PHGC on plant growth in terms of number of leaves, length and diameter of the trunk and the quality of the production using red okra plant.

1.5 Significant of the Study

i) The developed model can be used to estimate the water absorption capacity of polymer hydrogel composite of different content of APS, MBA, NaOH and natural microfiber.
ii) The prepared materials of hydrogel composite are environmentally friendly, can be used for agricultural field application as slow release system or as soil conditioner.

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