

**PREPARATION OF CHITOSAN-G-PMMA FOR ADSORPTION-DESORPTION  
BEHAVIOR OF UREA**

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PREPARATION OF CHITOSAN-G-PMMA FOR ADSORPTION-DESORPTION  
BEHAVIOR OF UREA

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*Specially dedicated to my amazing parents  
Abd Ghapar bin Abd Kadir and Samsiah binti Hamat,  
My beloved friends, all my family members, and my beloved ones*

*“Thank you for the endless support and everything “*

*I love you, Lillahi Taala*

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## ABSTRACT

This study focused on grafting of poly(methyl methacrylate) (PMMA) onto chitosan beads to develop a controlled-released fertilizer material which can act as carrier molecule for fertilizers. Chitosan grafted with PMMA (chitosan-*g*-PMMA) was successfully synthesized using potassium persulfate (KPS) as the initiator and characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy and X-ray diffraction (XRD). Grafting yield of 51.47% was obtained at 70°C,  $6.58 \times 10^{-3}$  mol/L of KPS and 1 mL of monomer. FTIR results showed successful grafting between PMMA and amino group of chitosan through the increasing intensities observed in the absorption peaks at 1726 and 1147  $\text{cm}^{-1}$ . Surface morphology of the beads showed that grafted chitosan bead has smoother surface compared to pure chitosan bead and XRD spectrum for chitosan-*g*-PMMA bead also showed a shift of  $2\theta$  due to the grafting of PMMA onto the chitosan backbone. The maximum amount of water absorbed into the chitosan beads is 5.70 g after 80 minutes of immersion whereas grafted chitosan beads only adsorbed 1.25 g of water even after 180 minutes of immersion indicating that grafted chitosan beads showed a slow increase in degree of swelling compared to pure chitosan beads. The optimum time for maximum adsorption of urea into the chitosan beads was found to be at 12 hours with 0.33% urea adsorption whereas grafted chitosan beads has maximum adsorption at 24 hours which is 0.24% of urea. Desorption of urea from the chitosan beads showed that more than 90% desorption of urea occurred within 6 hours compared to grafted chitosan beads in which desorption occurred more than 24 hours. As the structure of both beads still remain unchanged even after adsorption and desorption of urea, the beads can be recycled.

## ABSTRAK

Kajian ini memberi tumpuan kepada cangkukan poli(metil metakrilat) (PMMA) kepada manik kitosan untuk membangunkan bahan baja pelepasan terkawal yang boleh bertindak sebagai molekul pembawa bagi baja. Kitosan yang dicangkuk dengan PMMA (kitosan-g-PMMA) telah berjaya disintesis menggunakan kalium persulfat (KPS) sebagai pemula dan dicirikan menggunakan spektroskopi inframerah transformasi Fourier (FTIR), mikroskopi elektron pengimbas dan pembelauan sinar-X (XRD). Hasil cangkukan sebanyak 51.47% telah diperoleh pada 70°C,  $6.58 \times 10^{-3}$  mol / L KPS dan 1 mL monomer. Keputusan FTIR menunjukkan cangkukan antara PMMA dan kumpulan amino kitosan telah berjaya melalui peningkatan intensiti pada puncak penyerapan 1726 dan 1147  $\text{cm}^{-1}$ . Morfologi permukaan manik menunjukkan bahawa manik chitosan yang dicangkuk mempunyai permukaan yang lebih licin berbanding manik kitosan tulen dan spektrum XRD bagi manik kitosan-g-PMMA juga menunjukkan perubahan  $2\theta$  disebabkan oleh cangkukan PMMA ke tulang belakang kitosan. Jumlah maksimum air yang dijerap ke dalam manik kitosan ialah 5.70 g selepas 80 minit rendaman sedangkan manik kitosan yang dicampur hanya menjerap 1.25 g air walaupun selepas 180 minit rendaman menunjukkan bahawa manik kitosan yang dicangkuk menunjukkan peningkatan perlahan dalam tahap bengkak berbanding dengan manik kitosan tulen. Masa optimum untuk penyerapan maksimum urea ke dalam manik kitosan didapati pada 12 jam dengan penyerapan urea sebanyak 0.33% manakala manik kitosan dicangkuk mempunyai penyerapan maksimum pada 24 jam iaitu sebanyak 0.24% urea. Penyahjerapan urea daripada manik kitosan menunjukkan bahawa lebih daripada 90% penyahjerapan urea berlaku dalam masa 6 jam berbanding dengan manik kitosan cangkukan di mana penyahjerapan berlaku lebih daripada 24 jam. Oleh kerana struktur kedua-dua manik masih kekal tidak berubah walaupun selepas penyerapan dan penyahjerapan urea, manik-manik boleh dikitar semula.

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## LIST OF SYMBOLS

mL	-	Milliliter
min	-	Minutes
M	-	Molar
%	-	Percentage
wt %	-	Weight Percentage
L	-	Liter
cm	-	centimeter

## LIST OF ABBREVIATIONS

MMA	-	Methyl methacrylate
PMMA	-	Poly(methyl methacrylate)
NaOH	-	Sodium hydroxide
HCl	-	Hydrochloric acid
NMR	-	Nuclear Magnetic Resonance
FTIR	-	Fourier Transform Infrared Spectroscopy
SEM	-	Scanning Electron Micrograph
FRP	-	Free Radical Polymerization
KPS	-	Potassium Persulfate
XRD	-	Xray Diffraction

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background**

Fertilizers are chemical compounds used to enhance the plant's growth which is applied either through the soil or by foliar spreading [1]. However, high dissolution of normal fertilizers increase the accumulation of fertilizers in soil and limits the uptake of nutrient by the plant. Recently, Controlled Release Fertilizers (CRFs) has become a new method in agriculture industries in order to improve the fertilizer released. CRFs are fertilizers granules intercalated within the carrier molecule which is applied to control the nutrient release so that nutrient release at slower rate [2]. They are ideally coated with a natural or semi-natural, environmentally friendly macromolecule material or placed inside a carrier molecule that can retard fertilizer release so that the single application can meet the nutrient requirements for model crop growth [3].

It has been reported that chitosan beads can act as a carrier for drug delivery, meanwhile a few other studies have been attempted to discover the potential of chitosan beads as a controlled release of fertilizers [1, 4, 5]. Hasaneen et al. reported that the weakness of the chitosan beads to be used as CRFs is typically due to the difficulties in controlling the initial burst effect in releasing large quantities of fertilizers [1]. Porosity is an important key to utilize the chitosan beads so that it can be used as slow released fertilizers. However, the natural behavior of chitosan with ability to absorb large amount

of water in a short period of time bring disadvantages toward this. This is due to the hydrophilic behavior of chitosan that has many inter- and intra-molecular hydrogen bonding interactions, leading to the failure release of CRFs. Therefore, poly(methyl methacrylate) (PMMA) grafted to the chitosan beads was proposed to overcome the limitation of chitosan beads by reducing the hydrophilic properties so that it can be used as a carrier molecules for the urea fertilizers.

There have been few reports on grafting of PMMA onto chitosan. The preparation of microspheres using chitosan/chitosan-g-PMMA, the encapsulation and the controlled release of ampicillin from the chitosan and the chitosan/chitosan-g-PMMA microspheres has been studied by Changerath et al. (2008) [6]. Lagos and Reyes, reported on the preparation of graft copolymerization of methyl methacrylate onto chitosan with Fenton's reagent as a redox initiator in the presence of atmospheric oxygen [7]. It has been reported PMMA/chitosan showed a potential in drug release applications due to the degradation and porosity of the blend in the synthetic body fluid. It is also reported the swelling properties of the PMMA/chitosan blends increase with increasing chitosan percent [8]. Both chitosan and PMMA have been successfully used in drug delivery system, therefore they may also be used in this study to act as carrier molecule for urea.

Adsorption method is used to incorporate urea inside the chitosan beads. According to Zhao et al. (2007), the chitosan beads have high inherent porosity which induced high diffusion ability. It was found that the adsorption capacity is strongly related to the binding sites composed of the functional groups which are four amino groups or two amino groups and two hydroxyl groups collaborating with each other to make an appropriate space conformation for binding nutrient ions. Therefore, the adsorption capacities correspond to the porosity and the binding sites behavior [9]. Haseena et al. (2016) reported that chitosan can be used in removing ammonium-nitrogen ( $\text{NH}_4^+\text{-N}$ ) from aqueous solution using adsorption method and the exhausted adsorbent enriched with nitrogen can be recovered and reused as a fertilizer [10].

Several studies showed the potential of coating to control the release of fertilizers to the soil [2]. The type of materials for coating can be divided into organic polymer coatings such thermoplastic or resin, and inorganic coating materials such as sulphur or mineral based coatings. The use of coated fertilizers in agriculture practices is quite common, for instance, sulphur-coated urea was developed at the Tennessee Valley Authority laboratories and manufacture commercially for almost 30 years [2]. Therefore, developments of chitosan as a coating materials or carrier molecule in CRFs will significantly improve the nutrient released from the fertilizers due to its porosity and cationic characteristics that may react with negatively charged molecules. The modification of chitosan could control its high swelling properties and also to control the release of the adsorbed urea.

## **1.2 Problem Statement**

It has been reported that 40 to 70% of nitrogen, 80 to 90% of phosphorus, and 50 to 70% of potassium of the normal fertilizers are lost to the environment and not absorbed by plants, causing intrinsic economic and resource losses and dangerously increasing environmental pollution [1]. Most commercial fertilizers are easily soluble in water thus increasing mineral compounds in the soil. When the concentration of nutrient exceeds the plant's intake capability, the processes such as rinsing out, vaporization and precipitation are activated to decrease its concentration [11].

This may cause serious problems in environmental aspect such as soil pollution and acid rain, as well as in term of economic aspect. Material losses, spent energy and human work effort affect the total economic balance of the whole agrochemical production process [11]. It is important to increase the effectiveness of nutrients uptake by the plant and to decrease material losses while limiting the amount of fertilizer's waste material produced at the same time. These can be achieved through the development of

the fertilizers which can release mineral components according to the nutrient requirements of the plants.

CRFs has been employed to improve the release properties of the fertilizers by applying coating to the commercial fertilizers or by incorporating the fertilizers inside a carrier molecule. Polymeric materials such as polyolefin, rubber, thermoplastics and resins, offer many advantages as coating materials for the CRFs since they are biologically inert against microbial attack, can supply nutrients consistent with the crops metabolic needs over longer period of time and also have an ability to retain both micro and macronutrients within the helical polymer chain matrix. However, polymer coating may cause environmental effects since it can lead to soil pollution due to non-biodegradable polymer coating which will be left on soil surface after all the nutrient has been released [12].

Therefore, to overcome the polymer coating problems, biopolymer which is chitosan seems to be an alternative way to be used as carrier molecules for fertilizers since it has shown great potential in the development of versatile delivery system due to its gel beads and film-forming ability properties. However, chitosan is a very hydrophilic in nature since it can form strong hydrogen bonding with water molecule. For a material to be as coating materials for CRFs, it should absorb water however cannot has high water absorbency since this will lead to burst effects and failure release of fertilizers will occur. Therefore, the grafting of chitosan with PMMA would be a great implementation for the controlled release formulation to reduce water absorbency of chitosan.

### **1.3 Objective**

The objectives of this study are:

1. To synthesise the chitosan-*g*-PMMA beads and characterize using FTIR, XRD and SEM.
2. To investigate the grafted copolymer swelling properties.
3. To study the adsorption and desorption behavior of urea using chitosan-*g*-PMMA beads.

### **1.4 Scope of Study**

The scope of this study consists of four parts. The first part is the preparation of chitosan beads and grafting the PMMA onto the chitosan beads (chitosan-*g*-PMMA beads). The chitosan-*g*-PMMA beads were prepared by free radical polymerization (FRP) method. The second part was to investigate the swelling properties of chitosan and chitosan-*g*-PMMA beads in order to be used as a carrier molecules. The third part was characterization of the grafted polymer beads. The grafted polymer beads was characterized using FTIR to study the presence of functional groups and XRD to study the crystallography behavior of the polymer beads. The morphology of the cross section of the beads was observed by Scanning Electron Microscopy (SEM). The last part involves the simulation of adsorption and desorption behavior of the materials prepared in order to study the adsorption and desorption of urea into the target area.

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