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COMPARISON OF GAMMA RADIATION CROSSLINKING AND CHEMICAL CROSSLINKING ON
PROPERTIES OF METHYLCELLULOSE



Mr. Korapat Somsaeng

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย
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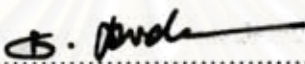
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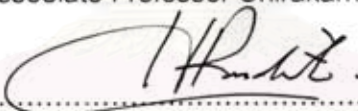
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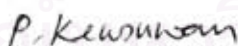

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งานวิจัยนี้มีจุดประสงค์เพื่อที่จะปรับเปลี่ยนเมธิลเซลลูโลสซึ่งเป็นพอลิเมอร์ที่ย่อยสลายได้ทางชีวภาพโดยมีแนวทางในการพัฒนาด้วยการเชื่อมขวาง 2 วิธีคือ การเชื่อมขวางด้วยการฉายรังสีแกมมา และการเชื่อมขวางด้วยการเติมสารเคมีชนิดกลูตาวัลดีไฮด์ เพื่อทำให้เกิดการเชื่อมขวางกันระหว่างสายโซ่โมเลกุลของเมธิลเซลลูโลส และทำการเปรียบเทียบสมบัติต่างๆ ของฟิล์มเมธิลเซลลูโลสที่เกิดโครงสร้างตาข่ายจากการเชื่อมขวางทั้ง 2 วิธีกับเมธิลเซลลูโลสที่ไม่ได้ผ่านการเชื่อมขวาง ทางด้าน สมบัติทางความร้อน การดูดซับความชื้น ปริมาณเจล พฤติกรรมการบวมตัวของเจล และการย่อยสลายตัวทางชีวภาพในดิน ผลการทดลองพบว่า ในระบบของการเกิดพันธะเชื่อมขวางของเมธิลเซลลูโลสทั้งสองวิธีไม่ส่งผลต่อสมบัติทางความร้อนของฟิล์มเมธิลเซลลูโลสยกตัวอย่างเช่น อุณหภูมิเปลี่ยนสถานะคล้ายแก้ว และอุณหภูมิสลายตัวของเมธิลเซลลูโลส ในด้านพฤติกรรมการบวมตัวของฟิล์มเมธิลเซลลูโลสพบว่า ฟิล์มที่ได้จากการเชื่อมขวางด้วยการฉายรังสีแกมมามีความเป็นขั้วสูงกว่าเจลที่ได้จากการเติมสารกลูเตอรัลดีไฮด์ จากการสังเกตการบวมตัวในน้ำของฟิล์มเมธิลเซลลูโลสทั้งสองชนิดพบว่า ฟิล์มที่ได้จากการฉายรังสีแกมมามีลักษณะเป็นเจลแบบวิวิธพันธุ์หรือไม่เป็นเนื้อเดียวกัน แต่ฟิล์มที่ได้จากการเติมสารกลูเตอรัลดีไฮด์มีลักษณะเป็นเอกพันธุ์หรือเป็นเนื้อเดียวกัน และในการทดสอบการย่อยสลายตัวทางชีวภาพในดินพบว่า ฟิล์มเมธิลเซลลูโลสที่ทำการเชื่อมขวางด้วยการเติมสารกลูเตอรัลดีไฮด์ที่ 0.3 และ 0.5 เปอร์เซ็นต์โดยน้ำหนักสามารถยึดช่วงเวลาในการย่อยสลายตัวทางชีวภาพออกไปได้

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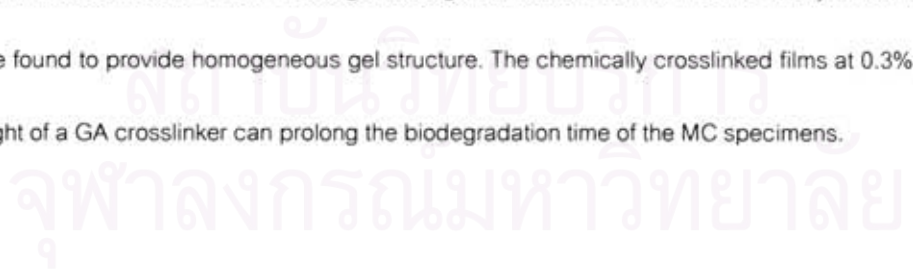
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KORAPAT SOMSAENG: COMPARISON OF GAMMA RADIATION CROSSLINKING AND CHEMICAL CROSSLINKING ON PROPERTIES OF METHYLCELLULOSE. THESIS ADVISOR: ASST. PROF. SARAWUT RIMDUSIT, Ph.D., THESIS COADVISOR: ASSOC. PROF. SIRIPORN DAMRONGSAKKUL, Ph.D. AND PRARTANA KEWSUWAN, Ph.D., 72 pp.

This research aims to modify properties, particularly biodegradability, of methylcellulose (MC), by utilizing two crosslinking methods. The first method is gamma irradiation treatment to form insoluble MC gel by intermolecular crosslinking. The second one is the use of a glutaraldehyde (GA) crosslinker to promote hemi-acetal linkages between MC polymer chains. In comparison of the rendered MC films from the two crosslinking methods, some important characterizations such as moisture adsorption, thermal properties, gel content, degree of swelling, and composting degradation were determined. MCs prepared from both crosslinking techniques show negligible effects on thermal properties such as T_g and T_d . In the swelling behavior, the radiation crosslinked MC films show higher polarity than chemically crosslinked MC films. From the visual observation of water-swelled crosslinked MC films, the radiation crosslinked MC films were observed to render heterogeneous gel structure whereas the chemically crosslinked MC films were found to provide homogeneous gel structure. The chemically crosslinked films at 0.3% and 0.5% by weight of a GA crosslinker can prolong the biodegradation time of the MC specimens.

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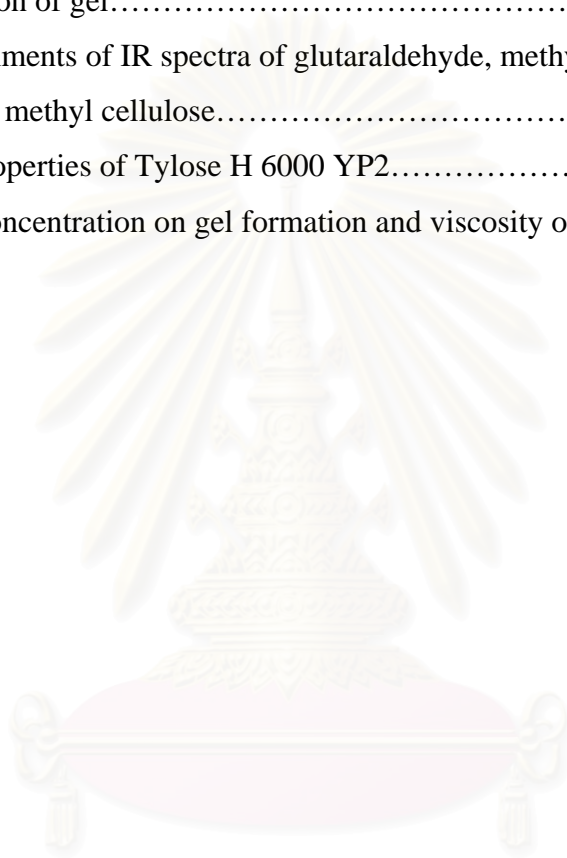
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CHAPTER I

INTRODUCTION

1.1 Introduction

In the past 20 years, the production and the use of plastics in the world have been enormously increased, worsening the problems of the waste disposal. The growing interest in environmental impact of discarded plastics has directly researched on the development of plastics that degrade more rapidly in the environment, leading to a complete mineralization or bioassimilation of the plastics [1, 2 and 3]. Biopolymers should be used in those applications where biodegradability and/or the derivation of natural resources gives added value, particularly, where valuable petroleum-based plastics are used for applications with a short life time [4]. For these reasons, throughout the world today, the development of biodegradable materials with controlled properties has been a subject of great research challenge to the community of material scientists and engineers [5].

Methylcellulose (MC), a biodegradable polymer, is a modified type of cellulose which is the most abundant biopolymer in nature. MC is well known and of interest to be used as environmental friendly products, especially as coating or mulching film, because of its large availability, low cost, and easy processability. However, due to a limitation in biodegradable behavior of MC, it can be used only in some applications.

Crosslinking is one of the most popular methods used to modify water-soluble polymer in order to achieve desired properties. Some polymer characteristics could be altered by crosslinking such as swelling, permeability drug releasing, transport properties, water uptake, mechanical properties, chemical stability, sponge structure as well as biodegradation rate [6 and 7]. Irradiation of water-soluble polymer in aqueous solution, due to the high yield of radicals, is often used for formation of hydrogel. Gamma irradiation, which is a very clean, easy and cost effective process, has been regarded as a very useful method in order to get macroscopic three dimensional able to swell lattice [8 and 9]. Several crosslinking agents for MC have been employed including dialdehyde. However, one of the most popular crosslinkers is glutaraldehyde (GA), a small molecule dialdehyde [6].

In this work, MC films are prepared by solution intercalation using a homogenizer at the MC gelatinized temperature of 50-55°C. Crosslinked MC is prepared by using gamma radiation and GA as a crosslinking agent in an aqueous solution. The effects of dose of gamma radiation and GA crosslinking agent content on the gel content and swelling behavior, physical observation, thermal properties and dynamic mechanical properties of radiation crosslinked and chemical crosslinked films will be investigated.

1.2 Objectives

To compare the effects of radiation crosslinking and chemical crosslinking on thermal properties, mechanical properties, moisture absorption, water solubility and biodegradability of methylcellulose.

1.3 Scope of Research

1. Investigating the effects of gamma radiation doses at 5, 10, 15, 20 and 25 kGy in aqueous MC solution on:
 - Thermal properties will be studied by DSC, DMA and TGA.
 - Crosslinking density will be observed by gel content, swelling behavior and moisture absorption.
 - Mechanical properties will be examined by DMA.
 - Biodegradability will be investigated by composting degradation.
2. Determining the effects of the amount of GA at 0.05, 0.1, 0.2, 0.3, and 0.5% by weight in aqueous MC solution on:
 - Thermal properties will be studied by DSC, DMA and TGA.
 - Crosslinking density will be observed by gel content, swelling behavior and moisture absorption.
 - Mechanical properties will be examined by DMA and universal testing machine.
 - Biodegradability will be investigated by composting degradation.

3. Comparing the biodegradability of MC film undergoing radiation crosslinking and chemical crosslinking. Determining the range of biodegradability of the systems in (1) and (2).



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CHAPTER II

THEORY

2.1 Biodegradable Polymers

The term “biodegradable” materials is used to describe those materials which can be degraded by enzymatic action of living organisms, such as bacteria, yeasts, fungi. The ultimate end-products of the degradation process are CO₂, H₂O, and biomass under aerobic conditions and hydrocarbons, methane and biomass under anaerobic conditions [10].

The degradation of biodegradable polymer proceeds either by hydrolysis through the bulk and/or by enzymatic degradation. The latter comprises of endoenzyme and exoenzyme as shown in Figure 2.1. Hydrolysis (so called bioerosion) necessitates a certain degree of hydrophilicity of the polymer, so that water molecule can access to sample bulk. Materials such as PET characterized by a strong hydrophilic character and/or a high degree of crystallinity will generally show good tolerance to hydrophilic breakdown. Enzyme attacks a polymeric material from the surface, degrading first the amorphous and easily accessible regions [11].

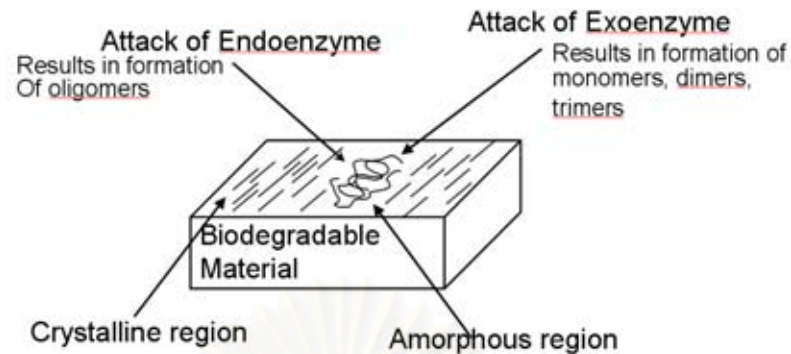


Figure 2.1: Biodegradation by surface of biodegradable material: action of exo- and endo-enzymes [11].

2.2 Cellulose and Methylcellulose

2.2.1 Cellulose

Cellulose constitutes the main structural component of plants and the most abundant source of carbohydrate in nature. Cellulose consists of $\beta(1,4)$ -glycopyranose units. Cellulose exhibits a strong tendency to form intra- and inter- molecular hydrogen bonding. Because of its highly crystalline nature, it is insoluble and unswellable in water. In order to solubilize cellulose e.g. for processability purpose, various substituents have been incorporated into its anhydroglucose backbone to decrease its crystallinity [12, 13 and 14].

2.2.2 Methylcellulose

In methylcellulose (MC), some hydroxyl groups are replaced with methoxyl groups and thus the hydrogen-bonding, which is responsible for the crystallinity of cellulose, is weakened. For this reason MC becomes water soluble. MC is prepared on a commercial scale by the etherification of alkali-cellulose with methyl chloride [15]. Chemical structure of MC is showed in Figure 2.2.

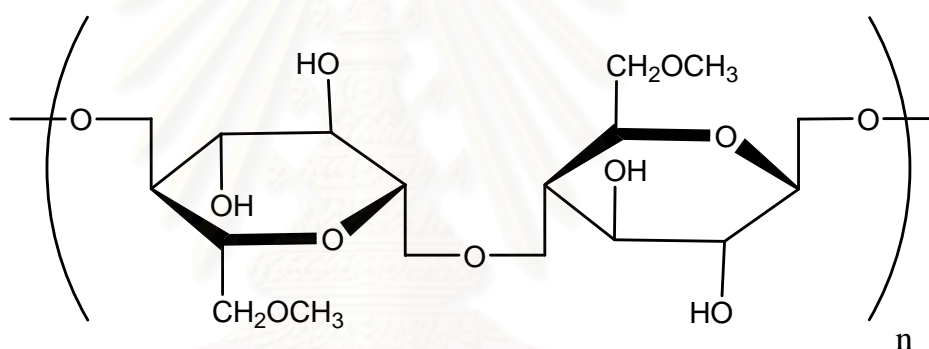


Figure 2.2: Methylcellulose.

MC is a powder which can be mixed with distilled or de-ionized water to form a paste. It is not lumpy (completely soluble in water) and has a neutral pH (pH 6.5-8.5 at 1% solution), non-toxic, odorless and smellless. It is soluble even in cold water because of the existing of hydrophilic group. MC provides high-strength films which are transparent, water soluble, oil resistant, and have low oxygen and moisture vapor transmission rates [15 and 16]. Its biodegradability rate is rather high, i.e. 55 to 73 wt% of polymer degraded in 20 days using bath-type activated sludge tests [17].

2.3 Gels [18]

Gels are defined as "polymers and their swollen matters with three-dimensional network structures that are insoluble in any solvents." The dictionary also states that the relationship between the crosslinked structure of gels and characteristics of swelling matter is one in which "linear and branched polymers absorb, swell, and eventually disperse as individual molecules into good solvents. On the other hand, the degree of swelling of crosslinked polymers is limited due to the three-dimensional network structure, although they can swell by the interaction with the solvent.

2.3.1 Classification of gels

A gel consists of both a 3D network structure and a medium. Although it is possible for the medium to be a gas, it is generally a liquid. It will be considered here that gels are 3D network polymers swollen by liquids (solvents). Gels are classified based on the type of crosslinking that creates their 3D networks, as well as whether they are natural or artificial, the shape and size of the gel configuration, and the types of solvents. Table 2.1 presents many of the classifications of gels to which this work will refer.

Table 2.1 Classification of gels [18].

Crosslinking system (semi-crosslinking)	<ul style="list-style-type: none"> • Covalent bonding • Coulombic force • Hydrogen bonding • Coordination bonding • Entanglement 	<ul style="list-style-type: none"> • Crosslinking agents (chemical crosslinking) • Gamma ray, electron beam, UV radiation • Polyelectrolytes • Natural gels, frozen gels • Small molecules (ions) • High degrees of polymerization, branches, weak in strength
Structural polymers	<ul style="list-style-type: none"> • Natural gels • Hybrid gels • Synthetic gels 	<ul style="list-style-type: none"> • Food, proteins, polysaccharides, tissue living in the natural world • Medical materials, artificial skin, artificial cornea, artificial pancreas model • Organic polymer , contact lenses, high water absorbance resins, silica gels
Configuration size	<ul style="list-style-type: none"> • Micro-gel • Macro-gel 	<ul style="list-style-type: none"> • Intramolecular crosslinking: doesn't enlarge • Intermolecular crosslinking: normal gel
Solvent	<ul style="list-style-type: none"> • Air • Water • Oil 	<ul style="list-style-type: none"> • Aerogel, Xerogel • Hydrogel • Lyopic (organo) gel

2.3.2 Method of Crosslink Formation

Gels can be formed via covalent bonding, the coulombic force, hydrogen bonding, and coordination bonding, and although physical interaction (such as entanglement) is not a form of chemical crosslinking, gels can be formed this way.

Most synthetic matter is of the covalent bonding type, generally polymerized by adding crosslinking agents when polymers are synthesized. The crosslinked structure is strong. Those gels using coulombic force are poly-ion complexes between polyelectrolytes with opposite charges or polyelectrolytes with multivalent ions, such as calcium.

The gels liquefy and a sol-gel transition occurs when the coulombic force is overcome by changing either pH or ionic strength. The hydrogen bonding system, created when crosslinked structures are formed by hydrogen bonding between the polymers, is seen mostly in natural matter. In these cases, gels will change to sols when hydrogen bonding is broken by the environment, for example, by heating. Coordination bonding is created when crosslinked structures are formed between polar groups of a polymer and the material that is coordinated. Situations that do not involve crosslinking were mentioned previously. Polymer chains become entangled and a gel is created when the molecular weight of the polymer is large or there is branching. In this case, the crosslink point is not specified and the gel configuration is unstable. As bonding strength is weak, in time it will disperse in the solvent and dissolve.

2.3.3 Chemical Gels

In the creation of network structures by chemical bonding (covalent bonding), there is a method of: (1) crosslinking at the same time as polymerization; or (2) crosslinking by chemical reaction after linear polymer chains have been synthesized. The latter method can be divided into the addition polymerization in the presence of

divinyl compounds (radical polymerization, anionic polymerization, ionic polymerization, etc.) or the formation of crosslinked structures by polycondensation of multifunctional compounds. In the addition reaction, free radical polymerization is generally utilized. In this free radical polymerization method, initiators are usually used, but light, radiation, and plasmas can also be used.

2.3.4 Methods of crosslinking among polymer chains

2.3.4.1 The method for crosslinking using the functional group of polymer

A polymer containing isocyanate ($R-N=C=O$) can undergo polyaddition reactions with such compounds as diols or diamines, crosslink and become a gel. This polyaddition reaction results in urethane and urea bonds. There are other functional groups that can create gels if the crosslinking agent is selected. Several of these possibilities will be noted later. This crosslinking method can achieve the creation of gels with uniform networks, compared to methods in which linking is done simultaneously with polymerization.

2.3.4.2 Radiation crosslinking

By irradiating using γ -rays, it is possible to crosslink poly(vinyl alcohol), poly(methyl vinyl ether), polyethylene, polystyrene, polyacrylate and natural rubber in water. The crosslinking is considered to take place by splitting water molecules by radiation, extracting the hydrogen from the main chain by the resultant free radicals, and coupling the polymer free radicals formed. Radiation crosslinking is affected by the following: (1) condition of the irradiation (total dose, rate of irradiation, test

specimen size, temperature, pressure, etc.); and (2) properties of the polymer (multiple bonding, etc.).

2.4 Crosslinking of Methyl Cellulose

Crosslinking of MC, which could be used as biodegradable materials, can be considered as a useful approach to prepare non-water soluble polymer with interesting moisture barrier properties. Keslter and Fennema [19] studied the method to enhance barrier characteristics by crosslinking modified polysaccharides chains. They reported that, crosslinking would decrease polymer chain mobility, and increases the resistance to vapor and gas transport. This study corresponds to the reports of Coma et al. [7]. They reported that crosslinking of the hydroxypropylmethylcellulose (HPMC), hydrophilic polymers, induced a strong influence on water solubility and an improvement in the water vapor barrier of about 34% under conditions of 50% RH and 23°C. It is evident that highly water soluble MC crosslinked to various extents should offer the possibility to modulate its biodegradability.

2.4.1 Crosslinking Reaction of Methyl Cellulose with Glutaraldehyde

Crosslinking agents for MC have been employed in various reports such as dialdehyde (e.g. glutaraldehyde (GA), glyoxal, succinaldehyde, trichlorotriazine, epihalohydrin, benzoquinone and bisepoxiranes) in the presence of a strong acid to generate a hydrogel [20 and 21]. However, the most popular crosslinker is GA, a

small molecule dialdehyde. That is due to the fact that GA provides higher crosslink density than other crosslinking agents with the same consumption [6].

Using acid as a catalyst, crosslinking reaction between MC and GA occurs from hydroxyl groups of MC and aldehyde groups of GA via hemiacetal formation, as shown in Figure 2.3 [22]. This reaction starts with the breakages of O-H bonds in alcohol and C=O in aldehydes. Then, carbonyl groups of aldehydes react with H⁺ ions of alcohols from O-H. In addition, RO⁻ ions of alcohol form with carbon atoms of aldehydes to be C-RO.

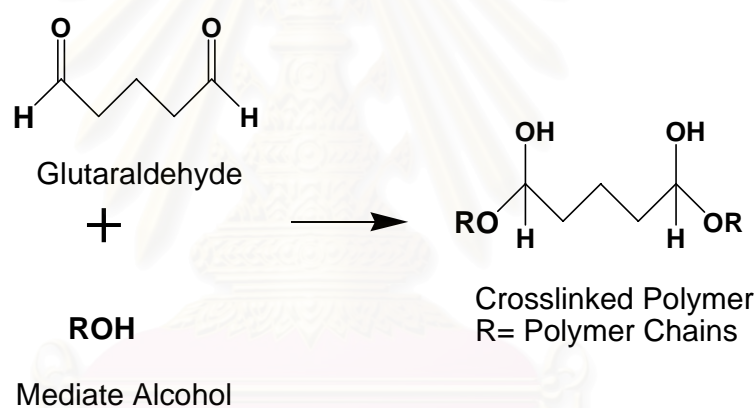


Figure 2.3: Aldehyde-mediated crosslinking of polymers containing hydroxyl groups [22].

2.4.2 Crosslinking procedure of methylcellulose with glutaraldehyde

Crosslinking reaction between MC with GA depends on temperature, concentration of MC, concentration of GA and the amount of employed acid. Moreover, crosslinking condition plays important roles in the obtained MC properties. These methods can be divided into two categories, i.e. homogeneous crosslinking [23

and 24] and heterogeneous crosslinking [25 and 26]. Homogeneous crosslinking is the method that a crosslinking agent is mixed with MC solution. Heterogeneous crosslinking is the method that MC in solid form is soaked in a crosslinking agent. Homogeneous crosslinking method is easier because crosslinker can be well dispersed in MC solution. Hence, homogeneous crosslinking method is used in this study.

2.6.3 Techniques Used for the Characterization of Crosslinked MC

Crosslink reaction of MC with GA is easily observed by Infrared (IR) spectroscopic technique. There are many absorbance peaks related to crosslinking reaction. Kurita et al. [27] reported that the excess glutaraldehyde shows the absorption peak at 1710 cm^{-1} (aldehyde group in FTIR spectra). Peak assignment of the spectra is listed in Table 2.2

Table 2.2: Peak assignments of IR spectra of glutaraldehyde, methyl cellulose and crosslinked methylcellulose ([7, 27, 28 and 29].

Peak (cm^{-1})	Possible assignment
GA	
2740, 2855	C–H stretching vibration
1710	C=O stretching vibration
1645	C=O stretching vibration (shift by conjugating)
1114	C–O stretching vibration of trimer or polymer
MC	
3430	O–H stretching vibration

3000-2800	C–H stretching vibration
1645	C=O stretching vibration
1371	C–H stretching vibration of methyl group
1153	C–O stretching vibration (asymmetric oxygen bridge)
1066	C–O stretching
948	ring stretching
Crosslinked MC	
1710	C=O stretching vibration

2.5 Radiation [5]

In physics, the term “irradiation” defines emission of electromagnetic waves (the field theory) or photons (the corpuscular) theory, as well as other corpuscular emissions: α - and β -particles, neutrons, protons and nuclei. The class of electromagnetic radiation includes:

- X-rays and γ -irradiation – electromagnetic emissions at the wavelength between 10^{-11} and 10^{-7} cm, which represent the short-wave region of the spectrum.
- Charged particles having kinetic energy enough for ionization act as they pass through the medium: electrons, protons, deuterons, α -particles, polyvalent ions, nuclear fission product of heavy elements.

2.5.1 The Effect of Ionizing Radiation

As ionizing radiation hits the substance, it ionizes and excites atoms and molecules in the substance. The ionization act (electron removal from electron shell of an atom or molecule) is accompanied by occurrence of two oppositely charged ions: positively charged ion (an atom or a molecule which lost an electron) and negatively charged ion (an atom or a molecule obtaining electron).

Excited state of atoms or molecules are formed under the impact of ionizing radiation on them, which induced electron transition from basic to excited orbital. At the reverse transition from excited to basic orbital the energy is emitted as photons of visible, UV light or X-rays.

The ionizing radiation loses its energy in three basic processes: photoelectrical absorption, Compton scattering and pair production. The photo effect dominates at low energy values, Compton's effect – at moderate energy values and the pairing effect – at high energy of photons. Also Compton's effect dominates in materials with low atomic number (biological media), in the range between 1 keV and 2 MeV

2.5.2 Key Terms of Radiation Chemistry

For the absorbed radiation dose they take the energy of ionizing radiation, absorbed by specific mass of radiated matter. Gray (Gy) is the unit of absorb dose. The specific unit (1 Gy) equals absorption of 1 Joule of any kind of ionizing radiation by 1 kg of the matter. For X-ray and γ -radiation, absorbed and exposure doses are

distinguished. The exposure dose is measured in Coulombs per kilogram (C/kg). The dose of X-ray and γ -radiation is the radiation measure based on its ionizing ability. Let them consider this more comprehensively, using the Gaussian system of units for higher visualization. In this system the exposure radiation dose is measured in roentgens ($1 \text{ R} = 2.58 \times 10^4 \text{ C/kg}$). the specific dose of 1 R corresponds to the dose at which in 1 cm^3 of air (e.g. 0.001293 g) radiation under normal conditions ($T=273 \text{ K}$, $P=1013 \text{ hPa}$) ions carrying charges of 1 electrostatic unit of each sign are produced. As known from electrochemical data, 1 electrostatic unit of electricity equals 2.1×10^9 specific charge of each polarity e.g. this amount of ionic pairs is formed in 1 cm^3 of air, which absorbed 1 R radiation dose. On average, formation of 1 ionic pair consumes 34 eV ($1 \text{ eV} = 1.6 \times 10^{-12} \text{ erg}$). Thus at 1 R dose 1 cm^3 of air absorbs $(2.1 \times 10^9) \times 34 = 0.114 \text{ erg}$ or 87 erg per air gram, respectively

Previously, radiobiology and radiation chemistry present such notions as Roentgen-equivalent-physical (Rep) and Roentgen-equivalent-man (Rem). Rep is the dose, at which water or tissue absorbs the same amount of energy, as under impact of 1 R dose. Rem is the unit of radiation dose equivalent (the amount of any radiation type), which causes the same biological damage compared with 1 rad dose impact of X-rays (within the energy range between 100 and 1000 keV). In the SI system the dose-equivalent is measured in Joule per kilogram (J/kg):

$$1 \text{ Gy} = 1 \text{ J/kg} = 100 \text{ rad} = 107.5 \text{ Rep} = 6.24 \times 10^{15} \text{ eV/g.}$$

The absorb dose intensity represents energy of ionizing radiation absorbed by specific mass of radiated substance during specific time (Gy/s, Gy/min, Gy/h). In SI

system the intensity unit of exposure dose equals Ampere per kilogram (A/kg). The relation between dose intensity and dose value is presented by the formula:

$$P = \frac{D}{t}.$$

Radiation intensity is the radiation energy, which hits 1 cm² of this matter surface transversal to the radiation ray direction during 1 s.

Also, radiobiology studies dependence of biological organism survivability on radiation dose (survivability curves). Survivability curves are subdivided to linear, exponential, sigmoid, and combined curves. The combined curves are frequently represented by a sum of two components. The notion of radiation dose (D₃₇), which the quantity of survived organisms equals 37% (the second case of survivability curves), is used for specification of radiosensitivity of organisms in the study of survivability curves.

2.5.3 Gamma Rays

The first scientist, who was found the phenomena of radioactivity is Henri Becquerel in March, 1896. Gamma ray is electromagnetic wave that it has no mass and weight, no deviation in the magnetic field and has the power of high through. It is the result of nuclear process that is generated from the degradation of nucleus of atom that is radioisotope or named radioactive source such as Cobalt-60 (⁶⁰Co). The gamma

rays has short wavelengths in the region of 3×10^{-9} cm to 3×10^{-11} cm or becomes approximately 40 keV to 4 MeV.

^{60}Co is the radioactivity which it has concentration of ray amount of 42,814 curies that found by George Brandt, Swedish Chemist in 1735 and use in 1950 by curing the cancer. In commercial gamma radiation factory will use gamma ray from ^{60}Co , because it is very cheaper than other isotope and have half-cycle is 5.25 years. ^{60}Co has resistant under the environment that has high radiation and can use in high temperature of 1000 degree by using in maturing of material and increase resistant to plastic sheets for cross linking of molecule. It gives off two gamma rays/disintegration, one with 1.17 MeV energy and the other with a 1.33 MeV or a total of 2.5 MeV energy/disintegration.

In the present of oxygen, oxidative degradation dominates, leading to the introduction of hydroxyl and carbonyl groups, as well as chain scission. The oxidative degradation is caused by the free radical reactions that lead to the formation of the peroxy, as well as chain scission and cause deterioration of mechanical properties. It occurs not only during radiolysis in the presence of air or oxygen, but, if oxygen is available, it can take place for months during the post-irradiation period. Several factors affect the extent of oxidative degradation such as solubility of oxygen, dose and thickness of the sample (oxygen diffusion).

2.5.4 Radiolysis of Aqueous Biopolymers

The interest raised in 1950s to radiolysis of aqueous biopolymer and other biologically active compounds was mostly defined by the task of radiobiology: a living cell protect against ionizing radiation and vice versa stimulation of its decomposition, for example, in the case of cancer therapy. To solve these problems, the primary stages of radiolytic processes proceeding in all microareas of the living cells must be known.

Aqueous solutions of biopolymers represent a suitable model for radiobiological investigates, because on average a cell contains up to 80%, and some parts of it represent a set of organic and inorganic compounds in different concentrations. At the same time the cell also contains components forming a solid phase and interphases form membranes. Therefore, the task of taking into account radiolytic processes proceeding in this complex heterogeneous system, the living cell, for the above-formulated purpose of practical radiobiology and medicine must be reduced to estimation of direct and indirect (via water radicals) action of irradiation in all components of the system.

Biopolymers represent water radical acceptors, formed by the radiation impact. The information about the role of water radiolysis products in conversion of biopolymers were obtained with the help of various methods used in radiation chemistry.

CHAPTER III

LITERATURE REVIEWS

Park and Ruckenstein[6] studied the preparation of MC gel crosslinked with glutaraldehyde (GA) in the presence of hydrochloric acid by solution casting method. In case of GA-crosslinked MC, 5wt% MC solutions was prepared by dissolving MC powder in water with constant stirring at room temperature and then GA and hydrochloric acid were added for crosslinking. The films were fabricated by casting on a glass plate. Films with the thickness of 50-80 μm were obtained by drying at ambient temperature for 72 hr. The swelling test has shown that the MC gels were insoluble in water with GA content of over 5.0×10^{-3} mol/l, and hydrochloric acid concentrations of more than 1.0×10^{-2} mol/l. The swelling ratio of MC gel, which is a measure of their degree of crosslinking density, was observed to increase with increasing GA and hydrochloric acid concentrations. The tensile strength was increased through crosslinking while the elongation was slightly decreased.

Mi et al. [30] showed the effects of TPP/genipin crosslinking mechanism of chitosan beads on degradable properties. Figure 3.1 presents the degradation profile of the TPP/genipin crosslinked chitosan beads in terms of the increments in free amino group content within 8 weeks of lysozyme incubation. It was showed that the increment in free-amino-group content of medium incubated with fresh chitosan gel

bead (without crosslinking) was significantly greater than that observed in the media incubated with the TPP/genipin co-crosslinked chitosan beads. The biodegradation rates of TPP/genipin co-crosslinked chitosan networks were slower than fresh chitosan gel beads.

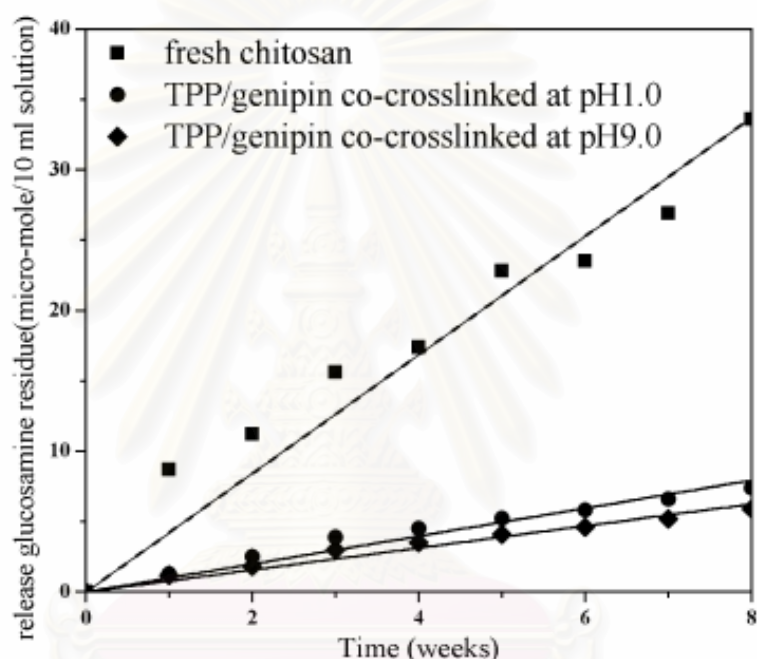


Figure 3.1: Degradation profile of the TPP/genipin crosslinked chitosan beads in terms of the increments in free amino group content in the incubation medium vs. time [30].

Wach et al. [31] studied the formation of carboxymethylcellulose (CMC) hydrogel by ionizing radiation at highly concentrated aqueous solutions. They prepared the highly concentrated aqueous solutions of CMC at natural pH (~ 7.8). Irradiation was carried out using γ -irradiation from ^{60}Co source at a dose rate of

10kGy/h at inert temperature. Figure 3.2 presents the tensile strength of hydrogels prepared from aqueous solutions of CMC. Tensile strength of hydrogels in relaxed state (after irradiation with the original water content) was related the concentration of polymer that increased with the increasing of concentration. It was considered that intermolecular crosslinking reactions occur by a radical route engaging side chain. They pointed the propable place of crosslinking that was on the α -carbon atom of the side chain, due to the stability of such radical.

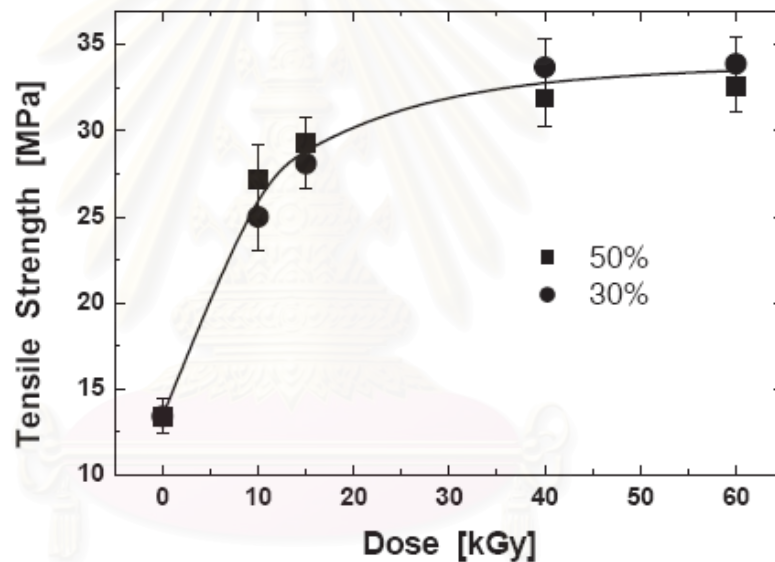
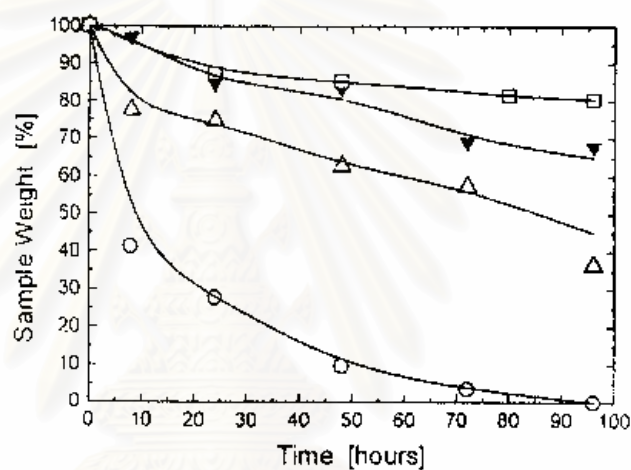


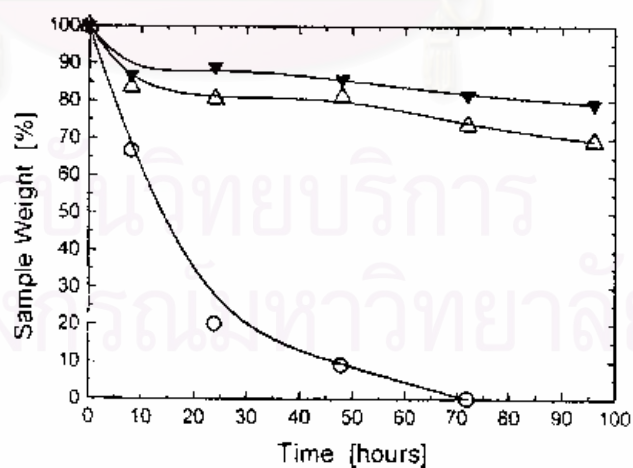
Figure 3.2: Tensile strength of CMC hydrogel film in dry state. Hydrogel were formed from CMC aqueous solution at various concentrations by γ -irradiation [31].

Wach et al. [32] investigated the effect of high-energy radiation on carboxymethylcellulose (CMC) with biodegradability. They found that hydrogel of a lower crosslinking density degraded faster than that crosslinked more tightly by higher

energy because the number of intermolecular bonds was far greater in the latter. Figure 3.3 presents the biodegradation profile of radiation crosslinked CMC. CMC films formed from 50 and 30% solutions by 15 kGy degrade completely after 95 and 72 h, respectively. In case of CMC films formed by 10 kGy, the specimens disappeared before 8 h of incubation. The degradation time increased with increasing dose of radiation.



(a)



(b)

Figure 3.3: Biodegradation of crosslinked CMC by the cellulose enzyme C-0901 (pH 5.0). Hydrogels were prepared from (a) 50 and (b) 30% CMC

aqueous solutions at different doses of irradiation: (○) 15, (△) 40, (▼) 60, and (□) 100kGy [32].

Wach et al. [9] investigated the effect of ionizing radiation on aqueous solutions of methylcellulose (MC) and hydroxyethylcellulose (HEC) with swelling and biodegradability. They prepared the sample by irradiating the aqueous solution of MC and HEC with γ -rays generated from ^{60}Co source at a dose rate of 10 kGy / h at inert temperature. Swelling depends on the density of intermolecular links, also swelling can replace the crosslink density. Figure 3.4 presents schematic of intermolecular crosslinking and degradation with irradiation. It shows that the crosslinking density did not depend on the dose. Figure 3.5 presents the biodegradation of hydrogels at various dose of irradiation. Hydrogels formed at higher dose degraded slower than lower dose.

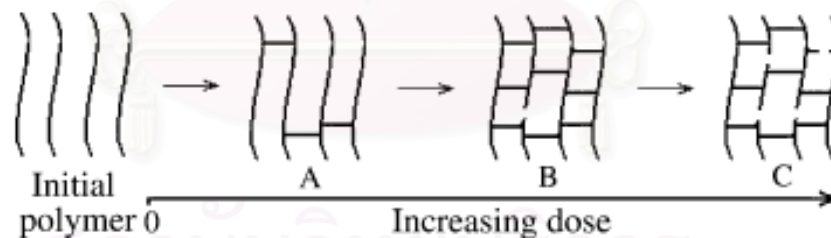


Figure 3.4: Schematic representation of intermolecular crosslinking of polymer chains and their degradation with continuous irradiation [9].

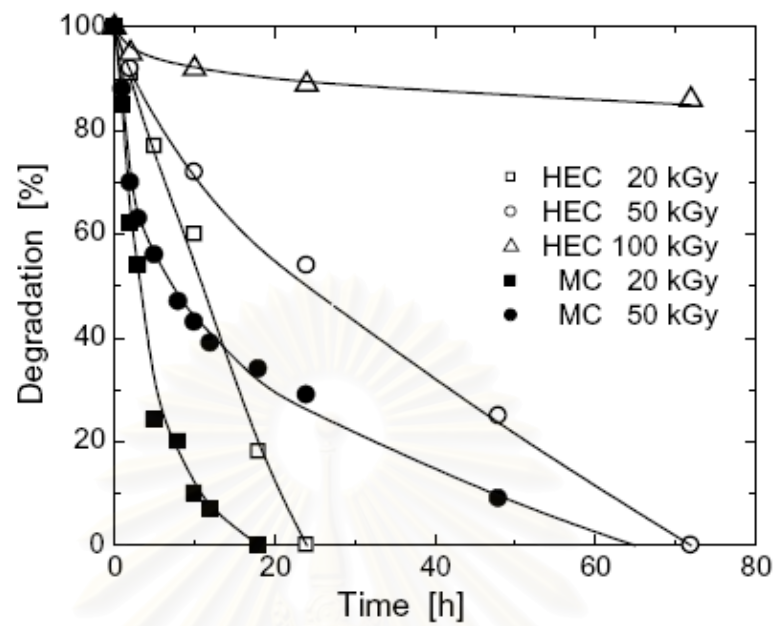


Figure 3.5: Biodegradation of hydrogels by the cellulose enzyme C-0901 (pH 5.0). Hydrogels were prepared by irradiation of 20% MC and HEC solution [9].

CHAPTER IV

EXPERIMENTAL

4.1 Materials

- Methylcellulose (MC), Tylose H 6000 YP2, was purchased from ShinEtsu Co.,Ltd.

Table 4.1 Specific properties of Tylose H 6000 YP2

Specific Properties		Unit	Method
<i>Texture/Physical form</i>		powder	
<i>Solubility</i>		soluble in water of any temperature	
<i>Ionicity</i>		nonionic	
<i>Moisture, as packed</i>	max. 6	%	7130
<i>Ash content, as Na₂SO₄</i>	max. 5	%	7140
Particle size			
<i>< 0.180 mm (through 80 mesh)</i>	min. 95	%	7010
<i>< 0.100 mm (through 140 mesh)</i>	min. 45	%	7010
Viscosity			
<i>1.9% absolutely dry, 20 °C, 20 °GH</i>			
<i>Grade, Hoppler falling ball viscometer</i>	6000	mPas	7320
<i>Range, Brookfield RV, 20 rpm, sp. 4</i>	6000 - 7500	mPas	7270

- Glutaraldehyde (GA) solution (25wt%, MW = 100.11, Bp = 106°C)

under trade name of UNILAB was obtained from Ajex Finechem, New Zealand.

4.2 Preparation of Crosslinked MC Films

4.2.1 Preparation of Radiation Crosslinked Methylcellulose Films

Aqueous MC solutions (5wt%) are prepared by dissolving MC powders in water and mixed for 1 min at 80°C using a homogenizer (IKA T25 basic) with a speed of 13500 rpm. About 20 ml of the obtained MC solution was poured into a Petri dish. 5wt% MC solutions are evaporated to 25wt% MC solutions. Gamma radiation is radiated to MC solutions at various doses of 5, 10, 15, 20 and 25 kGy. Dried films were obtained after the solvent was evaporated in an air-circulated chamber at ambient temperature. The yielded thickness of the radiation crosslinked MC film was in the range of 100-120 μm .

4.2.2 Preparation of Chemically Crosslinked Methylcellulose Films

Aqueous MC solutions (2wt%) are prepared by dissolving MC powders in water and mixed for 1 min at 80°C using a homogenizer with a speed of 13500 rpm. GA and hydrochloric acid are added after the MC solution is cooled to room temperature. The investigated GA contents are varied at 0.05, 0.1, 0.2, 0.3, and 0.5 wt%. In each solution, 2 drops of hydrochloric acid are added to yield a solution of

pH 3. The homogeneous blend solution is obtained using a magnetic stirrer at 700 rpm for 1 hr. Finally, the resulting dried films are washed by distilled water for 3 hr to neutralize the film. About 30 ml of the obtained MC solution was poured into a polystyrene mold, as shown in Figure 4.1. Dried films were obtained after the solvent was evaporated in an air-circulated chamber at ambient temperature. The thickness of each chemical crosslinked MC film is approximately 70-80 μm .

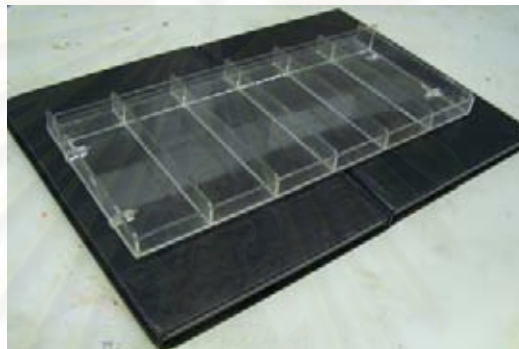


Figure 4.1: Polystyrene mold for chemically crosslinked MC film casting.

4.3 Specimen Characterizations

4.3.1 Viscometer

Viscosity of MC solution was measured by Physica Rheolab MC1: Standard measuring system MS-Z3 DIN/MC1, at shear rate of 10-1000 s^{-1} for 10 min. The volume of measured suspension was about 17-20 ml. The raw data was plotted between shear rate and viscosity of the solutions.

4.3.2 Moisture Absorption

The moisture absorption testing of ASTM D570-98 was modified to find out the moisture absorption of crosslinked MC films with 70-80 μm thickness. The test specimens with the dimension of $50 \times 50 \times 0.07 \text{ mm}^3$ were dried at 60°C for 24 hr, then cooled in a desiccator, and immediately weighed as the initial weight. The specimens were placed on the aluminum net inside a plastic box ($300 \times 200 \times 110 \text{ mm}^3$) at 100% RH for 24 hr.

After 24 hr, the specimens were then weighed immediately to obtain the final weight. The moisture absorption of the sample was calculated according to Eq. (1):

$$\text{Moisture Absorption (\%)} = \frac{(W_f - W_i)}{W_i} \times 100 \quad ; (1)$$

Where W_i and W_f are the weight of composite MC films before and after absorbing moisture.



Figure 4.2: Experimental set-up for moisture absorption test.

4.3.3 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of radiation and chemical crosslinked MC films were investigated by NETZSCH DMA 242C in the tensile mode at a frequency of 1 Hz. The samples were heated from 30 to 200°C at a rate of 2°C/min in nitrogen atmosphere. The films with dimensions of about 5×10×0.1 mm³ were subjected to sinusoidal deformation with a 5 μm amplitude. The storage modulus (G'), loss modulus (G''), and loss tangent (tan δ) were determined. The T_g was taken as the maximum point on the loss tangent curve in the temperature sweep tests.

4.3.4 Thermogravimetric Analysis (TGA)

The thermal stability of crosslinked MC was investigated by Mettler Toledo TG/DTA. The sample mass used was about 15 mg. The first heating scan, which was conducted to eliminate water residual, was carried out at a rate of 20°C/min from room temperature to 120°C. The second scan was heated from 40 to 800°C at a heating rate of 20°C/min in a nitrogen atmosphere. The nitrogen purging flow rate was 100 ml/min. Weight loss of a sample was measured as a function of temperature.

4.3.5 Gel Fraction and Swelling Behavior

Radiation and chemical crosslink MC films were immersed and extracted in de-ionized water for about 72 h at room temperature, and then were dried at 60°C in a

vacuum oven to constant weight. The gel fraction was calculated according to the following equation:

$$\text{Gel fraction (\%)} = (G_d / G_i) \times 100 \quad ; (1)$$

where G_i is the initial weight of dried sample, G_d is the weight of dry gel after removing water. Radiation and chemically crosslinked MC hydrogels with certain weight were immersed into de-ionized water and taken out at certain time to weight. Swelling degree was calculated as follows:

$$\text{Swelling degree} = (G_t - G_d) / G_d \quad ; (2)$$

where G_t is the weight of the swollen hydrogel after swelled for 3 days.

4.3.6 ATR FT-IR Spectroscopy

To investigate functional groups and the structure of crosslinked MC films, FTIR technique was used NICOLET 6700 (Thermo corporation) with CONTINUUM FT-IR microscope by using resolution of 4 cm^{-1} at 128 scans with mercury-cadmium-telluride (MCT) detector. The dome shape Ge μ IRE is developed for ATR FT-IR spectral acquisition using an infrared microscope. ATR spectra of crosslinked MC films pick up by the tip.

4.3.7 Composting Degradation

The film samples were placed on the mixed soil and stored under controlled conditions (100% RH at ambient temperature, as seen in Figure 4.3) in a plastic box ($300 \times 200 \times 110 \text{ mm}^3$). The test specimens were prepared in the dimension of

45×55×0.075 mm³. The film appearance was observed, and then the photographs were taken.

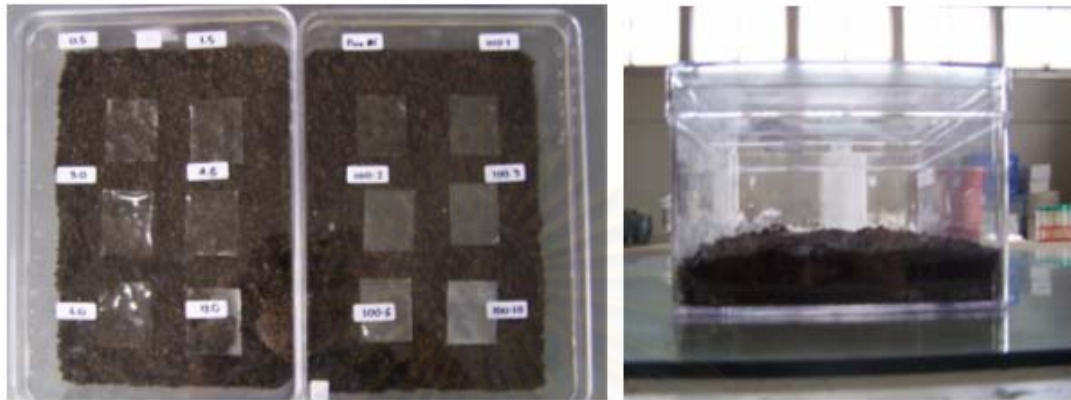


Figure 4.3: Experimental set-up for composting degradation test.

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CHAPTER V

RESULTS AND DISCUSSION

5.1 Preparing Radiation Crosslinked MC Films

5.1.1 Effect of Concentration of MC Solution on Gel Formation and Viscosity after Gamma Radiation Crosslinking

Irradiation of polysaccharide material evokes some effects depending on the type of polymers, parameters of irradiation, the phase of material under processing and others. The two main reactions, which influence the final properties of polymers include: (a) scission of main chain, leading to diminishing of the molecular weight of macromolecules and (b) crosslinking, the opposite process to degradation, which leads to the formation of macroscopic, insoluble material [33]. Table 5.1 shows the gel formation and the viscosity of the MC solution (before and after irradiation) at various concentration of the MC solution. From this table, the viscosity of radiated hydrogel is more than the un-radiated MC solution that imply the crosslinking in the MC solution can be generated by gamma irradiation. In addition, hydrogels by gamma irradiation at 5kGy can be formed at the concentration of MC of 4% to 25% by weight but the concentrations of MC solutions of 2% to 3% by weight are not formed. It implied that polysaccharides irradiated in solid state and in diluted aqueous solutions

suffer scission of acetal linkages in main chain. Several mechanisms have been proposed by Wach et al. [9]. They reported that the degree of substitution of gamma irradiation of CMC aqueous solution in air atmosphere is high at a relatively low concentration, while for the low degree of substitution, high concentrated solutions are necessary to form the gels. Random cleavage of glycoside bonds in the main chain, initialized by radicals placed on macromolecules was found to be a leading reaction.

5.2 Characterization of Crosslinked MC

5.2.1 Moisture Absorption of Crosslinked MC Films

The effects of doses of gamma ray (kGy) and glutaraldehyde (GA) crosslinker contents (wt% based on the MC) on moisture absorption capacity of crosslinked MC films is presented in Figure 5.1. The crosslinked MC films by gamma radiation were obtained using the radiation doses from 5kGy to 25kGy whereas those GA-crosslinked films were obtained with the GA content ranging from 0.05% to 0.5 wt%. Both methods yielded film specimens which were insoluble in water. Therefore, both techniques provided MC specimens with the potential formation of the three dimensional network structure thus inhibited the solubility of the uncrosslinked MC polymers.

When the doses of gamma ray and GA contents increased, moisture absorption also systematically decreased from 160% of uncrosslinked MC films to 104% of the radiation crosslinked MC films and 119% of the chemically crosslinked MC films. It

can be explained that as the crosslinking of MC increased, the number of hydroxyl groups of MC decreased [6]. As a result, the reaction between hydrogen bonds and water molecules reduced. Moreover, the crosslinking made the polymer chains difficult to move. As a result, the moisture absorption decreased with increasing doses of gamma ray and GA contents. This phenomenon was similar to that reported for chitosan crosslinked with tripolyphosphate and genipin at pH 7.4 [30] and HPC crosslinked with glutaraldehyde. They reported that, the moisture absorption decreased with increasing degrees of crosslinking.

5.2.2 Dynamic Mechanical Analysis of Crosslinked MC Films

The DMA constitutes a sensitive tool for the detection of the molecular relaxation of a polymer and leads to information about the molecular structure of the polymer. For all crosslinked MC films, significant enhancement of storage modulus (G') can be seen in the investigated temperature range as presented in Figure 5.2 and 5.3. The storage modulus at room temperature (30°C) was observed to systematically increase with the increasing contents of a GA crosslinker. However, in the radiation crosslinked case, the variation of doses of gamma ray had no obvious trend on the storage modulus at room temperature. Because radiation crosslinked MC films were heterogeneous structures that complicated to inspect the real storage modulus of these films. At 200°C (temperature in the rubbery plateau region), the increasing of a GA crosslinker increased the plateau modulus of the crosslinked MC films. The similar effect can be observed at various doses of gamma ray in radiation crosslinking method. From the result, we can infer that gamma irradiation and GA addition can

generate intermolecular crosslinking in the MC chains. An increase of storage modulus in the rubbery plateau region in principle relates to an increase in degree of crosslinking of the specimen. The higher degree of crosslinking leads to denser network structures, which decreases the mobility of the polymer chains. Therefore, the higher crosslinked materials tend to have greater rigidity in nature. The effects of radiation as well as chemical treatments on the MC crosslinking are relatively indifferent. The crosslinked MC film at 0.2% by weight of a GA crosslinker showed the highest crosslinking density in this result whereas the maximum value in the radiation crosslinked systems was observed at the radiation dose of 25kGy.

Figure 5.4 and 5.5 illustrated the plots between the mechanical loss tangent ($\tan \delta$) against temperature from the DMA experiment of the pure MC films, the radiation crosslinked MC films and the chemically crosslinked MC films. The $\tan \delta$ curves for the MC crosslinked films showed no effect on the α -relaxation with increasing the doses of gamma ray from 5kGy to 25 kGy or with the contents of a GA crosslinker from 0.1% to 0.2% by weight i.e. the α -relaxation peak corresponded to the glass transition temperature of the specimens and observed at 147°C for every specimen. This means that the glass transition temperature of the crosslinked MC films does not change with the levels of both crosslinking techniques used under this investigation. This phenomenon might also be attributed to the fact that the MC backbone was so rigid so that the network rigidity thus the glass transition temperature did not significantly change after crosslinking and the degree of the crosslinking may not be enhanced sufficiently to affect the glass transition temperature. This observation is similar to the report by Park and Ruckerstein [6] who revealed that the MC gels exhibited almost the same glass transition temperature of

MC after chemical crosslinking, indicating that effect of crosslinking was negligible. Moreover, from Figure 5.4 and 5.5, the heights of $\tan \delta$ are not different with the increase of doses of gamma ray and contents of a GA crosslinker. Generally, the $\tan \delta$ is related to the ratio between viscous and elastic behaviors. From the report of Huang et al. [34], they gave the reason that $\tan \delta$ is defined as the ratio of viscous components to elastic components, it can be assumed that the increased height is associated with the higher segmental mobility and more relaxing species. From the results, it is possible to conclude that the variation of gamma irradiation in this investigation rendered negligible effects on the viscoelastic behavior of the specimens. While the contents of a GA crosslinker increased the height of $\tan \delta$ peak slightly decreased. It can be implied that the elastic behaviors in the chemically crosslinked films were higher than uncrosslinked films.

5.2.3 Thermogravimetric Analysis of Crosslinked MC Films

The TGA approach in which a sample loses mass with increasing temperature directly provided the information about the thermal stability and the degradation mechanism for crosslinked film. The TGA thermograms of the pure MC films, radiation crosslinked MC films at various doses of gamma ray and chemically crosslinked MC films at various contents of a GA crosslinker are presented in Figure 5.6 and Figure 5.7, respectively. It can be noticed that a slight weight loss (~3%-7% by weight) of MC and crosslinked MC started below 100°C. Park and Ruckerstein [6] reported that the possible causes for the initial weight loss are probably due to moisture and high water-retention capacity of MC. In these figures, they show that the

variation of doses of gamma ray had negligible effect on the thermal stability of crosslinked MC films. While the contents of a GA crosslinker increased from 0.05 to 0.5% by weight the degradation temperature (at 10% weight loss) of chemically crosslinked MC films increased from 310°C to 339°C, respectively. From this result, it shows the effect of homogeneous crosslinked structures of chemically crosslinked MC films. The hemi-acetal linkages could slightly shift the thermal stability of MC films. However, the negligible effect of thermal stability on radiation crosslinked films might be caused of the heterogeneous crosslinked structure of films. The major weight decrease of pure MC films and crosslinked MC films in both techniques took place in the temperature range of 310-410°C possibly because of the structure degradation of MC. In general, the thermal stability of a polymer is improved by crosslinking. However, in this case, thermal stability of MC gels remained comparable to that of the uncrosslinked MC because of the rigid anhydroglucose unit of MC. This phenomenon was similar to that reported by Park and Ruckenstein [6] for MC crosslinked with GA. Beyond 450°C, all curves were approaching a plateau value as mainly char residue remained. The residual weight of these specimens at 700°C slightly increased with the increasing of doses of gamma ray and contents of a GA crosslinker. The increasing of char residues can be explained as due to the formation of the covalent bonding from intermolecular crosslinking of gamma irradiation and hemi-acetal formation of GA addition. The same behavior was reported by Huang et al. [34] in HPPA/DHMP system cured by UV radiation. They reported that the further degradation of the cured film is considered to be a competition between the crosslinking of unsaturated species with radicals being formed (to form the char), and

continued chain scission process occurring, evolving flammable materials which continue burning until there is nothing left.

5.2.4 Gel Contents of Crosslinked MC Films

Gelation dose, at which is the amount of insoluble polymer in any solvent [9]. Gel content at various doses of gamma ray (kGy) and different contents of a GA crosslinker (% by weight based on the MC) is presented in Figure 5.8. In this figure, it is clearly seen that the gel fraction of the crosslinked MC films increased with an increase of the doses of the gamma ray. The same trend was observed in the chemically crosslinked MC films with increasing the contents of a GA crosslinker. The gel content was determined to be 0% in the uncrosslinked MC specimen due to its water soluble thermoplastic nature. The gel fraction; however, increased drastically from 0% to 80% using the radiation dose of only 5 kGy and the similar level of gel fraction i.e. 81% was obtained using a GA crosslinker at the content of only 0.05wt%. Both crosslinking techniques also revealed a less dependence in gel fraction values with further treatments. In the chemical crosslinking process, the gel fraction changed from 81% at the GA level of 0.05% by weight to the gel fraction value up to 90% at the maximum GA content of 0.5% by weight. On the other hand, the gel fraction increased from 80% using a radiation dose of 5kGy to the value of 96% using a radiation dose of 40kGy. Wach et al. [32] reported that gamma irradiation on cellulose derivatives typically lead to the random formation of free radicals on polymer chains and hydrogen atoms. These free radicals are responsible for such reactions as grafting and intermolecular crosslinking. Pekel et al. [33] reported that

interactions of high-energy radiation with polysaccharides result in dehydrogenation, oxidative degradation, and depolymerization reactions and destruction of the basic monomer units. While GA crosslinking occurs specifically at the hydroxyls group at C(2) or C(3) of anhydroglucose unit which should be in the neighborhood of each other and can be linked by the GA molecule. Our results suggested that the adjacent hydroxyl groups have been mostly consumed at the 0.05% by weight of GA treatment to form an infinite network of MC. Therefore, further addition of GA beyond this level did not show significant increase in their gel fraction. However, greater level of gel fraction up to 96% can be obtained in the radiation crosslinking. This may imply that the crosslinked sites from gamma irradiation can be generated at a greater level than the crosslinked sites from GA addition which is relatively fixed. Furthermore, the tendency of crosslinking site formation in the radiation crosslinked MC specimens under gamma radiation was higher than that of chemically crosslinked MC specimens. As a result, the gel fraction of radiation crosslinked MC can be enhanced to a greater level than that of the chemically crosslinked MC.

5.2.5 Swelling Behavior of Crosslinked MC Gels

The crosslinked MC gels were characterized in term of their degree of swelling. The degree of swelling much depends on crosslink density hence irradiation dose [33]. The relationship between the degree of swelling of MC hydrogels and doses of gamma ray for MC gel as well as contents of a GA crosslinker (% by weight based on the MC) addition are illustrated in Figure 5.9. Both methods yielded film specimens which can swell at different degree in water. In this figure, it is clearly seen

that the degree of swelling of the crosslinked MC films decreased with the increasing the doses of gamma ray. The chemically crosslinked MC films showed no effect on various contents of a GA crosslinker. The same behavior was reported by Park and Ruckerstein [6]. They reported that the water uptake of the MC gels, which is a measure of their degree of crosslinking, decreased with the increasing of GA concentration. This indicates that the hydroxyl groups of MC backbone were crosslinked with GA to form a three-dimensional MC which is insoluble in water. Pekel et al. [33] gave a reason that volumetric expansion of the network reduces as a function of increasing crosslink density. Furthermore, the degree of swelling of radiation crosslinked gels decreased rapidly from 8.4 to 5.0 g water / g dry gel using the radiation doses ranging from 5 to 20kGy and then leveled off at 5.0 using radiation dose greater than 20kGy. The chemically crosslinked gels revealed a less dependence in degree of swelling. It leveled off at 1.3 g water / g dry gel at various contents of a GA crosslinker ranging from 0.05 to 0.5% by weight. Thus, it can be inferred that throughout gamma irradiation process the reaction of intermolecular crosslinking outweighs hemiacetal formation of chemical crosslinking from GA addition. Comparing the swelling values between radiation crosslinked and chemically crosslinked specimens, the swelling values of gamma irradiation crosslinked MC films are significantly greater than that of GA crosslinked MC films. It is also possible that the gamma irradiation crosslinking may cause some extra hydrophilic groups on the methylcellulose chains. Pekel et al. [33] reported that polarity and hydrogen bonding play decisive role in swelling of the radiation-treated gel. Gamma irradiation on MC could generate crosslink linkages at non-polar

functional group easier than polar functional group. This may be one reason why radiation crosslinked MC hydrogel had high degree of swelling.

5.2.6 FTIR Spectroscopy of Crosslinked MC Films

The FTIR spectroscopic technique was used to specify crosslinking moieties in anhydroglucose unit and level of crosslinking in both crosslinking methods. The FTIR spectra of pure MC film and radiation crosslinked MC films at various doses of gamma ray are showed in Figure 5.10. Pure MC had absorption bands related to O–H stretching at 3447 cm^{-1} , -CH_3 stretching in functional group on anhydroglucose unit at 2962 cm^{-1} , $\text{-CH}_2\text{-}$ stretching in functional group on anhydroglucose unit at 2860 cm^{-1} , C–O carbonyl stretching in the anhydroglucose unit of the cellulose at 1643 cm^{-1} , $\text{CH}_3\text{-O}$ in the plane bend at 1440 cm^{-1} , CH_3 symmetric bend (umbrella mode) at 1375 cm^{-1} , C–O stretching from asymmetric oxygen bridge at 1163 cm^{-1} , and ring stretching at 896 cm^{-1} . These values were consistent with those reported by Rimdusit et al. [35]. In this figure, it can be observed that the peak at 3447 cm^{-1} (O-H groups), 1643 cm^{-1} (C-O stretching in anhydroglucose unit), and 1440 cm^{-1} (C-OH groups in bend) decreased and the peak at 2860 cm^{-1} ($\text{-CH}_2\text{-}$ stretching), and the peak at 1375 (CH_3 symmetric) increased with the increasing of doses of gamma ray. In this observation, it is likely that the free radicals were produced from dehydrogenation at C(1), C(2), C(3), C(4), C(5) and C(6) of anhydroglucose repeating units of MC chains. The dehydrogenation of the functional groups of anhydroglucose could be happened easier than the others. This mechanism had been reported by Wach et al. [32]. The random crosslinking and scission of radiation crosslinked MC films showed

heterogeneous structure on them. Furthermore, the FTIR spectrum of 40kGy of dose of gamma ray irradiated on MC film showed the decreasing on the peak at 2860 cm^{-1} ($-\text{CH}_2-$ stretching) and 1163 cm^{-1} (C-O stretching from oxygen bridge). But the FTIR spectrums of 15kGy and 25kGy of radiation crosslinked film showed negligible effect of height on peak at 1163 cm^{-1} (C-O stretching from glycosidic linkages). It implies that the high dose of gamma irradiation caused the degradation in polymer chains. The same mechanism was founded in MC and HEC crosslinked by gamma ray and electron beam irradiation reported by Wach et al. [9]. They reported that breaking of chains inside the gel is directly reflected in swelling. Evidently, swelling starts to increase at higher doses, over 30kGy. It is known that after irradiation cellulose molecules are altered by breaking of glycosidic linkages and the introduction of carboxyl and carbonyl groups.

The FTIR spectra of pure MC film and chemically crosslinked MC films at various contents of a GA crosslinker are showed in Figure 5.11. For chemically crosslinked MC, the peak at 2860 cm^{-1} ($-\text{CH}_2-$ stretching in alkane group of GA) and the peaks at 1710 cm^{-1} (C=O stretching from aldehyde group of GA) were used to indicate the crosslinking reaction. With an increase in the content of a GA crosslinker ranging from 0.2 to 0.5% by weight in the chemically crosslinked MC, the peak at 2860 cm^{-1} ($-\text{CH}_2-$ from hemi-acetal crosslinked linkages) and the peak at 1163 cm^{-1} (C-O in hemi-acetal crosslinked linkages) slightly increased, but the peak at 1440 cm^{-1} (C-OH in plane bend) rapidly decreased. In this result, it can be explained that the dialdehyde groups of a GA crosslinker reacted with the hydroxyl groups at C(2) and C(3) in the anhydroglucose units of MC generating the three-dimensional crosslinked structure between MC chains. The peak at 2860 cm^{-1} ($-\text{CH}_2-$ from hemi-

acetal crosslinked linkages) and the peak at 1163 cm^{-1} (C-O in hemi-acetal crosslinked linkages) could imply the crosslink density of chemically crosslinked MC films that increased with the increasing of contents of a GA crosslinker. The appearance of the absorption spectrum also suggested the formation of intermolecular hydrogen bonding, resemble to the results reported for MC crosslinked with GA [35] and chitin crosslinked with GA [27].

5.2.7 Visual Observation of Crosslinked MC Films

Figure 5.12 shows the radiation crosslinked and chemically crosslinked MC film as well as the untreated MC film. From this figure, it can be seen that the chemically crosslinked MC film at 0.5% by weight of GA and the radiation crosslinked film at 25 kGy of dose of gamma ray are clear transparent films. The surface textures of radiation MC films were rough because of the non-uniform intensity of gamma ray. It happened because gamma ray was scattered in the ^{60}Co gamma irradiator's cell.

The water solubility of pure MC film, radiation crosslinked MC film, and chemically crosslinked MC film is exhibited in Figure 5.13. This figure illustrates that pure MC dissolved readily in water but both crosslinked MC films were insoluble in water. It can also be observed that the volume of the swollen gel of the radiation crosslinked MC was larger than that of the chemically crosslinked MC. This is maybe due to the radiation crosslinked hydrogel was more hydrophilic than the chemically crosslinked hydrogel. The appearances of radiation crosslinked hydrogel and chemically crosslinked hydrogel are also significantly different. The chemically

crosslinked hydrogel was a relatively uniform gel possibly because of the homogeneous crosslinking in the gel to form a homogeneous network as shown in Figure 5.13b. The radiation crosslinked hydrogel; however, rendered a rather non-uniform gel. The structure of the radiation crosslinked MC gel was likely a heterogeneous network which had crosslinked units locally concentrated in the hydrogel. Radiation crosslinked MC gel formed some gel clusters which were scattering in the MC gel specimen as shown in Figure 5.13c. Osada et al. [18] provided the reason for heterogeneous network formation in their gel samples as possibly due to the non-uniform radiation intensity irradiated on the material surface compared with at the inside or the other side of the sample. The non-uniform radiation intensity might be caused by the irradiated condition of ^{60}Co gamma irradiator. The gamma ray which irradiated on stuck specimens scattered in the cell.

5.2.8 Composting Degradation of Crosslinked MC Film in Mixed Soil

Biodegradable polymer after use is transformed to carbon dioxide and water by digestion and by bacterial degradation in the soil. This property is an advantageous characteristic of hydrogels developed in agricultural, medical and other fields [36]. Figure 5.14 and 5.15 illustrate the physical appearance of radiation crosslinked MC films and chemically crosslinked MC films placed on mixing soils at various observing times, respectively. The effect of doses of gamma ray on the degradation behavior of films was presented in Figure 5.14. The degradation behavior of all radiation crosslinked films started with swelling appearance. Then they decayed and finally disappeared. This period of consumption time can be prolonged when doses of

gamma ray was increased. It can be noticed that at the observation period of 4 days, the film with was the only one that 20kGy of radiation crosslinked film was not disappeared. In Figure 5.15, the appearance of the chemically crosslinked films with all compositions was the wet film-formed gel. The observation for 4 days illustrated that the chemically crosslinked films at 0.3% and 0.5% by weight were not disappear. This appearance is the same with MC film crosslinked by GA reported by Rimdusit et al. [35]. It can be concluded that the radiation crosslinked MC structure was heterogeneous because it was observed to form wet gel clusters on the mixed soil. Whereas the chemically crosslinked MC structure was homogeneous because it appeared to be uniformly swollen film. The degradation time at various doses of gamma ray and contents of a GA crosslinker increased with the increasing of both the dose of gamma ray and the GA content. This phenomenon is similar to the MC and HEC systems crosslinked by electron beam irradiation reported by Wach et al. [9]. The authors reported that hydrogel of lower crosslinking density degrades faster than that crosslinked more tightly at higher dose. It is because of greater number of intermolecular bonds in the latter.

Table 5.1: Effect of concentration of MC solutions on gel formation and viscosity

Concentration of MC Solution (% wt/wt base on water)	Gel Formation After Irradiation	Viscosity at shear rate 125 s^{-1} (cP)	
		Before Irradiation	After Irradiation
2	No	819	Very Low
3	No	1,627	Very Low
4	Yes	1,707	3,257
5	Yes	1,989	4,389
7	Yes	6,010	NA
25	Yes	Too High	NA

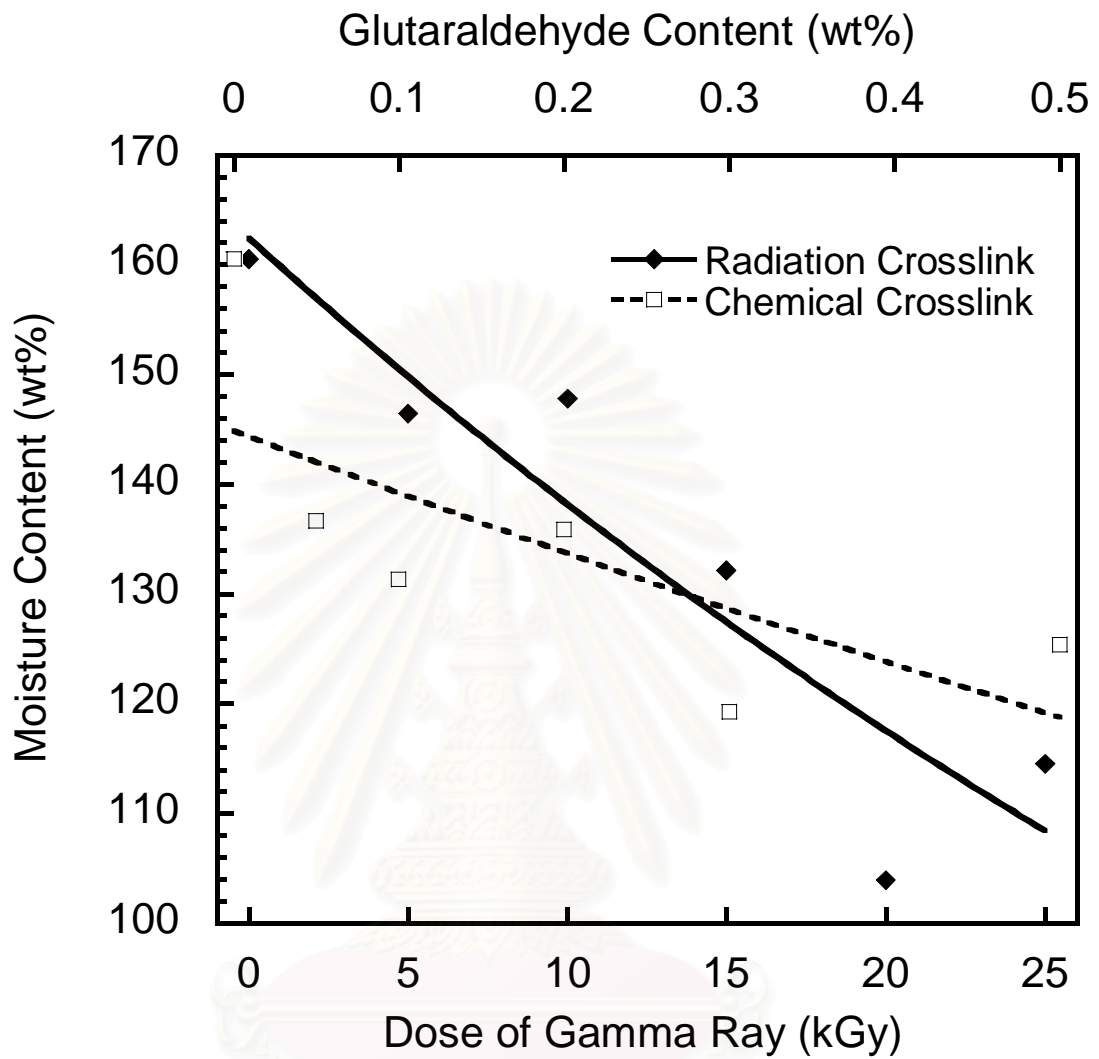


Figure 5.1: Moisture absorption of crosslinked MC films at various doses of gamma ray and contents of glutaraldehyde.

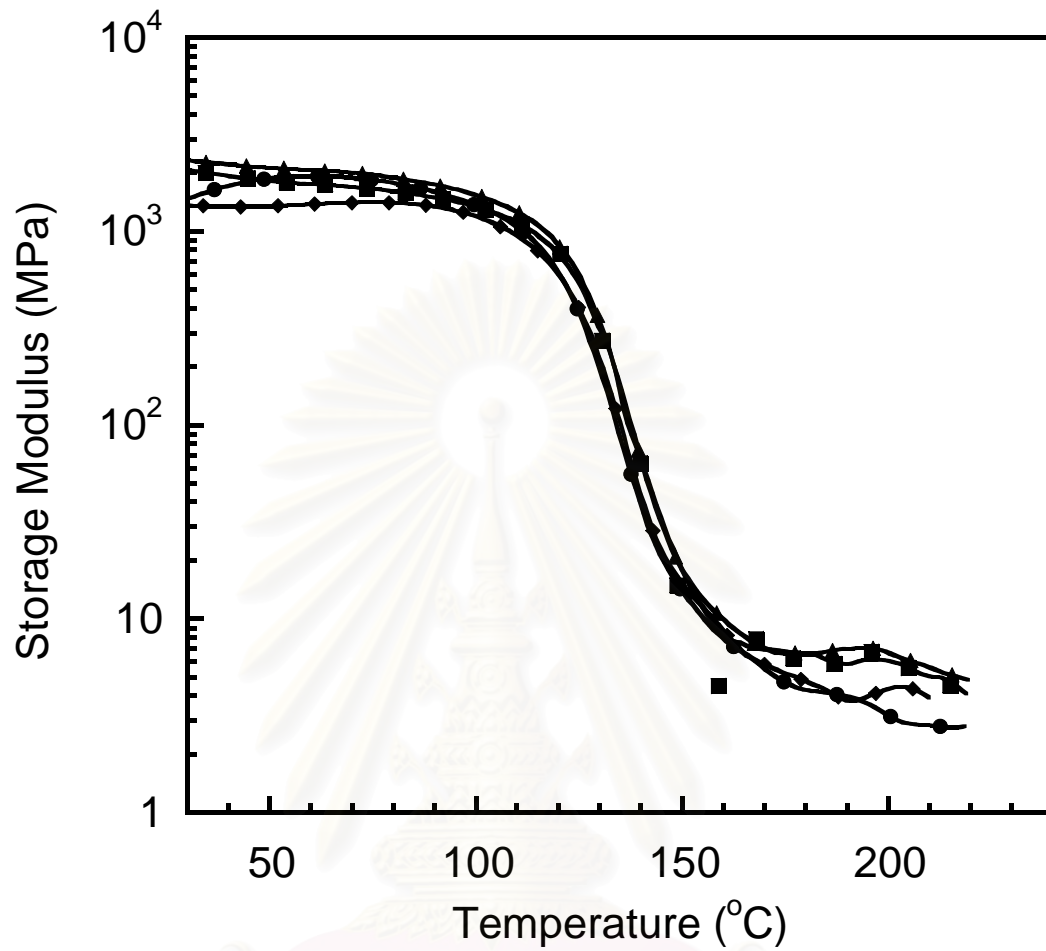


Figure 5.2: Storage modulus of pure MC and radiation crosslinked MC films at various doses of gamma ray: (●) pure MC, (■) 5kGy, (◆) 10kGy and (▲) 25kGy

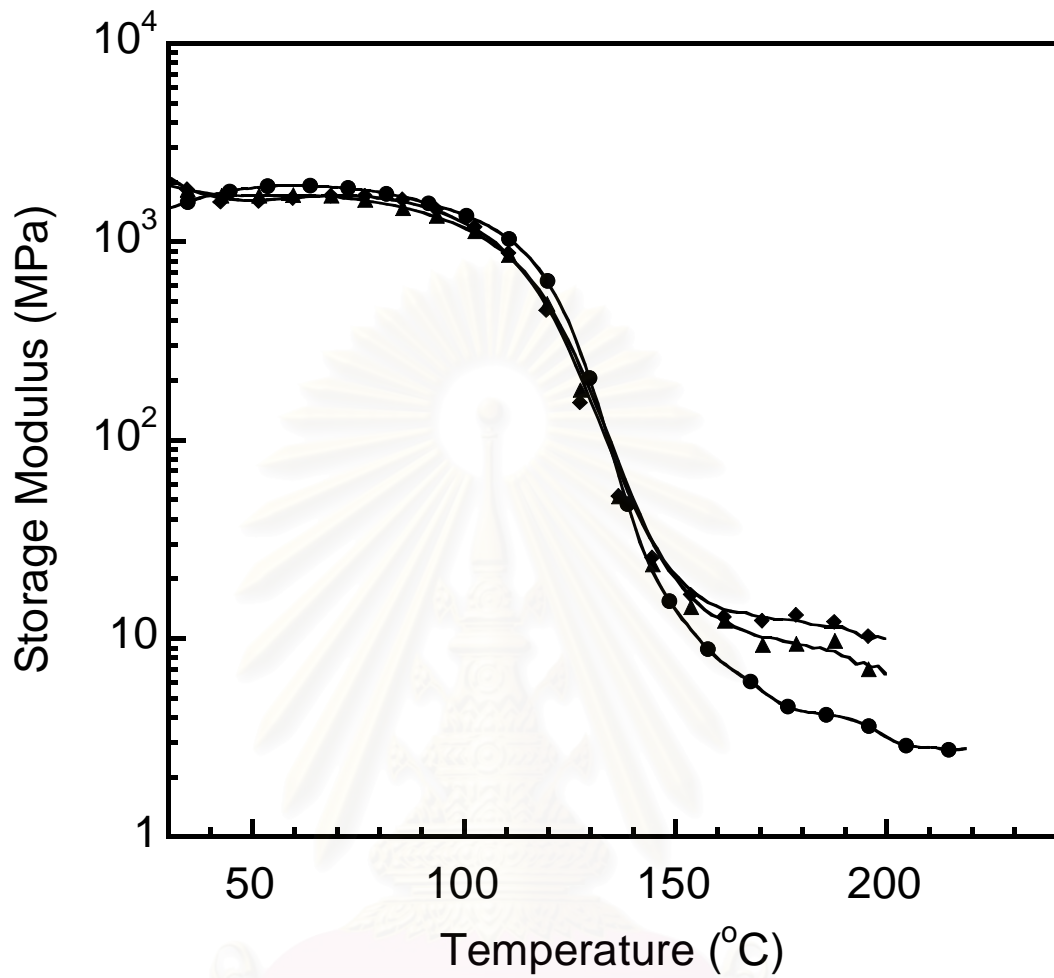


Figure 5.3: Storage modulus of pure MC and chemically crosslinked MC films at various contents of glutaraldehyde: (●) pure MC, (▲) 0.1wt% and (◆) 0.2wt%

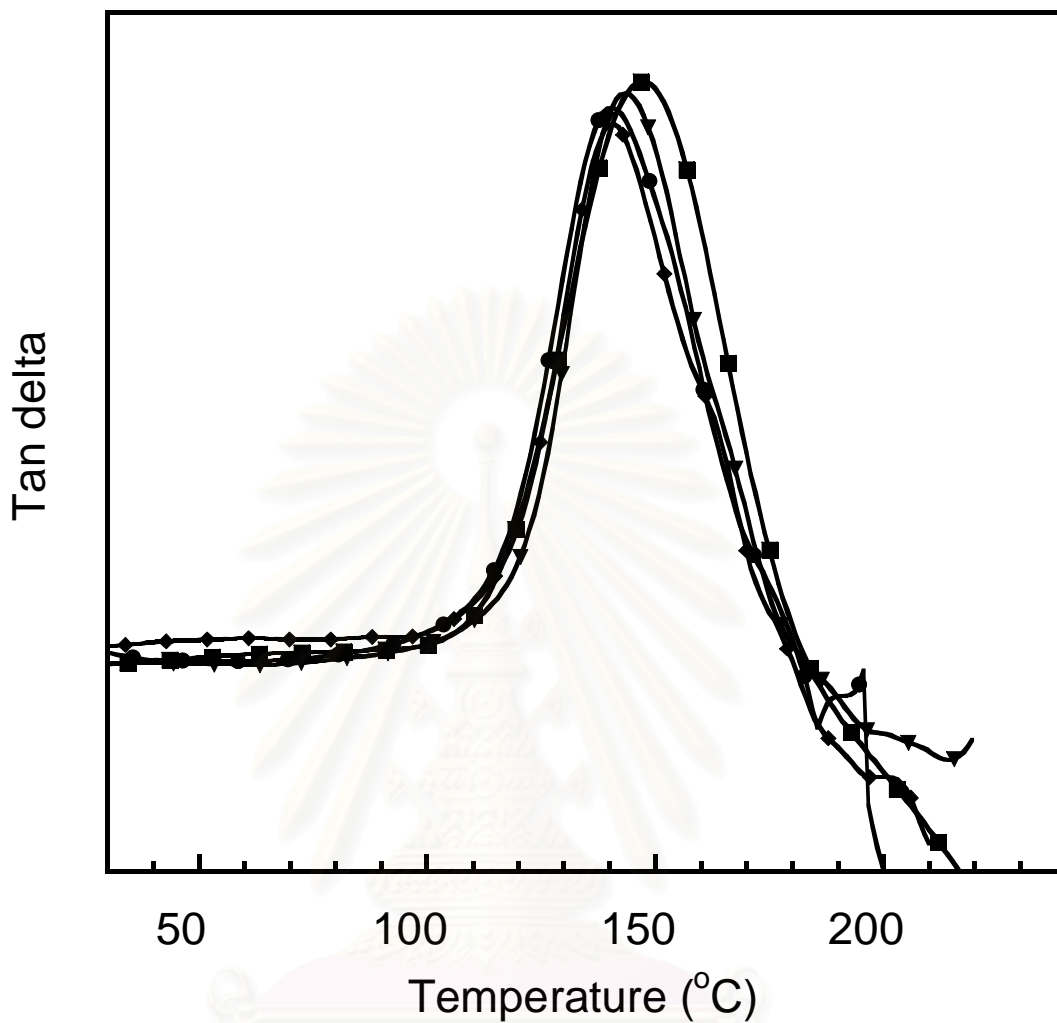


Figure 5.4: Loss tangent of pure MC and radiation crosslinked MC films at various doses of gamma ray: (●) pure MC, (■) 5kGy, (◆) 10kGy and (▼) 25kGy

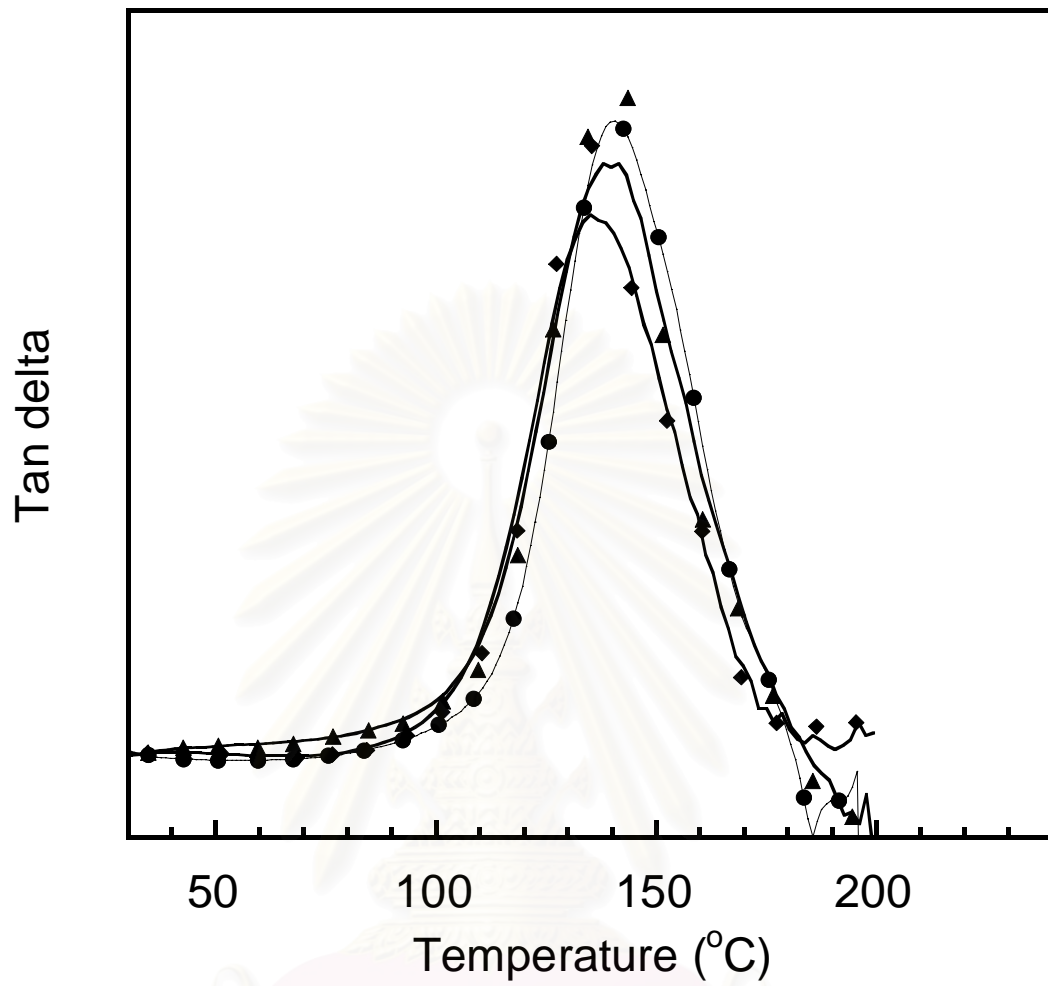


Figure 5.5: Loss tangent of pure MC and chemically crosslinked MC films at various contents of glutaraldehyde: (●) pure MC, (▲) 0.1wt% and (◆) 0.2wt%

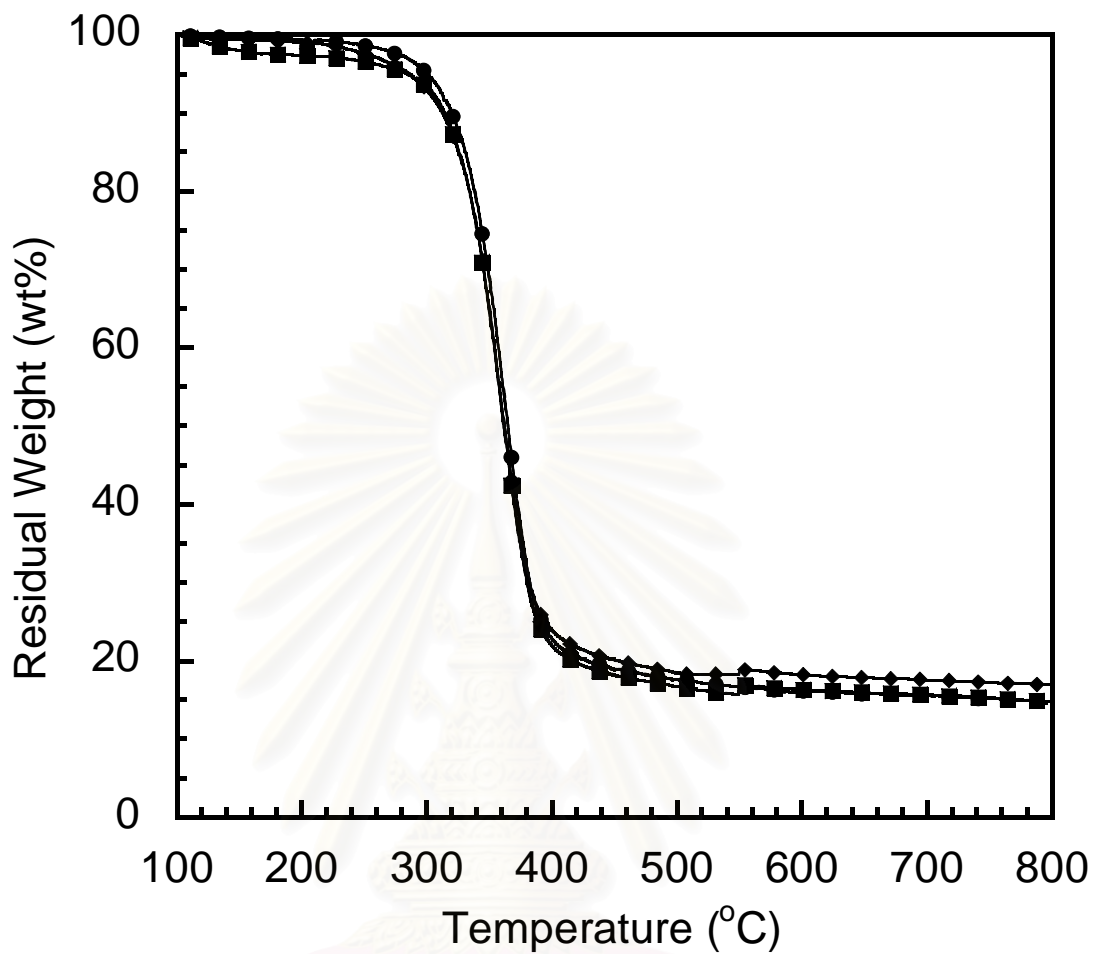


Figure 5.6: TGA thermograms of radiation crosslinked MC films at various doses of gamma ray: (●) pure MC, (■) 5kGy and (◆) 10kGy

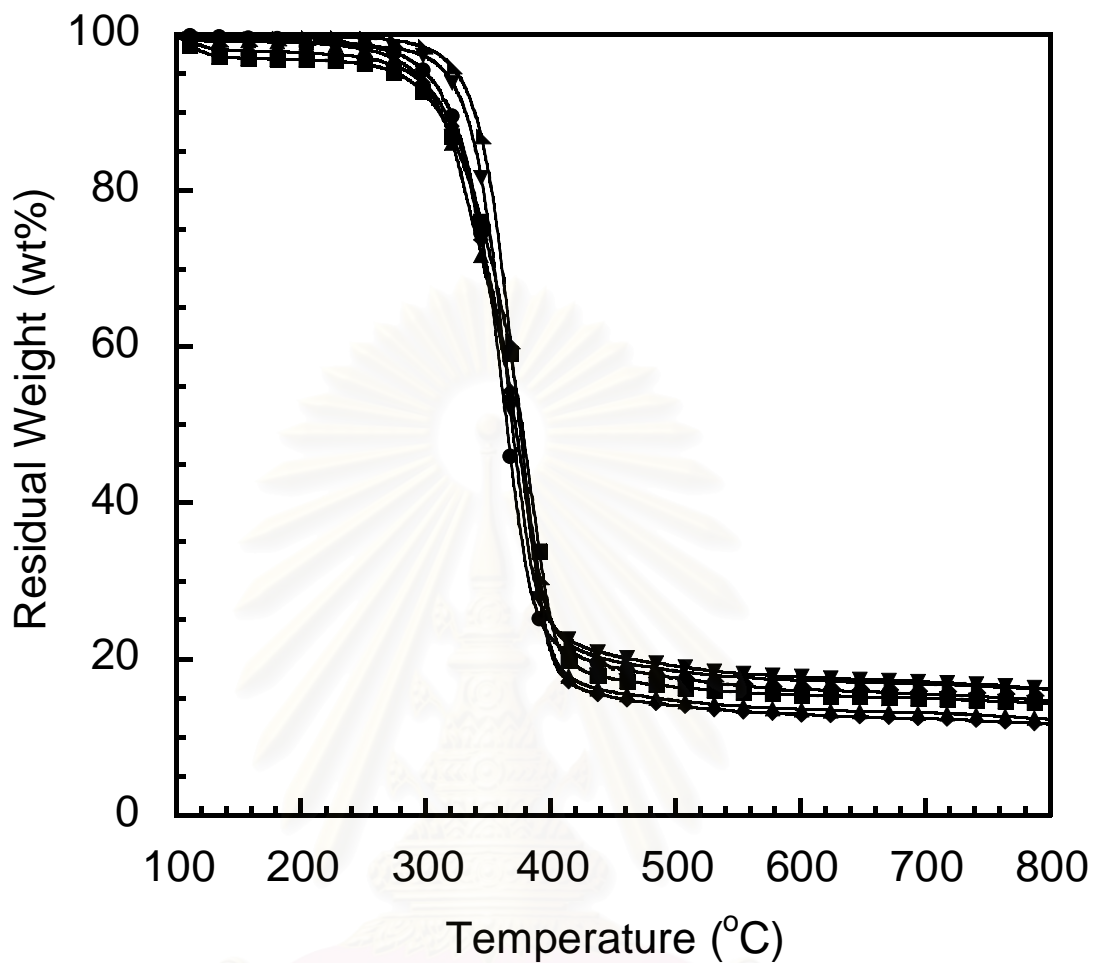


Figure 5.7: TGA thermograms of chemically crosslinked MC films at various contents of glutaraldehyde: (●) pure MC, (■) 0.05wt%, (◆) 0.1wt%, (▲) 0.2wt%, (▼) 0.3wt%, and (▲) 0.5wt%

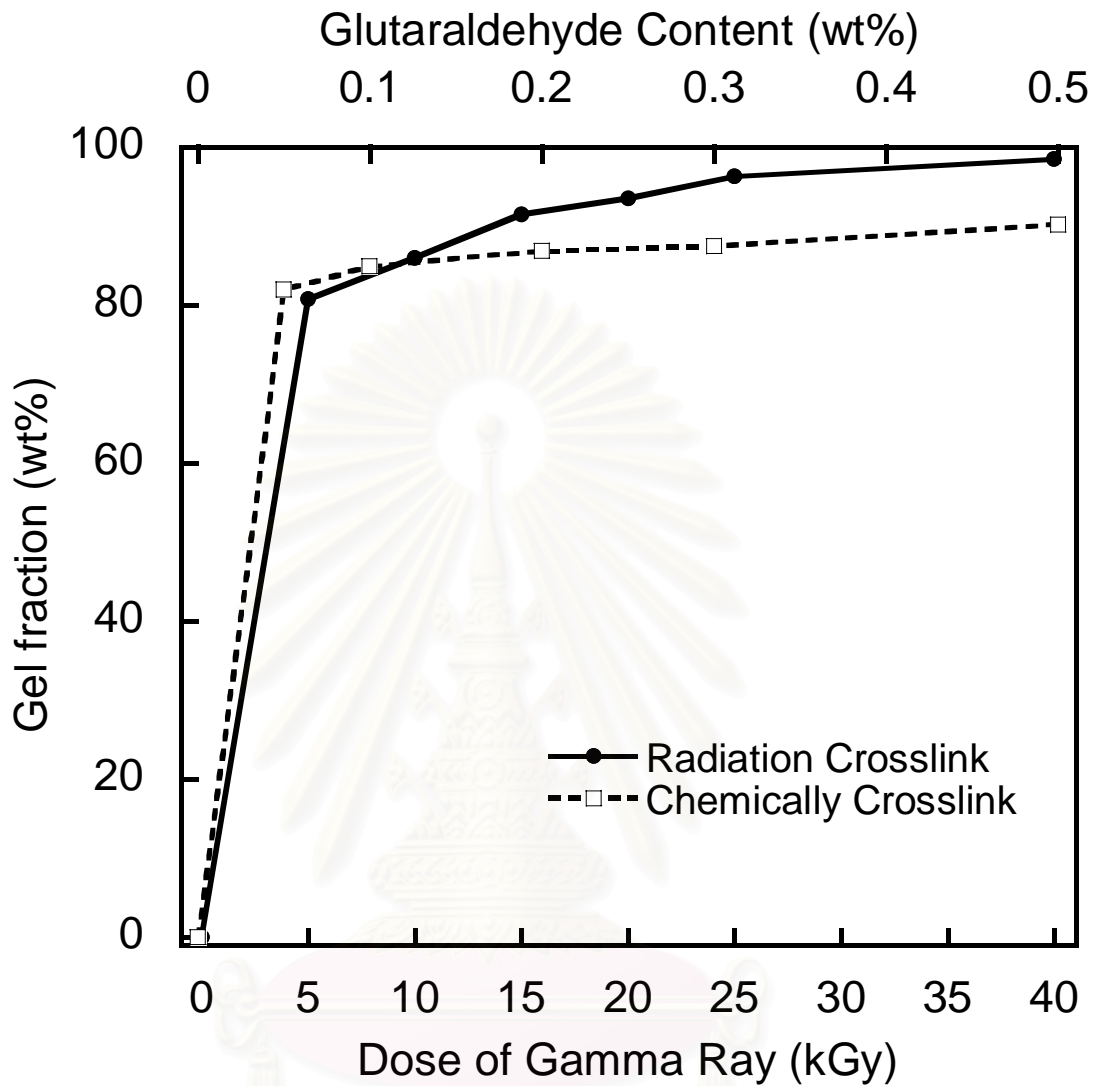


Figure 5.8: The gel content of crosslinked MC gels at various doses of gamma ray and contents of glutaraldehyde.

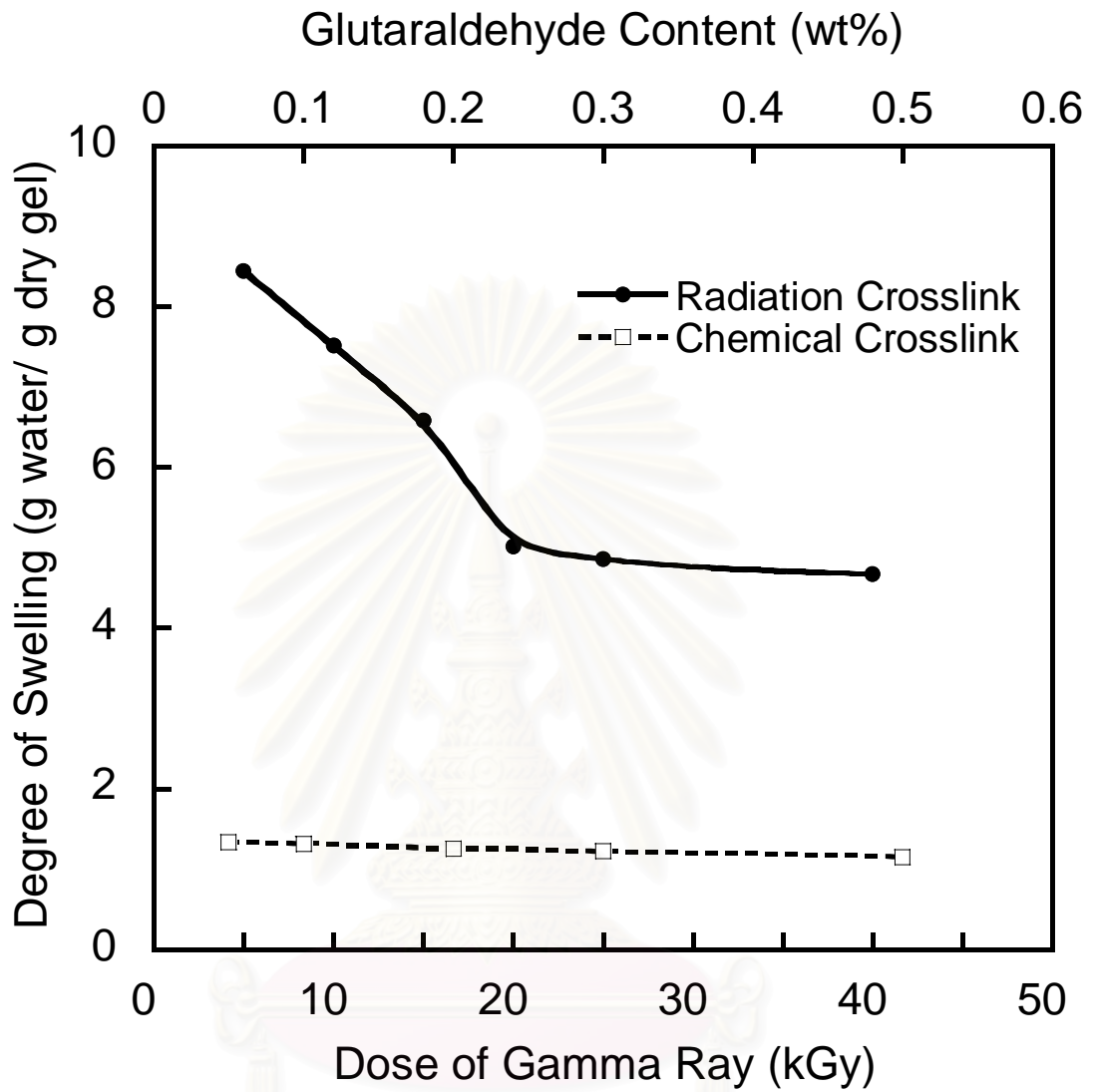


Figure 5.9: The degree of swelling of crosslinked MC gels at various doses of gamma ray and contents of glutaraldehyde.

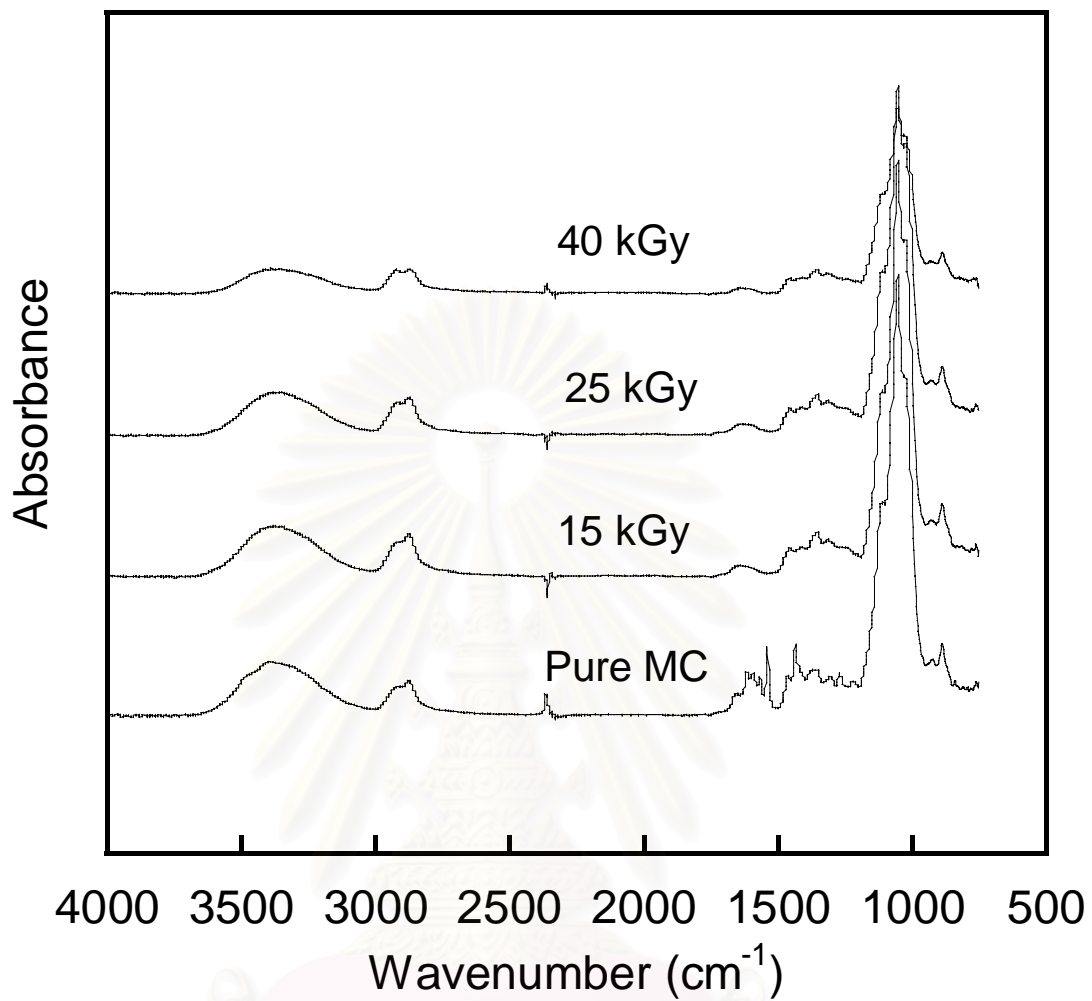


Figure 5.10: FTIR spectra of pure MC and radiation crosslinked MC films at various doses of gamma ray.

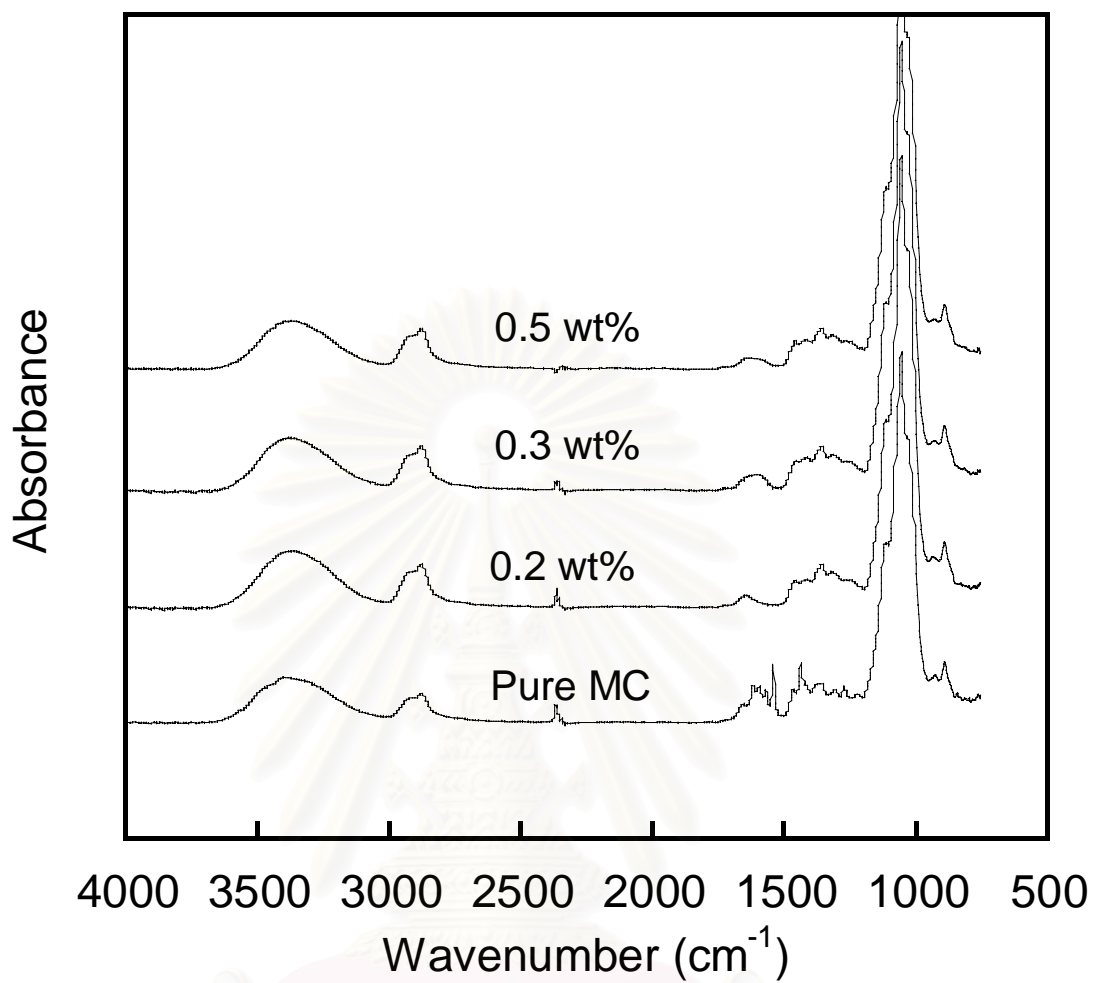


Figure 5.11: FTIR spectra of pure MC and crosslinked MC films at various contents of glutaraldehyde.

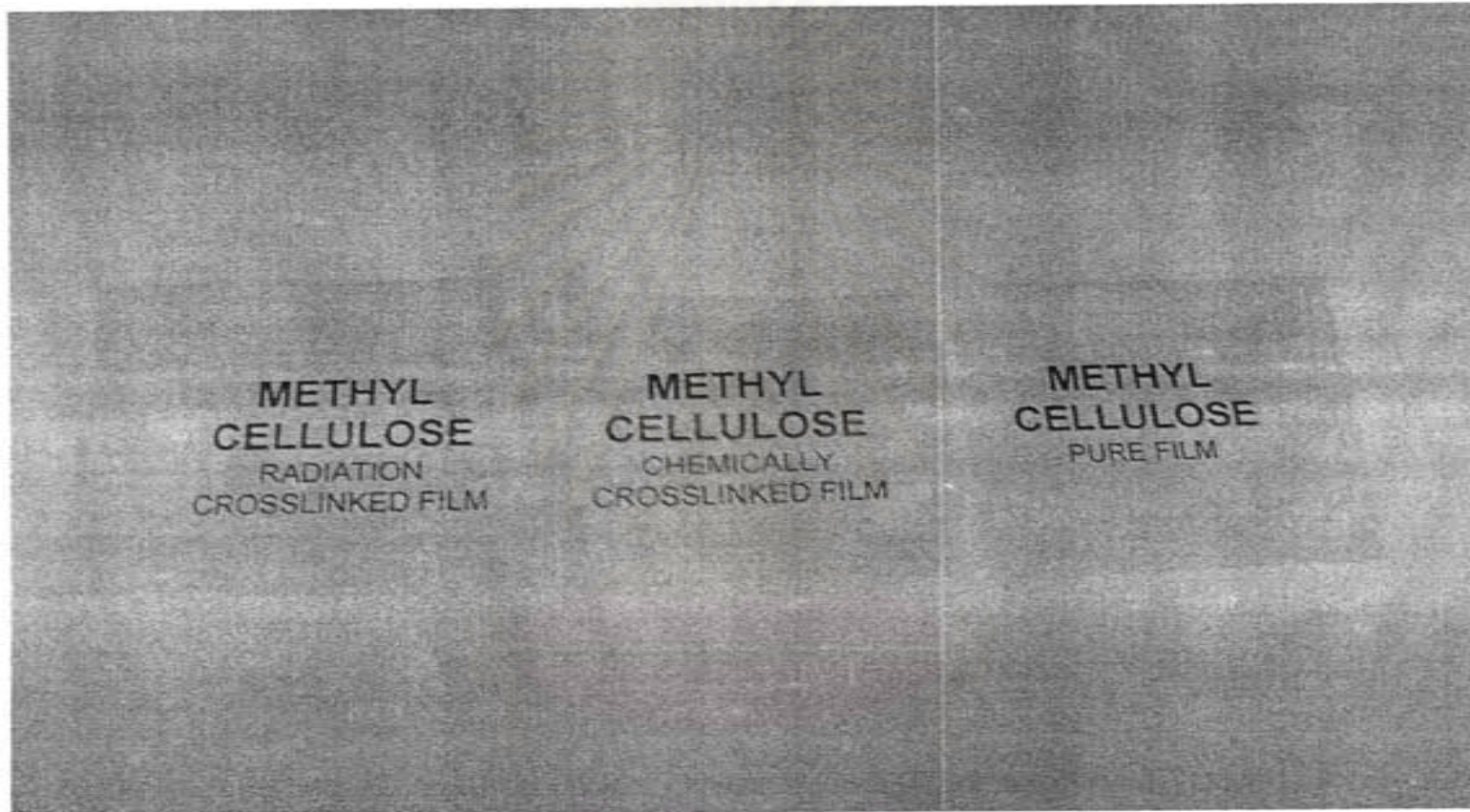


Figure 5.12: Pure MC, radiation crosslinked MC and chemically crosslinked MC films

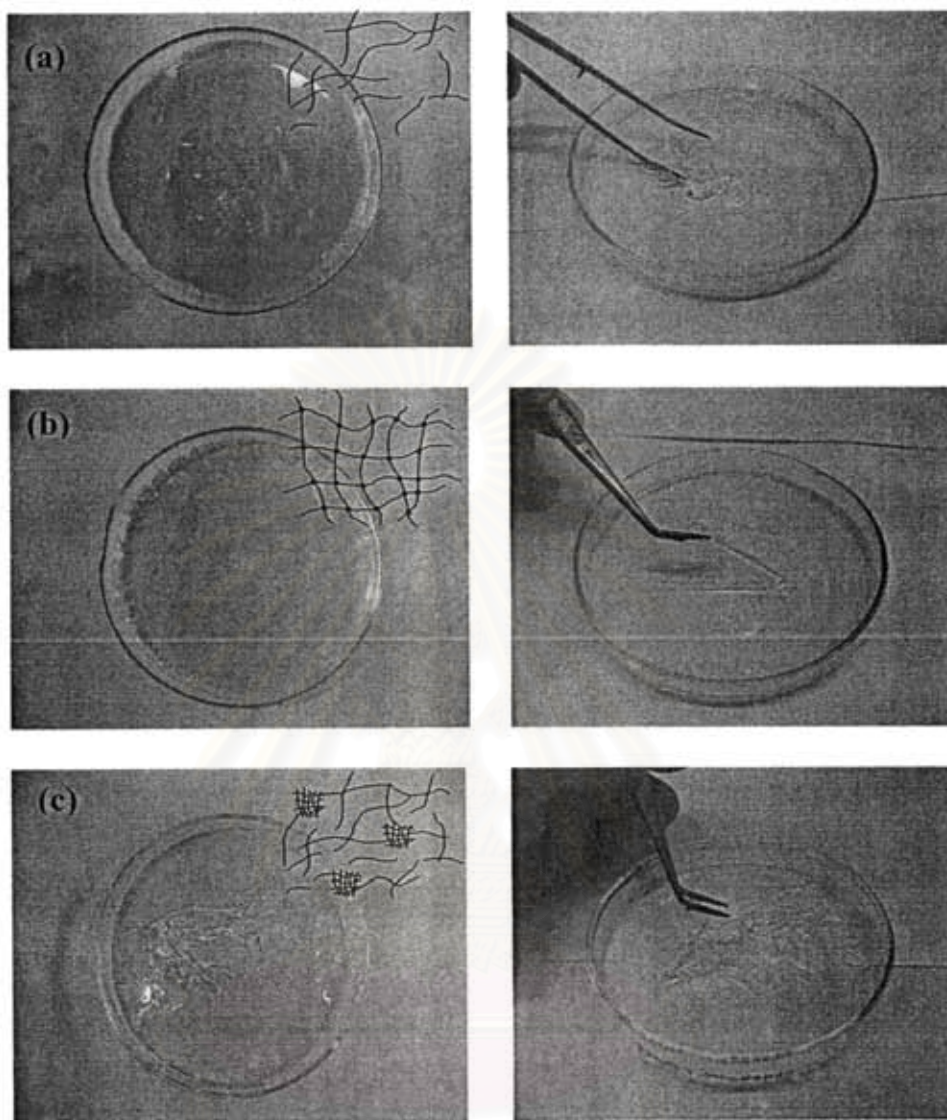


Figure 5.13: Water solubility of methylcellulose films: (a) pure MC, (b) chemically crosslinked MC, and (c) radiation crosslinked MC

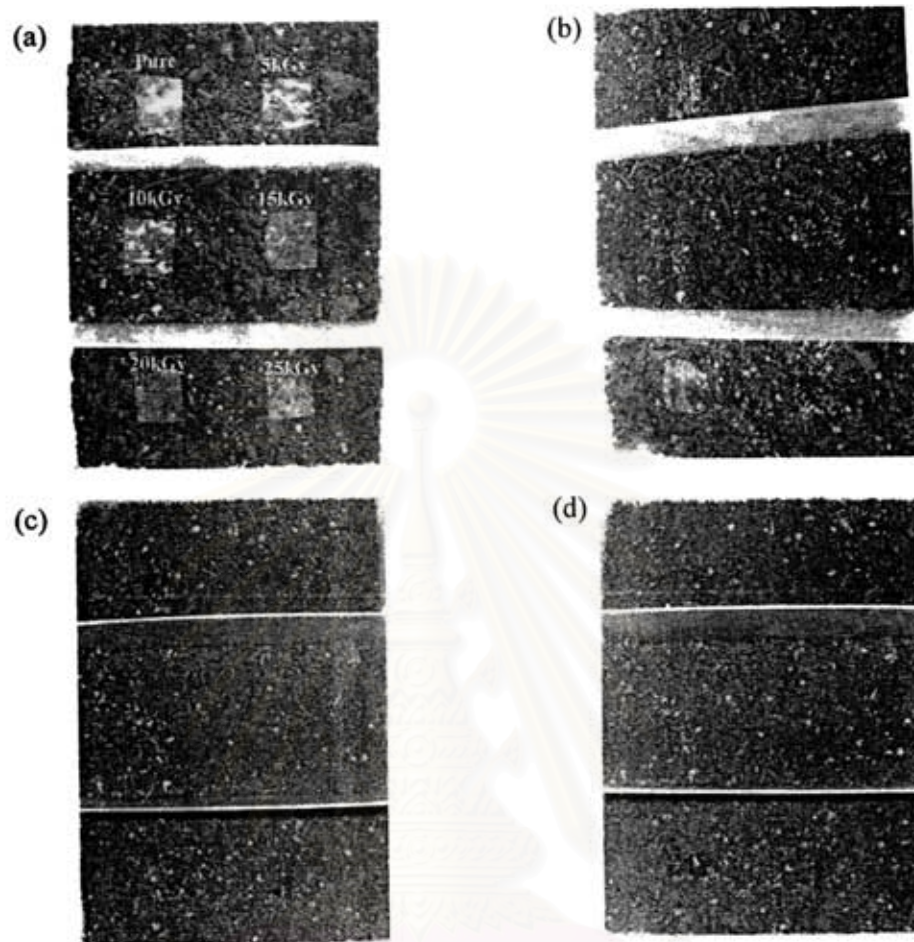


Figure 5.14: Biodegradability of pure MC and radiation crosslinked films at various dose of gamma ray under soil field with time at (a) 1 day, (b) 2 days, (c) 3 days, and (d) 4 days.

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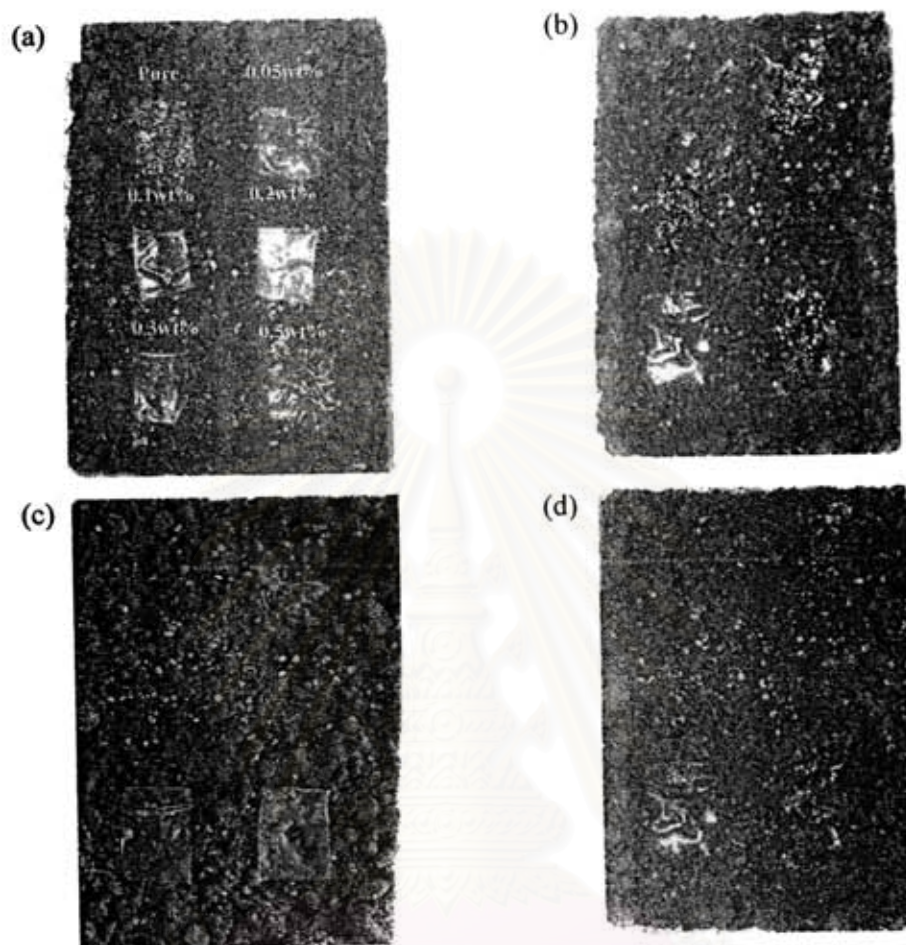


Figure 5.15: Biodegradability of MC crosslinked films various contents of glutaraldehyde under soil field with time at (a) 1 day, (b) 2 day, (c) 3 days, and (d) 4 days.

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CHAPTER VI

CONCLUSIONS

Crosslinked MC polymers prepared by gamma irradiation and GA addition were achieved. The results showed that the concentration of MC solution had significant effects on gel formation of radiation crosslinked MC hydrogels. The concentration of MC solution should be higher than 4% by weight of MC solution. In this study, the proper condition for radiation crosslinking to form MC hydrogel was 25% by weight of MC solution. Moisture absorption of radiation crosslinked film at various doses of gamma ray ranging from 0 to 25kGy decreased about 51% and chemically crosslinked film at various contents of GA crosslinker ranging from 0 to 0.5% by weight decreased about 27%. From the DMA and TGA thermograms, the various doses of gamma ray showed negligible effect on T_g and T_d of radiation crosslinked MC film. While the contents of a GA crosslinker range from 0.05% to 0.5% by weight increased the decomposition temperatures of chemically crosslinked MC films increased from 310°C to 339°C. In addition, the radiation crosslinking provided MC specimens with greater gel content and degree of swelling than chemical crosslinking. For radiation crosslinked MC films at 15kGy (at constant level of gel content), the gel contents rapidly increased from 0 to 91% but the gel contents of chemically crosslinked MC films at 0.05% by weight rapidly increased from 0 to 82%. The degree of swelling of radiation crosslinked MC gel at 15kGy was 6.5 but the degree of swelling of chemically crosslinked MC gel at 0.05% by weight of GA

was 1.3. Furthermore, the FTIR spectra suggested that the radiation crosslinking had more chance to form crosslink networks than chemical crosslinking. In the biodegradation test, the biodegradable period of MC polymers can be prolonged by chemical crosslinking techniques. The chemically crosslinked films at 0.3% and 0.5% by weight of contents of a GA crosslinker can prolong the period of biodegradability but the radiation crosslinked films range from 5 to 25kGy of doses of cannot enhance this property. In comparison, the chemical crosslinking technique had more potential to hinder the biodegradation process. The main reason is the structures of gel that radiation crosslinked gel was heterogeneous but chemical crosslinked gel was homogeneous.

In summary, both radiation and chemical crosslinking methods can provide infinite network of MC hydrogels. Thermal properties of radiation crosslinked MC films and untreated film were not different. For radiation crosslinked MC film, gel contents and degrees of swelling were greater than chemically crosslinked MC films. The radiation crosslinked MC hydrogel was observed to be heterogeneous but the chemically crosslinked MC hydrogel was homogeneous gel. The chemically crosslinked films at 0.3% and 0.5% by weight of a GA crosslinker can increase the period of biodegradability.

REFERENCES

- [1] Aminabhavi, T. M.; Balundgi, R. H.; and Cassidy, P. E., A review on biodegradable plastics, Polym-plast. Technol. 29 (1990): 235-262.
- [2] Crosby, N. T., Food packaging material. Aspects of analysis and migration of contaminants, London: Applied Science Publisher Ltd., 1981.
- [3] Doi, Y., Microbial polyesters, New York: VCH Publishers, Inc, 1990.
- [4] Avella, M.; Vlieger, J.J.; Errico, M.E.; Fischer, S.; Vacca, P.; and Volpe, M.G., Biodegradable starch/clay nanocomposite films for food packaging applications, Food Chem. 93 (2005): 467-474.
- [5] Sharpatyi, V.A., Radiation Chemistry of Biopolymers, Leiden, The Netherlands: Koninklijke Brill NV, 2006.
- [6] Park, J.-S. and Ruckenstein, E. Viscoelastic properties of plasticized methylcellulose and chemically crosslinked methylcellulose. Carbohydr. Polym. 46 (2001): 373-381.
- [7] Coma, V.; Sebti, I.; Pardon, P.; Pichavant, F.H.; and Deschamps, A., Film properties from crosslinking of cellulosic derivatives with a polyfunctional carboxylic acid, Carbohydr. Polym. 51 (2003): 265-271.
- [8] Cheng, S. and Kerluke, D.R., Radiation processing for modification polymer, ANTEC (2003): 2694-2699.
- [9] Wach, R.A.; Mitomo, H.; Nagasawa, N.; and Yoshii, F., Radiation crosslinking of methylcellulose and hydroxyethylcellulose in concentrated aqueous solutions, Nucl. Instrum. Meth. B. 211 (2003): 533-544.

- [10]Doi, Y. and Fukuda, K., Biodegradable plastics and polymers (pp. 479-497), Amsterdam: Elsevier, 1994.
- [11]Chiellini, E. and Solara, R., Biodegradable polymers and plastics, New York: Kluwer Academic Plenum, 2003.
- [12]Hirrien, M.; Desbrieres, J.; and Rinaudo, M., Physical properties of methylcellulose in relation with the conditions for cellulose modification, Carbohydr. Polym. 31 (1996): 243-252.
- [13]Sarkar, N. and Walker, L.C., Hydration-dehydration properties of methylcellulose and hydroxypropylmethylcellulose, Carbohydr. Polym. 27 (1995): 177-185.
- [14]Hirrien, H.; Chevillard, C.; Desbrieres, J.; and Rinaudo, M., Thermogelation of methylcellulose: new evidence for understanding the gelation mechanism, Polymer. 39 (1998): 6251-6259.
- [15]BeMiller, J.N., Encyclopaedia of polymer science and engineering, (p.601) New York: Wiley, 1986.
- [16]Park, H. J.; Weller, C. L.; Vergano, P. J.; and Testin, R. F. Permeability and mechanical properties of cellulose-based edible films. J. Food. Sci. 58(1993): 1361-1364.
- [17]Blanchard, F.A.; Takahashi, I.T.; and Alexander, H.C., Biodegradability of [¹⁴C]methylcellulose by activated sludge, Appl. Environ. Microbi. 32 (1976): 557-560.
- [18]Osada, Y and Kajiwara, K., Gels handbook (pp. 4-20), Academic Press, San Diego (2001).
- [19]Keslter, J. J. and Fennema, O. R. Edible films and coatings: a review. Food Technol. Biotech. 48 (1986); 47-59.

- [20]Tomita, E. and Ikeda, Y. Crosslinking of hyaluronic acid with glutaraldehyde. J. Polym. Sci. Pol. Chem. 35 (1997): 3553-3559.
- [21]Gimenez, V, Reina, J.A.; Mantecon, A.; and Cadiz, V., Unsaturated modified poly(vinyl alcohol). Crosslinking through double bonds, Polymer. 40 (1999): 2759-2767.
- [22]Hennink, W.E. and Nostrum, C.F., Novel crosslinking methods to design hydrogels, Adv. Drug Deliver. Rev. 54 (2002): 13-36.
- [23]Oungbho, K. and Muller, B.W. Chitosan sponges as sustained release drug carriers. Int. J. Pharm. 156 (1997): 229-237.
- [24]Fang, Y.E.; Cheng, Q.; and Lu, X.B., Kinetics of in vitro drug release from chitosan/gelatin hybrid membranes, J. Appl. Polym. Sci. 68 (1998): 1751-1758.
- [25]Andrady, A.L. and Xu, P., Elastic behavior of chitosan films, J. Polym. Sci. Pol. Phys. 35 (1997): 517-521.
- [26]Denkbas, E.B. and Odabasi, M., Chitosan microspheres and sponges: preparation and characterization, J. Appl. Polym. Sci. 76 (2000): 1637-1643.
- [27]Kurita, K.; Koyama, Y.; and Taniguchi, A. Studies on chitin.IX. Crosslinking of water-soluble chitin and evaluation of the products as adsorbents for cupric ion., J. Appl. Polym. Sci. 30 (1986): 1169-1176.
- [28]Sannino, A.; Pappada, S.; Madaghiele, M.; Maffezzoli, A.; Ambrosio, L.; and Nicolais, L. Crosslinking of cellulose derivatives and hyaluronic acid with water-soluble carbodiimide. Polymer. 46 (2005): 11206-11212.
- [29]Zaccaron, C.M.; Oliveira, R.; Guiotoku, M.; Pires, A.; and Soldi, A., Blends of hydroxypropyl methylcellulose and poly(1-vinylpyrrolidone-co-vinyl acetate): Miscibility and thermal stability, Polym. Degrad. Stabil. 90 (2005): 21-27.

- [30]Mi, F.-L.; Sung, H.-W.; Shyu, S.-S.; Su, C.-C.; and Peng, C.-K. Synthesis and characterization of biodegradable TPP/genipin co-crosslinked chitosan gel beads. Polymer. 44 (2003): 6521-6530.
- [31]Wach, R.A.; Mitomo, H.; Yoshii, F.; and Kume T. Hydrogel of biodegradable cellulose derivatives. II. Effect of some factors on radiation-induced crosslinking of CMC. J. Appl. Polym. Sci. 81 (2000): 3030-3037.
- [32]Wach, R.A.; Mitomo, H.; Nagasawa, N.; and Yoshii, F., Radiation crosslinking of carboxymethylcellulose of various degree of substitution at high concentration in aqueous solutions of natural pH, Radiat. Phys. Chem. 68 (2003): 771-779.
- [33]Pekel, N.; Yoshii, F.; Kume, T.; Güven, O., Radiation crosslinking of biodegradable hydroxypropylmethylcellulose, Carbohyd. Polym. 55 (2004): 139-147.
- [34]Huang, Z and Shi, W., UV curing behavior of hyperbranched polyphosphate acrylate/di(hydroxypropyl methacrylate) piperazine and properties of the cured film, Prog. Org. Coat. 59 (2007): 312-317
- [35]Rimduisit, S.; Jingjid, S.; Damrongsukkul, S.; Tiptipakorn, S.; Takeishi, T., Biodegradability and property characterizations of methyl cellulose: effect of nanocompositing and chemical crosslinking, Carbohyd. Polym. 72 (2008): 444-455.
- [36]Nagasawa,N.; Yagi, T.; Kume, T.; Yoshii, F., Radiation crosslinking of carboxymethyl starch, Carbohyd. Polym. 58 (2004): 109-113.



APPENDIX

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

APPENDIX

LIST OF PUBLICATIONS

International conferences:

Somsaeng, K.; Rimdusit, S.; Damrongsakkul, S.; Kewsuwan, P., Comparison of gamma radiation crosslinking and chemical crosslinking on properties of methylcellulose, POLY-2008 Advances in Polymer Science and Technology, New Delhi, India, 28-31 January, 2008.



สถาบันวิทยบริการ
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