SYNTHESIS AND CHARACTERIZATION OF CHITOSAN-BASED HYBRID POLYMER

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By

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ABSTRACT

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Chitosan is one of the most abundance natural polysaccharide which can be prepared chemically or enzymatically from chitin. Chitosan has the properties of biodegradability, biocompatibility, non-toxicity and anti-bacterial properties. The present study was carried out to produce a chitosan-based hybrid polymer in the presence of vinyl monomers via radical polymerization process. The polymer samples were characterized by total solids content, tensile test (to determine tensile strength), differential scanning calorimetry, thermogravimetric analysis, fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and flame test. In order to find out the optimum condition to produce the polymer with better tensile strength, degradation temperature and melting temperature, different initiator system as well as different processing temperature were studied. Besides that, crosslinker was also added during polymerization with the intention to improve the mechanical strength of the hybrid polymer.

ABSTRAK

SINTESIS DAN PENCIRIAN KITOSAN BERASASKAN POLIMER HIBRID

CHEN YOU WEI

Kitosan adalah salah satu semulajadi polisakarida yang paling banyak yang boleh disediakan secara kimia atau enzim dari kitin. Kitosan mempunyai sifat biodegredasi, bioserasi, tidak toksik dan anti-bakteria. Kajian ini telah dijalankan untuk menghasilkan polimer hibrid berasaskan kitosandengan menggunakan vinil monomer melalui proses pempolimeran radikal. Sampel polimer telah disifatkan oleh jumlah kandungan pepejal, ujian tegangan kalori pengimbasan kebezaan, analisis Termogravimetri, Spektroskopi, sinar-X, mikroskopi elektron imbasan dan ujian api. Untuk mendapatkan keadaan yang paling sesuai untuk menghasilkan polimer dengan kekuatan yang baik tegangan, suhu degradasi dan suhu lebur, sistem pendayautamaan berbeza serta suhu pemprosesan yang berbeza telah dikaji. Di samping itu, crosslinker juga ditambah semasa pempolimeran dengan tujuan untuk meningkatkan kekuatan mekanik polimer hibrid.

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Finally, a special thanks to my family. Words cannot express how grateful I am to my parents that always support me all the time. I would also like to thank all of my friends who supported me especially my team mates.

DECLARATION

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

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Chen You Wei

APPROVAL SHEET

This project reports entitled **"SYNTHESIS AND CHARACTERIZATION OF CHITOSAN-BASED HYBRID POLYMER"** was prepared by CHEN YOU WEI and submitted as partial fulfillment of the requirements of the degree of Bachelor of Science (Hons) in Chemistry at Universiti Tunku Abdul Rahman.

Approved by:

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PERMISSION SHEET

It is hereby certified that **CHEN YOU WEI** (ID No: **11ADB01838**) has completed this thesis entitled "**SYNTHESIS AND CHARACTERIZATION OF CHITOSAN-BASED HYBRID POLYMER**" under the supervision of **DR. CHEE SWEE YONG** from the Department of Chemical Science, Faculty of Science.

I hereby give permission to the University to upload the softcopy of my thesis in pdf format into the UTAR Institutional Repository, which may be made accessible to the UTAR community and public.

Yours truly,

_____

(CHEN YOU WEI)

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LIST OF ABBREVIATIONS

AA	Acrylic Acid
ASTM	American Society for Testing and Materials
BA	Butyl Acrylic
^{O}C	Degree Celsius
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
g	Gram
IPN	Interpenetrating Polymer Network
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
mL	Milliliter
MMA	Methyl Methacrylate
PMMA	Poly (methyl methacrylate)
SEM	Scanning Electronic Microscopy
T_d	Degradation temperature

T_m	Crystallinity melting temperature
TGA	Thermogravimetric Analysis
TMVS	Trimethoxyvinylsilane
TSC	Total Solids Content
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Chitin and chitosan

About 70% of the Earth surface is covered by water sources such as oceans, ponds, and lakes. For centuries, seafood has served as energy and nutrients sources for mankind. Nowadays, it has been discovered that seafood has useful bio-chemicals such as chitin. Chitin is one of the most abundant polysaccharides in the world. It is a hard, inelastic and nitrogenous polysaccharide. The sources of chitin are found in naturally occurring organisms such as fungi and yeast. It is the main component in the exoskeleton as well as in internal structure of invertebrates of sea organisms such as Dungeness crab (*Cancer magister*), Pacific shrimp (*Pandalus borealis*), crawfish shells, and lobster. (Knorr, 1991)

In the past, chitin had become a source of waste material pollution in coastal area all around the world. However, appropriate utilization of chitin and chitosan can bring about economic and academic prosperity for the country. Many researches are done all over the world with the intention to adapt and impart the required functionalities to chitin and chitosan to maximize their utility. (Dutta, Dutta and Tripathi, 2004)

Chitin, poly (ß-(1-4)-N-acetyl-D-glucosamine), is normally available from the waste products of crabbing and shrimping industries, while chitosan is only found in small quantities on some fungi such as *Mucoraceae*. However, the main factor limiting the utilization of chitin is its poor solubility in solvents and this has restricted the investigation of its properties and structure. (Aranaz, et al., 2009)

Chitin has low solubility in all solvents due to its fibrous structure. Chitin is only soluble in solvents which are highly toxic such as dimethylacetamide and lithium chloride. However, chitosan has better solubility than chitin and it is able to dissolve in some natural organic acids such as acetic acid, citric acid, glycolic acid, tartaric acid and ascorbic acid. (Chen, et al., 2007) Therefore, chitosan is no longer just the waste from seafood processing industries and it is generally more useful than chitin.

In different fields, ranging from pharmaceutical and medical to water and waste treatment, different properties of chitosan are required and these properties are affected by the degree of acetylation as well as the molecular weight of chitosan. (Dutta, Dutta and Tripathi, 2004)

Chitosan is similar to cellulose which is also a kind of fiber. However, it is different from plant fiber due to the fact that chitosan has unique properties such as is ability to produce in film form and it possesses positively ionic charge that reacts with bile acids, lipids and fats which carry negative charge. (Sandford,

1992) In addition, it is also an attractive bioactive polymer and a renewable source of natural polymer with wide applications. This is because of its chemical and physical properties such as biocompatibility, anti-fungal, biodegradability, non-toxicity and anti-bacterial properties.

When chitosan is dissolved in acidic solvent, it forms a cationic polymer because amino groups in chitosan are protonated by the protons from acid. Therefore, organic acids are frequently used as solubility agent in the preparation of chitosan solution.

As chitosan can be dissolved in acidic solution, it is hardly soluble in alkaline solutions, water or other common organic solvents. This is because when chitosan reacts with those solvents, it results in the formation of intermolecular hydrogen bonds between its molecules. (El-hefian, Yahaya and Misran, 2009)

1.2 Deacetylation of chitin

Chitosan used for industrial purposes is normally obtained from chitin through enzymatic or chemical processing treatments of shells of crab and prawn. Although limited quantities of chitosan are found in nature, it can be obtained from chitin through the N-deacetylation process.

Chitin is a linear chain polymer that consists of acetylglucosamine groups. During the N-deacetylation process, some of the acetyl (CH_3-CO) side groups on the chitin long chain are converted to NH_2 groups. This process is known as deacetylation. (No and Meyers, 1992) Chitin is referred to as chitosan when it is deacetylated to at least 50%. (Pati and Nayak, 2012)

Properties of chitosan are mainly affected by the degree of deacetylation on its long chain. The amount of free amino acids available on chitosan is controlled by the degree of deacetylation. The degree of deacetylation of chitin is greatly affected by factors such as concentration of alkali used, density of chitin, previous treatment and particle size of chitin. (Aranaz, et al., 2009) Chitosan carries positive charge after the free amino groups have been protonated. This charge allows chitosan to become highly reactive polysaccharide because it can be reacted with negatively charged molecules through electrostatic interactions. (Mohammad and Bashar, 2003)

This process can be carried out by alkaline hydrolysis of chitin with sodium hydroxide at the concentration of 30-50% weight/volume at 120^{o}C for 1-3 hours. 40%-80% of deacetylated chitosan is produced by this alkaline treatment. Therefore, chitosan is a hetero-polymer which consists of (1→4) 2-amino-2-deoxy-ß-D-glucose units (D-glucosamine) together with (1→4) 2-acetamido-2-deoxy-ß-D-glucose (N-acetyl-D-glycosamine) units in the polymeric chain which as shown in Figure 1.1. (Rani, Agarwal and Negi, 2010)

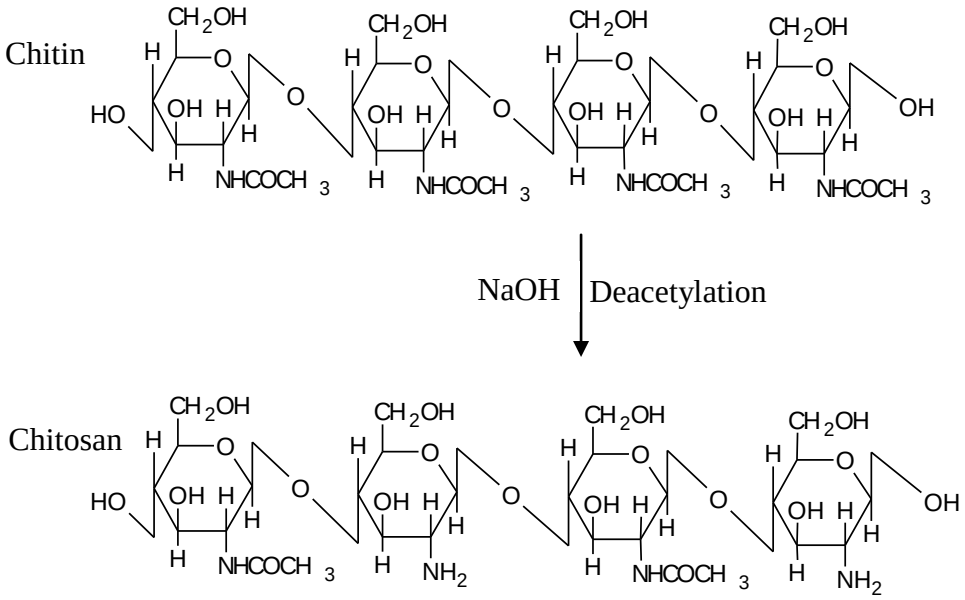
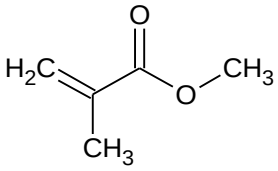
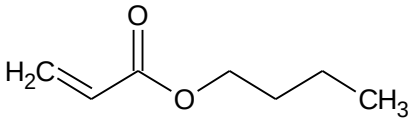
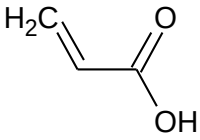


Figure 1.1: Structure of chitin and chitosan (Rani, Agarwal and Negi, 2010)

1.3 Monomers

According to IUPAC definition, molecule which can undergo polymerization process and can contribute the constitutional units to a macromolecule's structure is known as monomer molecule. (Jenkins, et al., 1996) In this study, three types of monomers are used, including methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA). These monomers are colorless liquid which act as building blocks for homo- or copolymer. Methyl methacrylate and butyl acrylate are esters of acrylic acid. The molecular structures of these monomers are shown below:

Table 1.1: Molecular structure and nomenclature of three monomers

Structure	Nomenclature
	Methyl methacrylate
	Butyl acrylate
	Acrylic acid

1.4 Copolymerization

If a polymer consists of at least two different monomers, it is known as copolymer.

Several polymerization methods have been used to produce copolymers, such as step growth, free radical, group transfer, coupling, macro initiators, and metathesis. Polymers formed by the copolymerization process are different from their respective homopolymer, which gives more flexibility for designing new polymers.

There are four different types of copolymer patterns that may be formed during the copolymerization process:

- Regular copolymers: Monomers molecules are arranged in regular sequences in the polymer chain.

  -A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-

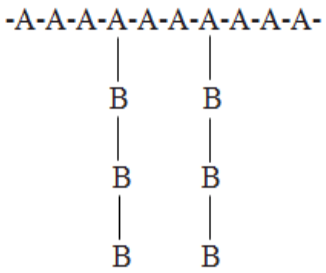
- Random copolymers: Distribution of monomers have no definite sequence, it is in random distribution.

  -A-A-B-A-B-B-B-A-A-B-A-B-B-A-A-

- Block copolymers: Block of one monomer is connecting to a different block linearly.

  -A-A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B-

- Graft copolymers: Unlike block copolymer, graft copolymer consists of one type of polymer linking to another type through a branched structure.



Note: A and B refer to two different types of monomer units

1.5 Objectives

The objectives of this project are:

1. To develop chitosan based polymer via radical polymerization process using methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA) as monomers.

2. To characterize the polymers by doing tensile test, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electronic microscopy (SEM) and flame test.

3. To find the optimum conditions for the production of the best polymer in terms of tensile strength, degradation temperature (T_d), crystalline melting temperature (T_m) and morphology.

4. To investigate the effect of processing temperature and type of initiator system on the properties of polymers.

1.6 Scope/ Limitations

In this study, monomers such as methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA) will be grafted onto chitosan in acidic

condition, with potassium persulfate as thermal initiator, and the combination of potassium persulfate and sodium hydroxymethanesulfinate hydrate as redox initiator. In addition, N,N'-methylenebis(acrylamide) is used as crosslinker. Acetic acid acts as proton donor to protonate chitosan in order to dissolve it in water. Throughout this study, we will find out whether the grafting process could be done successfully under different processing conditions. Besides, the optimum conditions for the grafting of polymers will be determined. At the same time, the effect of processing temperature and initiator systems on the properties of polymer produced will be examined.

Several physical tests will be carried out to characterize the polymers produced, such as tensile test, TGA, DSC, XRD, SEM and flame test. From these tests, the physical properties of the polymers such as tensile strength, melting temperature, degradation temperature and morphology will be determined.

Due to time constraint, only the effects of processing temperature and initiator systems will be the main focus for the polymerization process in this study. Other parameters such as concentration of initiator, ratio of monomers to chitosan, monomer concentration, and pH of the mixture as well as polymerization time will not be looked into in this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Industry applications of chitosan

Chitosan is widely used in areas such as food industry, agriculture, cosmetics products, textile industry, paper industry, photography, and water treatment as well. Besides that, chitosan can also be used in various applications in biomedical field.

2.1.1 Food industry

Chitosan has a wide range of usage in food application. Its principal applications commercially are as food preservatives, clarifying agents, anti-cholesterol additives and food additives.

Chitosan based films are high effective in the prevention of microbial growth in food and delay the spoilage or decay of fruits and vegetables, such as apples, strawberries, tomatoes, etc. at different storage temperature. (El-ghaouth, et al., 1992) Chitosan film can function as a protective barrier when it's coated on vegetables and fruits. Hirano and Nagao (1989) found that chitosan with low molecular weight tend to have greater inhibitory effect toward phyto-pathogens compared with chitosan with high molecular weight. For example, N,O-

carboxymethyl chitosan films are selectively permeable to certain gases such as oxygen and carbon dioxide. As reported by Setha, Kanlayanarat and Gemma (2000), banana that was coated with chitosan can delay its ripening period up to thirty days while apple coated with chitosan can maintain its freshness for six months.

Besides that, chitosan can function as clarifying aid which is able to prevent the browning effect in apple juice and pear juice. This could be due to the ability of chitosan to remove the particulate matter found in these juices, and eventually prohibiting the enzymatic browning process. (Sapers, 1992) As reported by Soto-Peralta, Muller and Knorr (1989), chitosan can be used to replace typical clarifying aids such as gelatin, silica sol, tannins or bentonite in the fruit juice industry.

Chitosan has de-acidifying properties and it is normally used in coffee industry. In beverage industry, it is used to clarify wine, fruit juices and beer. Besides, chitosan can be used to purify drinking water, precipitate out caseins in bovine milk and involved in cheese production. (Gavhane, Gurav and Yadav, 2013)

In addition, there are results that showed that chitosan is able to reduce the total cholesterol level in the body. Chitosan possesses hypocholesterolemic activity which is able to reduce the cholesterol level in human body by

minimizing the absorption of cholesterol into human body while interfere bile acid absorption. (Sugano, et al., 1988) Tsugita (1990) reported that chitosan can be one of the important dietary fiber added in the diet. In Japan, cookies and foods which contain chitosan are available in the market and it is a new type of health food. (Hirano, 1989)

Other than that, chitosan can function as a thickener and stabilizer for food, especially in the production of sauces and other culinary dishes. (Gavhane, Gurav and Yadav, 2013) Researches had shown that chitosan and chitin have the properties of enzymes immobilization, which could be used as emulsifying agent, thickening and stabilizing agent as well as color stabilization agent. For example, microcrystalline chitin can function as emulsifying, superior thickening and gelling agent to stabilize food. (Dutta, Dutta and Tripathi, 2004)

2.1.2 Agriculture

In agriculture, chitosan functions as natural seed treatment medium and is able to enhance the growth of plants. Chitosan has the properties of anti-fungal infections. Therefore, it can be a bio-pesticide which is environmentally friendly. (Naeem, et al., 2010) Chitosan can enhance the plant growth through increasing the photosynthesis rate, nutrient uptake as well as germination process of plants. When chitosan is used in seed treatment, it triggers the defensive mechanism in plants. (Gavhane, Gurav and Yadav, 2013)

In addition, it has the ability to help plants to develop healthy roots by destroying harmful parasites without affecting the beneficial organisms. For example, chitosan is coated onto cotton seeds, potatoes, sugar beets, wheat and tomatoes for the purpose. (Smiley, Cook and Pauliz, 2002)

2.1.3 Cosmetics

As reported by Srisombat, et al. (2005), chitosan and its derivatives are applied in three major areas of cosmetics, which are skin care, oral care and hair care. Chitosan can be used in skin care products such as moisturizer. This is due to its two unique properties:

1. It carries positive charge.
2. It's low molecular weight which enables it to penetrate human skin.

Therefore, chitosan is suitable in the production of cream, lotions, foundations, eye shadows and bath agents. Fine acrylated chitosan particles in organic diacid anhydride are used for skin care. In addition, facial mask prepared by curcuminoids and chitosan can greatly reduce the probability of skin irritation problem. (Dutta, Dutta and Tripathi, 2004)

For the application in oral care, chitosan products are able to freshen breath, to prevent tooth decay and minimize the formation of plaque. Therefore, these products are normally used in toothpaste, mouthwashes as well as chewing

gums. In addition, the unpleasant taste in toothpastes which is caused by silicon dioxide can be covered when salts of chitosan is added. (Dutta, Dutta and Tripathi, 2004)

Chitosan is one of the main ingredients for hair care, especially in commercial shampoos and conditioners. There are several reasons to use chitosan:

1. It is physiologically safe because it does not contain any harmful monomers.
2. It is able to form a clear elastic film on hair due to the difference in charge.

Therefore, shampoos made of chitosan are able to increase the softness and suppleness of hair, which is also less statically charged during combing. It also enhances the mechanical strength of hair as well as its smoothness. (Dutta, Dutta and Tripathi, 2004; Rout, 2001)

2.1.4 Textile industry

Chitin derivatives are normally used in printing and the final stage of preparations for the textile industry. This is because chitin is antistatic with soil repellent properties. When applied on textile, it will ensure the textile products to be always in good condition.

On the other hand, chitosan-based textile products such as threads, sutures and fibers have contributed much to the medical field. (Dutta, et al., 2009) These products are popular in medical field because of their protection against inflections their moisture retention property and their capability in wound healing. (Dutta, Dutta and Tripathi, 2004)

Textile industry tends to release a large amount of toxic textile chemicals to the environment during processing. Hence, chitosan can be used to replace these chemicals as it is an eco-friendly product. Due to this reason, chitosan is normally used in textile dyeing process and finishing. (Lim and Hudson, 2003)

2.1.5 Paper industry

Chitosan has been involved in paper production industry. This is because chitosan molecules have high similarity with cellulose molecules which are the main component of plant walls. There are several advantages of chitosan-based paper over typically cellulose-base paper, which are:

- Able to use less chemical additives
- Increase product output
- Produce paper with smoother surface
- More resistant to moisture

Other than that, chitosan is also used for the production of toilet paper, cardboard and wrapping paper. As reported by Dutta, Dutta and Ravi Kumar (2002), hydroxymethyl chitin and its derivatives are biodegradable which are used in paper and packaging material production for food wrapping purposes. (Dutta, Dutta and Tripathi, 2004)

2.1.6 Photography

Chitosan plays an important role in photography. This is due to its optical characteristics, high abrasion resistance and ability to form film. (Muzzarelli, 1997) In color photography, chitosan can function as fixing agent for acid dyes in gelatin. It also helps to improve the diffusion process during photograph development. (Dutta, Dutta and Tripathi, 2004)

2.1.7 Water treatment

As reported by No and Meyers (1992), chitosan that was produced from crawfish waste had been used as coagulant for the recovery of organic materials in wastewater. The study found that crawfish chitosan has better coagulant properties than chitosan obtained from crab and shrimp shell waste. Chitosan has natural chelating properties and acts as heavy metal trapper due to its polycationic nature. Chitosan is able to bind and remove metal ions that are normally found in wastewater. Example:

- Poly(acrylonitrile) grafted onto chitosan has been modified to become a better absorbent for metal ions such as Cu^{2+}, Pb^{2+} and Mn^{2+}, compared to crosslinked chitosan. (Lee, et al., 2009)

- Chitosan-graft-carboxymethylcellulose can be prepared by thermal initiated graft copolymerization process and it has the ability to remove heavy metal in the wastewater. (Lee, et al., 2009)

- Chitosan N-benzyl sulphonate functions as adsorbent to remove heavy metal ions under acidic condition. (Weltroswki, Martel and Morcellet, 1996)

Bhavani and Dutta (1999) reported that chitosan was used as adsorbent to remove dyes from dye industries. Dyes are toxic to the aquatic organisms and are normally hard to remove due to its resistance toward degradation by light, chemical or microorganisms. Due to the unique molecular structure of chitosan, it has very high affinity toward many classes of dyes such as anionic, sulfur, vat, reactive, direct, naphthol, acid and disperses. For example, chitosan was found to give a maximum adsorption capacity of acid blue 25 of 77.4 mg/g. However, chitosan has low affinity towards the basic dye. (Ravi Kumar, 2000; Rout, 2001)

2.1.8 Biomedical applications of chitosan

2.1.8.1 Burn treatment

Chitosan can produce films which is biocompatible, tough with good water-absorbency. Due to these properties, chitosan is suitable to use for burn treatment. Besides that, chitosan film allows excellent oxygen permeability to prevent oxygen-deprivation of tissues at injured area. (Mi, et al., 2001) In addition, chitosan membrane is highly effective in controlling the evaporative water loss and is able to enhance the fluid drainage ability. (Dutta, Dutta and Tripathi, 2004)

Chitosan naturally has the anti-microbial property and it is able to form a strong protective film. Therefore, chitosan membrane is able to inhibit the attack of microorganisms that come from outside environment. (Mi, et al., 2001) As reported by Yan, Khor and Lim (2000), polymer film which was formed by mixing chitosan-alginate polyelectrolyte has shown good wound dressing capability. Due to this reason, chitosan is used in conjunction with typical bandages to form a chitosan-based bandage. This kind of bandage can provide the protection to wound from bacteria or microorganisms from surrounding environment, at the same time maintaining a moist condition around the wound to accelerate the healing process. (Senel and McClure, 2004; Ueno, Mori and Fujinaga, 2001)

The most important feature of chitosan film is that it is able to absorb water and be degraded by body enzymes safely and naturally. This means that chitosan film needs not be removed after the wound is healed. For most of the time, extra operation to remove wound dressing may cause further harm to the injured area again. (Dutta, Dutta and Tripathi, 2004)

2.1.8.2 Wound healing

Chitosan has exhibited acceleratory effect on wound healing process by accelerating migration of cells to the injured area. (Chen, Chang and Chen, 2008; Ueno, Mori and Fujinaga, 2001) These cells are macrophages which are able to kill microorganisms, remove dead cells at injured area as well as stimulate the immune system in the body. Therefore, this can reduce infection at the injured area. (Lee, et al., 2009) For example, regenerated chitin fibers and films have exhibited an increase in healing of wounds by at least 30%. (Dutta, Dutta and Tripathi, 2004)

Chitosan can react with glycosaminoglycans and this product has the properties of enhancing cell growth. In addition, chitosan is able to connect to cell wall of bacteria. Thus, retards the ability of bacteria synthesis. (Martino, Sittinger and Risbud, 2005) As reported by Wu, et al. (2004), membrane of chitosan-cellulose blend can be used for wound protection to minimize dehydration and inflection at injured area.

2.1.8.3 Opthalmology

Chitosan film is optically clear with sufficient optical correction, partially permeable to oxygen, immunologically compatible, gas permeable, with good gas permeability, mechanical stability as well as wettability. Contact lens that is made of chitosan film is clear, tough, with good tensile/ tear strength and high water content.

All these characteristics fulfill the requirements for an ideal contact lens. Therefore, synthetic polymers have been replaced by chitosan in ophthalmological applications. (Dutta, Dutta and Tripathi, 2004) As reported by Jiang, et al. (1996), chitosan film is suitable for ocular bandage lens production because of its antimicrobial and better wound healing properties.

2.1.8.4 Tissue engineering

Chitosan is polycationic in nature which exists in many forms: filaments, fibers, sponges, films, composite and gels. Chitosan can be easily engineered for a specific application, used at a certain part in the body as well as in conjunction with body tissue. For tissue engineering, chitosan can be used to produce three-dimensional scaffolds which can function as artificial extracellular matrix. This matrix enables new tissue to form in the body while at the same time it can further integrate the new tissue system. (Li, et al., 1992; Senel and McClure, 2004)

The mechanical properties of the matrix are greatly dependent on its application, which will be enhanced or reduced to match the characteristics of the tissue that it is going to repair. Hence, the matrix can be modified to support the hard tissue (bones/ cartilage) as well as the soft tissue (muscles/ blood vessels). Martino, Sittinger and Risbud (2005) reported that chitosan can attach to glycosaminoglycans and this further enhances its ability for cell attachment and proliferation. As reported by Prasitslip, et al. (2000), cells are more likely to attach to a more highly deacetylated chitosan.

2.2 Chitosan/natural polymer beads

Several literatures have reported that different polymer beads had been prepared using chitosan with other natural polymers, such as alginate, gelatin, methyl cellulose, etc. Some of them are described briefly below:

2.2.1 Chitosan-alginate beads

As reported by Hari, Chandy and Sharma (1996), chitosan-calcium alginate beads were prepared for entrapment of albumin and insulin. Besides that, Coppi, et al. (2001) reported that chitosan alginate microparticles were used as a protein carrier in body system. In addition, chitosan-calcium alginate beads used for haemoglobin encapsulation were investigated by Huguet, et al. (1994). The results showed that the loading and release of haemoglobin were affected by the

molecular weight of chitosan and the pH of the releasing medium. (Rani, Agarwal and Negi, 2010)

2.2.2 Chitosan-gelatin beads

Yin, et al. (1996) reported the synthesis of chitosan-gelatin network of polymeric beads for the controlled release of cimetidine (heartburn and ulcers treatment). The results had shown that the release rate was dependent on the pH of the release medium, the degree of deacetylation of chitosan, and the composition of beads. (Rani, Agarwal and Negi, 2010) As reported by Yao, et al. (1995), chitosan-gelatin was also crosslinked with glutaraldehyde to form hydrogel, which was used for drug control release, such as for the release of cimetidine and chloramphenion (an antibiotic).

2.2.3 Chitosan-methyl cellulose beads

Interpenetrating polymer network (IPN) beads of chitosan and methyl cellulose had been prepared by Rokhade, et al. (2006). It was prepared by emulsion crosslinking in the presence of glutaraldehyde as crosslinker. IPN beads had been incorporated with theophyline (anti-asthmatic drug). The rate of drug release is affected by the extent of matrix crosslinking, the methyl cellulose content of matrix, and the amount of drug loading. (Rani, Agarwal and Negi, 2010)

2.3 Chitosan/synthetic polymer systems

2.3.1 Chitosan-polyacrylic acid system

As reported by Peniche et al. (1999) and Borzacchielo et al. (2001), chitosan-polyacrylic acid networks had been prepared through free radical polymerization of acrylic acid in the presence of chitosan. Under mild conditions during the polymerization process, some polyacrylic acid chains were grafted onto chitosan molecules and resulted in the formation of super absorbent hydrogels. According to Borzacchielo et al. (2001), copolymerization of acrylic acid with methyl acrylate can enhanced the mechanical properties of the hydrogels without losing its swelling property.

Peniche et al. (2003) reported that chitosan-polyacrylic acid beads can be prepared using inverse suspension free-radical polymerization. This process involved the polymerization process between acrylic acid and chitosan in the presence of sunflower oil as continuous phase. These beads can be used in drug delivery system for meclofenamic acid (treatment for joint, arthritis and muscular pain) which is soluble in water. (Rani, Agarwal and Negi, 2010)

2.3.2 Chitosan-acrylamide-poly(vinyl alcohol) blends

As reported by Schellekens and Bastiansen (1991), poly (vinyl alcohol) is elastic and highly hydrophilic. Such properties make it possible to be blended with chitosan which is also hydrophilic.

According to Rao, et al. (2006), chitosan blended with acrylamide-grafted poly(vinyl alcohol) can produce a biodegradable blend system. This system is used for the control release of cefadroxil, an antibiotic drug. (Rani, Agarwal and Negi, 2010)

2.3.3 Chitosan-poly(ethylene glycol) beads

Semi-interpenetrating polymer network beads of chitosan and poly(ethylene glycol) crosslinked with glutaraldehyde have been synthesized for oral sustained drug delivery. (Gupta and Ravi Kumar, 2001) The rate of degradation and swelling of the matrix were controlled by crosslinking of biodegradable polymer. It was found that the degree of crosslinking and the pH of the solution affect the release of drug. Besides, crosslinking maximizes the drug entrapping capacity. (Rani, Agarwal and Negi, 2010)

2.3.4 Chitosan-poly(ethylene oxide) beads

As reported by Jagur-Grodzinski (1999) and Kreuter (1998), the beads formed by chitosan and poly (ethylene oxide) are hydrophilic. These spherical micro-beads have been used for administration of drug molecules and drug carriers. In order to increase the protein loading capacity, Calvo et al. (1997) had developed a new method to prepare these beads. Beads were formed by reacting chitosan and ethylene oxide with poly-anion sodium tri-phosphate which gave rise to greater loading capacity and provided a release process of one week. (Rani, Agarwal and Negi, 2010)

2.4 Improvement on the properties of chitosan film

As reported by Chen et al. (2007), properties of the polymer film can be improved by using natural organic acid such as glycolic acid and ascorbic acid. Normally, chitosan is dissolved into acetic acid; however, acetic acid has a strong and unpleasant smell. In this study, glycolic acid and ascorbic acid were used to replace acetic acid. The result proved that glycolic acid and ascorbic acid not only can dissolve chitosan; they can also enhance the properties of the polymer membrane formed.

With glycolic acid, a highly viscose solution was produced and the polymer produced was able to increase its water uptake by almost 100%

compared with that prepared in acetic acid. On the other hand, the polymer film produced using ascorbic acid has double its tensile strength compared with that obtained using acetic acid.

In conclusion, organic acids such as glycolic acid and ascorbic acid are able to improve the mechanical properties as well as the hydrophilicity of the polymer, which had extended its applications in biomedical field. (Chen, et al., 2007)

2.5 Vinyl graft copolymerization

Mino and Kaizerman (1958) were the first researches who reported the approach of generating graft copolymers by using ceric ion redox initiator system. The graft copolymers were prepared by initially generating the free radicals on the biopolymer backbone. These radicals served as macro-initiators for vinyl monomers. The technique of radical graft copolymerization was further developed especially for starch and cellulose. (Berlin and Kislenko, 1992; Jenkins and Hudson, 2001) Generally, medium to high molecular weight branches were observed along the polysaccharide long chains by free radical initiated graft copolymerization method. (Athawale and Rathi, 1999; Hebeish and Guthrie, 1981)

Besides using ceric ion, alkali-metal alkoxide can also be used to initiate the copolymerization process. However, this method is no longer in use due to the

difficulty of the process and that the branches grafted are low in molecular weight. (Fanta and Doane, 1986) As reported by Blair et al. (1987), chitosan was graft copolymerized with vinyl monomers (such as vinyl acetate, methyl methacrylate, acrylonitrile and methyl acrylate) in acetic acid solution using 2,2'-azobisisobutyronitrile as initiator. However, the grafting efficiency obtained was found being too low.

There are various initiator systems employed for the graft copolymerization of vinyl monomers and chitosan. Basically, it can be classified into two main classes: chemical initiation and radiation initiation.

2.5.1 Chemically-initiated vinyl polymerization

In order to initiate a graft copolymerization between the chitosan and the vinyl monomer, the used of a variety of chemical reagents have been reported. The most important chemical systems are ceric ion initiation and Fenton's reagent initiation.

Cerium (IV) ion is an oxidizing agent which is used in a redox initiator system. This system normally involves the graft copolymerization of polyacrylamide, poly(4-vinylpyridine) and poly(acrylic acid) onto chitosan. (Yilmaz, et al., 1998) The reaction is started with Ce^{4+} ion reacting with the primary amine group (at C-2) and the hydroxyl groups (at C-3) position of

chitosan unit to form a complex. When the complex is dissociated, the radicals are formed and these radicals subsequently initiate the polymerization between chitosan and vinyl monomers. (Pourjavadi, et al., 2003)

Fenton's reagent (Fe^{2+} / H_2O_2) is a redox initiator that is mainly used for grafting of methyl methacrylate (MAA) with chitosan. This redox system favors the process of grafting vinyl monomer onto chitosan. The reaction between Fe^{2+} ion and hydrogen peroxide leads to the formation of free hydroxide radicals and creates the macro-radicals on the backbone of polymer chain by hydrogen abstraction. As a result, the grafting process is initiated. (Lagos and Reyes, 1988; Yazdani-Pedram, 1995)

As reported by Prashanth and Tharanathan (2006), the reasons to use a combination of ferrous ion and hydrogen peroxides as redox initiator system are:

- Better yield of radicals formation
- Minimizes the probability of homo-polymerization formation
- Higher yield of grafting percentages
- Copolymerization process can occur at much lower temperature

Potassium persulfate is another type of free radical initiator. At 60^oC, potassium persulfate can undergo thermal degradation to generate free persulfate radicals. When potassium persulfate is combining with ferrous ammonium sulphate, it functions as a redox reaction system. (Hsu, Don and Chiu, 2002)

Hsu, Don and Chiu (2002) reported that, chitosan is degraded in aqueous media with potassium persulfate via radical mechanism. In the system with potassium persulfate and ferrous ammonium sulphate, grafting between methyl methacrylate and chitin can achieve between 300%-500% with the formation of 40%-50% homopolymer (PMMA). However, if potassium persulfate was used alone, only 80%-90% of grafting percentage can be achieved with the 40%-50% homopolymer (PMMA) yield. (Yazdani-Pedram, Lagos and Campos, 1992)

On the other hand, graft copolymerization initiated by potassium persulfate between acrylamide and chitosan can achieved high grafting percentage (~220%) in the presence of N-N'-methylenebisacrylamide, a cross-linker. The optimum conditions: 0.80 g chitosan, 2.40 g acrylamide, 0.002 M potassium persulfate and 50 mL 2% acetic acid under processing temperature of 60^{o}C for 30 minutes. (Yazdani-Pedram, Retuert and Quijada, 2000)

Azobisisobutyronitrile, hydrogen peroxide and ammonium persulfate were also used for initiating the copolymerization process. The polymerization reaction is similar to potassium persulfate initiated reaction where the first radicals produced react with the vinyl monomer and chitosan at the same time to create the macro-radicals. Eventually, a grafted chain consists of the vinyl monomer was produced. (Blair, et al., 1987; Jenkins and Hudson, 2001)

Other than that, tributylborane was used to initiate the grafting process as well. As reported by Kojima, Yoshikuni and Suzuki (1979), alkylborane-initiated polymerization process with chitosan and methyl methacrylate in the presence of oxygen has high homopolymer formation (~50%) and low percentage of graft yield (~40%). This means that this technique resulted in high homo-polymers production.

2.5.2 Radiation-initiated vinyl polymerization

Other than chemical-initiated vinyl polymerization, high-energy and low-energy radiation had been used in graft copolymerization between polysaccharides and vinyl monomers. Polymerization involving high-energy radiation such as beta, gamma and X-ray is highly effective. Radiation-based grafting is normally cleaner and more efficient than chemical initiation methods. However, the main disadvantage of this type of reaction is that it is difficult to control under technical conditions. (Beck, Fitton and Kricheldorf, 1992)

Pengfei, Maolin and Jilan (2001) reported the use of gamma-radiation to initiate the graft copolymerization of styrene onto chitosan. Besides, Singh and Ray (1994) conducted graft copolymerization reaction of 2-hydroxyethylmethacrylate onto chitosan films by cobalt-60 gamma radiation. The product was said being able to improve on its blood compatibility.

Other than using high energy photons, low energy photons such as ultraviolet light had also been used to initiate polymerization which involved vinyl/ acrylic monomers. This type of reaction needs to be carrying out in the presence of a photosentizer which functions as an activator. (Hebeish and Guthrie, 1981) Low energy irradiation involved the use of benzophenone or azo compounds (a photosentizer) had been reported although it is seldom used for this purpose. (Takahashi, Sugahara and Hirano, 1989)

CHAPTER 3

MATERIALS AND METHODS

3.1 Chemicals

Table 3.1: Chemicals used during polymerization

Chemical	Function	Producer
Chitosan	Organic modifiers	Nacalai tesque
Acetic acid	Acid	Systerm®
Methyl methacrylate	Monomer	Daejung
Butyl acrylate	Monomer	Daejung
Acrylic acid	Monomer	Merck Schuchardt
Potassium persulfate	Thermal initiator	Systerm®
Sodium hydroxymethanesulfinate hydrate	Redox initiator	Aldrich
N,N'-methylenebis(acrylamide)	Crosslinker	Sigma-Aldrich

3.2 Procedures

3.2.1 Removal of inhibitor in monomers

55 g of MMA and 40 g of BA were added into a 250 mL of separating funnel. The mixture was then washed with 50 g of 10% NaOH solution twice for 15 minutes each time. Two layers were formed. The aqueous layer, which was the

denser layer, was discharged while the monomers mixture was transferred into a plastic bottle. After that, 5 g AA was added into the methyl methacrylate and butyl acrylate monomer mixture with sufficient mixing.

3.2.2 Recipe and grafting process

Table 3.2: Recipe for polymer synthesis

Material	Quantity (g)
Distilled water	300.00
Chitosan	6.00
Monomers mixture	
Methyl methacrylate	23.10
Butyl acrylate	16.80
Acrylic acid	2.10
Catalyst used	
Potassium persulfate	0.42
Distilled water	12.00

Firstly, 6 g of chitosan was dissolved in 90 mL of 5 M acetic acid solution with 210 mL of distilled water in a beaker. The mixture was heated in a water bath at 80^{o}C with constant stirring for 30 minutes. When chitosan had fully dissolved, the mixture was cooled down to 60^{o}C. Then, 42 g of monomer mixture, with 5% of AA, 40% of BA and 55% of MMA, was added into the chitosan solution while the temperature of the mixture was maintained at 60^{o}C. After that,

0.42g potassium persulfate which was earlier dissolved in 14 mL of distilled water was added into the mixture. The mixture was stirred constantly for 90 minutes. To crosslink the polymer, 0.58 g of N,N'-methylenebis(acrylamide) was dissolved in 10 mL of distilled water and added into the mixture solution before the polymerization reaction was started.

For the redox initiator system, 0.20 g of sodium hydroxymethanesulfinate hydrate, which had been dissolved in 10 mL of distilled water beforehand, was added following with 0.42 g of potassium persulfate solution.

When the polymerization was done, the polymer mixture was cooled down to room temperature and transferred to a container for later use. The processes were repeated at different processing temperature (40^{o}C, $50\ ^{o}$C, 60^{o}C, 70^{o}C and 80^{o}C) for different initiator systems (thermal and redox).

3.2.3 Preparation of polymer films

About 15 g of polymer mixture was poured onto a plastic tray with the dimension of 7 cm × 15 cm. After that, the tray was dried in an oven at 50^{o}C for at least six hours. When the solvent in the mixture were completely evaporated, the polymer film was removed from the tray and kept in a dessicator for later use.

Before the film was characterized, it was conditioned in a dessicator with 50% relative humidity at 25^{o}C for at least two days before testing.

3.3 Characterization of the hybrid polymer

3.3.1 Total solids content (TSC) test

Total solids content test was one of the methods used to determine the percentage of polymer in the solution. Theoretically, when the monomers were grafted onto chitosan, polymer was formed which is in the solid state. Therefore, to determine the percentage of conversion of polymer, around 1 g of polymer solution was dried in an oven. This heating process was used to remove un-reacted monomers and excess amount of water present in the polymer solution. Once the polymer solution was dried completely, the residue left was the polymer solid. The experiment was repeated twice to obtain an average reading.

$$\text{Percentage of solid} = \frac{\text{Weight of residue left}}{\text{Total weight of solution}} \times 100\%$$

3.3.2 Tensile test

Five polymer strips with the dimension of 1.50 cm × 15.00 cm were prepared and conditioned with a relative humidity of 50% for at least two days at 25^{o}C. ASTM standard D638, which was a test method for determining the tensile

properties of polymer, was referred to. The brand of the tensile machine used was Tinius Olsen.

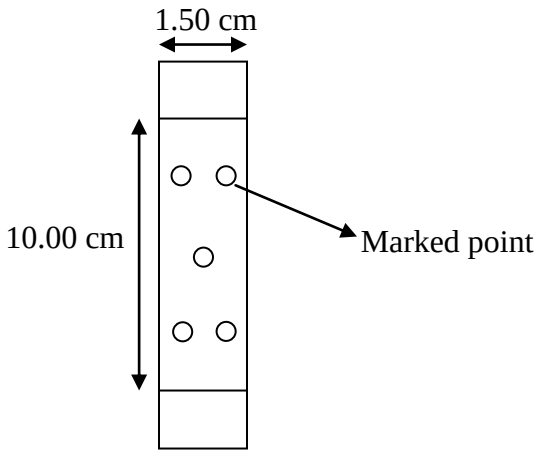


Figure 3.1: Dimensions of strip for tensile test

Thickness of each strip was measured at five points of the strip as shown in Figure 3.1 using an electronic digital thickness gauge. The average thickness was recorded for each strip before the tensile test was carried out.

The specimen was placed between the grips of tensile machine at 10 cm apart. The specimen was pulled until it broke. The stress versus strain was recorded in the system. At the end, the average tensile strength and elongation for five specimens were determined.

3.3.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is an analytical technique to determine the thermal properties of a polymer. In this study, the polymer sample was heated or cooled at 25^{o}C to 250^{o}C intervals of temperature. (Acharyulu, Gomathi and Sudha, 2013)

The crystalline melting point (T_m) of the polymer was determined using Mettler Toledo model DSC823^{e}. It was used under nitrogen gas atmosphere at a flow rate of 10 mL/min in order to minimize thermo-oxidative degradation. In all cases, aluminium pans were used to hold samples with weight ranging from 6 to 7 mg.

Table 3.3: Parameters for DSC

Temperature programmed	Dynamic (non-isothermal)
Initial temperature, ^{o}C	25
Final temperature, ^{o}C	250
Rate of heating, ^{o}C/min	10
Purge gas	Nitrogen
Flow rate of gas, mL/min	10
Sample size, mg	± 5.0
Sample holder, µL	Standard alumina 40

3.3.4 Thermogravimetric analysis (TGA)

TGA is commonly used to determine the thermal characteristics of polymers. TGA technique is helpful to determine the moisture content, degradation temperatures, and percentage of inorganic and organic components of the polymer samples. (Acharyulu, Gomathi and Sudha, 2013)

In this study, thermal degradation patterns of polymers were determined using TGA model SDTA851^{e}. About 5-6 mg of the sample was weighted into a 150 µL alumina crucible. Nitrogen purge was performed throughout the scan to minimize thermo-oxidative degradation with the flow rate of 20 mL/min.

3.3.5 Fourier transform infrared spectroscopy (FTIR)

Neat chitosan film and the grafted chitosan hybrid polymer thin films were analyzed by FTIR spectrometer, Perkin Elmer RX1, in the range between 4000 cm^{-1} and 400 cm^{-1}.

In order to obtain a more accurate result, the samples must be dried completely before running the test in order to prevent the OH peak found in the spectrum being due to excess water content in the samples. Besides, the films prepared had to be transparent and should be as thin as possible for better light transmission.

3.3.6 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a technique used to study the skeleton structures in semi crystalline polymers such as elastomers, thermoplastics and liquid crystalline polymers. (Acharyulu, Gomathi and Sudha, 2013) In this study, the crystallinity of the polymers was determined by XRD method. The samples were scanned between the range of 20^{o} to 90^{o} at a scan rate of 1.50^{o}/ min with the time constant of 0.80 second.

3.3.7 Scanning electron microscopy (SEM)

Surface morphology and features of the hybrid polymers were recorded using a SEM for samples with and without a crosslinker. The polymer samples were sputter coated with platinum for 30 s with the current of 45 mA in argon under the pressure of 200 mTorr to yield a coating thickness of ca. 50 Å.

3.3.8 Flame test

Five polymer strips of 1.50 cm by 15.00 cm were conditioned in a relative humidity of 50% at 25^{o}C for at least 24 hours. Before the flame test was conducted, average thickness of the strip was measured and recorded. Two reference lines were drawn 2.5 cm from the top end and the lower end of the strip as shown in Figure 3.2. The strip was clamped vertically from a retort stand.

A blue flame Bunsen burner was placed 20±5^{o} from vertical at the lower end of the polymer strip for 5±0.5 seconds and removed quickly. The stopwatch was started to record the time once the fire reached the first reference line. The time taken for the polymer to burn until the second reference line was recorded. The ASTM standard referred to is D 5048-03.

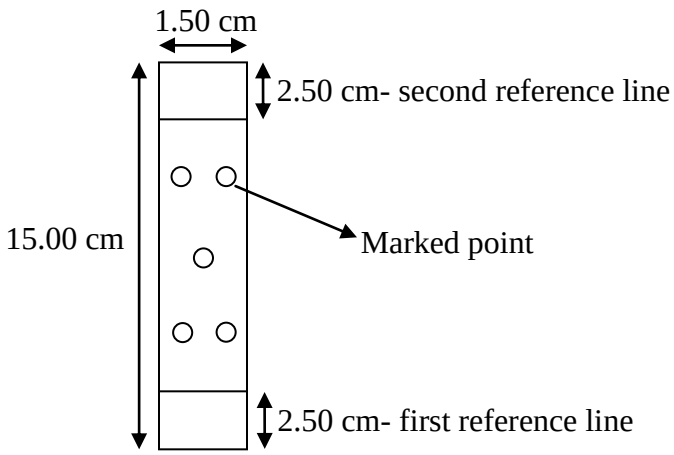


Figure 3.2: Dimensions of strip for flame test

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Dissolution of chitosan

Chitosan can only be dissolved under acidic condition (pH< 7). Organic acid such as acetic acid is able to donate its proton in water. When chitosan is reacted in acetic acid solution, its amino groups are protonated by the protons and eventually form a cationic polymer which is able to dissolve in the reaction mixture. In this study, the final pH of the polymer solutions produced was around pH 3-4 after the polymerization process was completed. (El-hefian, Yahaya and Misran, 2009)

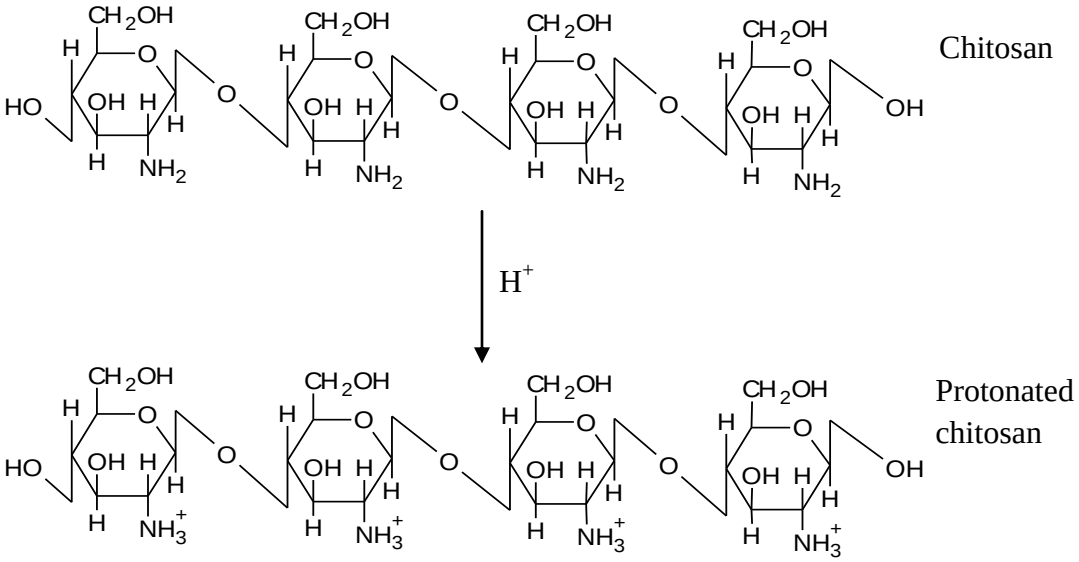


Figure 4.1: Protonation of chitosan by using acetic acid solution

4.2 Thermal and redox initiator system

In order to initiate a polymerization reaction between chitosan and monomers, a radical initiator must be used. Radical initiator functions as the substance that can produce radical species under mild condition and promote radical reactions.

Throughout this study, two different initiator systems, namely thermal and redox initiator systems were used. However, each initiator system had its own advantages and disadvantages. Pros and cons of each initiator systems are listed below:

Table 4.1: Pros and cons of thermal and redox initiator system

	Advantages	Disadvantages
Thermal initiator system	Polymer solution able to stir easily during polymerization	Polymerization process cannot occur at low temperature (below 60^{o}C)
	Dilute polymer solution formed which has higher processability	The polymer solution will precipitate out after some time
Redox initiator system	Polymerization process can proceed at wide temperature range (40^{o}C-80^{o}C)	A lots of bits formation during polymerization process
	Save energy and cost due to polymerization process can occur at lower temperature	Viscous solution formed which hard to cast films and difficult to produce smooth surface film

4.3 Total solids content (TSC) test

Table 4.2: Total solids content of polymers and percentage of conversion

	Types of initiator	Processing temperature (°C)	Percentage of total solids content (%)	Theoretical percentage of total solids content (%)	Percentage of conversion (%)
Without crosslinking	Thermal	80	13.40	13.43	99.78
		70	13.38		99.63
		60	11.05		82.28
		50	*	*	*
		40	*	*	*
	Redox	80	12.17	13.14	92.62
		70	10.42		79.30
		60	11.37		86.53
		50	10.92		83.11
		40	10.72		81.58
With crosslinking	Thermal	70	12.05	12.26	98.29
	Redox	50	9.77	10.94	89.31

*No polymerization reaction

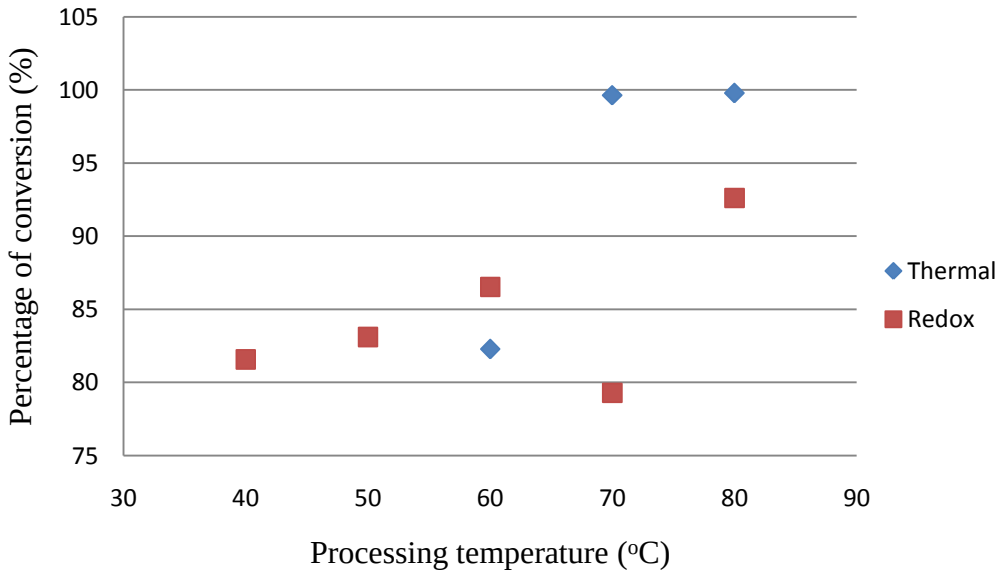


Figure 4.2: Total solids content of polymer solutions (without crosslinking)

Figure 4.2 shows that, most of the polymer solutions produced by thermal initiator system had shown higher percentage of total solids content. This may be due to more monomers were grafted onto chitosan to form polymer. Theoretically, the polymer formed was in solid form. Therefore, after the solution had dried, the solid left should be mainly the polymer.

On the other hand, redox initiator system showed lower percentage of conversion of polymer. This may be due to two reasons:

1. The amount of monomers grafted onto chitosan was reduced.
2. The grafted polymer produced was in short chain form rather than in long chain form polymer and eventually precipitated out as small bits.

This indicated that redox initiating system was less effective in this polymerization process compared with thermal initiator system. Therefore, percentage of polymers found in the former was lower.

However, this test cannot determine exactly which sort of initiator system can provide a better grafting process during polymerization. This is because the solids content in the polymer solutions may consist of un-reacted chitosan or synthetic copolymer as well as homopolymer which also exist in solid form. Therefore, in order to obtain a more accurate result, more physical tests, such as grafting efficiency test, should be done to confirm the results.

4.4 Tensile test

Table 4.3: Tensile strength of polymers

	Types of initiator	Processing temperature (°C)	Tensile Strength (MPa)
Without crosslinking	Thermal	80	9.220
		70	13.404
		60	12.302
		50	*
		40	*
	Redox	80	11.772
		70	10.281
		60	14.256
		50	14.670
		40	12.732
With crosslinking	Thermal	70	10.814
	Redox	50	12.351
Pure Chitosan			39.590

*No polymerization reaction

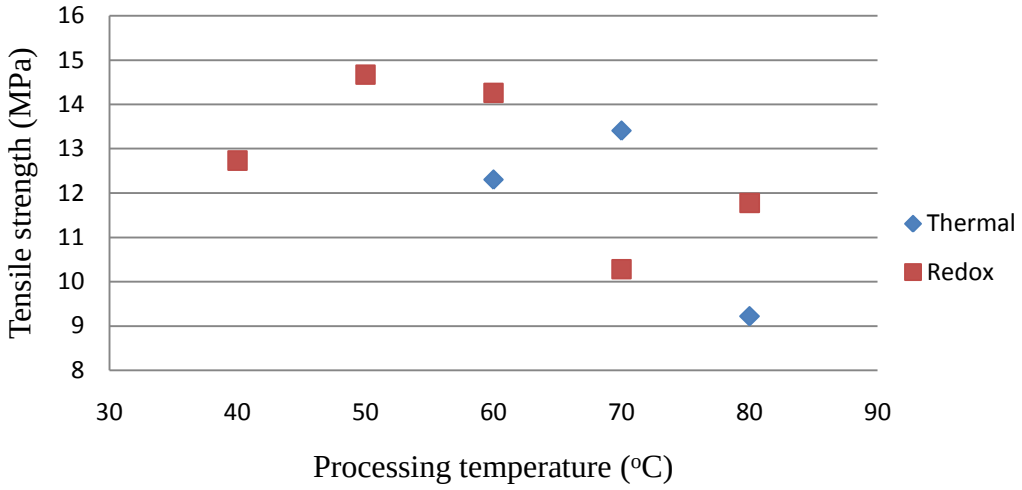


Figure 4.3: Tensile strength of polymers (without crosslinking)

Tensile test was carried out to study the mechanical strength of the polymers prepared at different processing temperature with different initiator system.

In the polymerization process, formation of low molecular weight polymer was favorable if the polymerization reaction is processing under high temperature especially when thermal initiator such as potassium persulfate was used to initiate the reaction. This is because at higher processing temperature, more kinetic energy was available for potassium persulfate to break its peroxide bond and formed persulfate radicals. Therefore, more persulfate radicals were produced under higher processing temperature.

When the amount of free persulfate radicals was increased, more radical sites were formed on the chitosan chain and the vinyl monomers. This had increased the probability of termination reaction between the radical sites and eventually terminated the polymerization process. Therefore, it reduces the possibility for polymer chains to grow longer and the increases probability of formation shorter polymer chains. As a result, the polymer produced had a lower molecular weight.

Figure 4.3 shows that thermal initiator polymers produced at lower processing temperature such as 60^{o}C and 70^{o}C had higher tensile strength compared with polymers produced at higher temperature (80^{o}C). This indicated

that polymer produced at 80^{o}C had lower molecular weight and eventually its tensile strength had decreased because lesser long polymer chains were formed to strengthen the polymer structure.

On the other hand, redox initiator normally has higher efficiency for polymerization reaction at lower temperature. Therefore, redox initiated polymerization reaction is favorable at lower temperature. At processing temperature above 60^{o}C, a sharp decrease of tensile strength for the polymers was observed. This may be again due to the formation of polymer with lower molecular weight.

Figure 4.3 shows that the polymer produced by redox initiator system at 50^{o}C had the highest tensile strength among all the grafted polymers produced in both the initiation systems. It suggested that polymer with higher molecular weight was obtained by redox initiation, which was carried out at lower temperature. Besides being higher in molecular weight, polymer that possessed higher tensile strength may indicate that there is more entanglement of the longer polymer chains and make it stronger to withstand the force applied on it.

Therefore, it can be concluded that redox initiator system had provided a better grafting condition to the polymerization process at lower temperature. The advantage for redox initiator system is that less energy is required for polymerization to occur.

In brief, it was found that redox initiator system was able to produce polymers with maximum tensile strength at 50^{o}C among the same initiator system as well as compared with thermal initiator system. On the other hand, the optimum temperature for thermal initiator system to produce the polymer with the best tensile strength was at 70^{o}C. These two polymerization conditions had been further studied by adding a crosslinker into the polymer system.

Theoretically, crosslinking reaction will further increase the tensile strength of polymers. This is because crosslinking process links one polymer chain to another in the system by either covalent bonds or ionic bonds. This will result in the formation of network structure in the polymer. Therefore, it further enhances the physical properties of the polymers such as tensile strength.

However, in this study, the tensile strength of the polymers did not increase as expected with the addition of N,N'-methylenebis(acrylamide) as a crosslinker. This indicated that the crosslinker did not function effectively in the polymer system. This could be that the crosslinking process has not been done successfully due to certain unknown reason.

Table 4.4: Percentage of elongation of polymers

	Types of initiator	Processing temperature (°C)	Elongation (%)
Without crosslinking	Thermal	80	116.46
		70	85.52
		60	53.90
		50	*
		40	*
	Redox	80	133.35
		70	39.16
		60	61.60
		50	68.50
		40	57.15
With crosslinking	Thermal	70	99.26
	Redox	50	91.70
Pure Chitosan			28.80

*No polymerization reaction

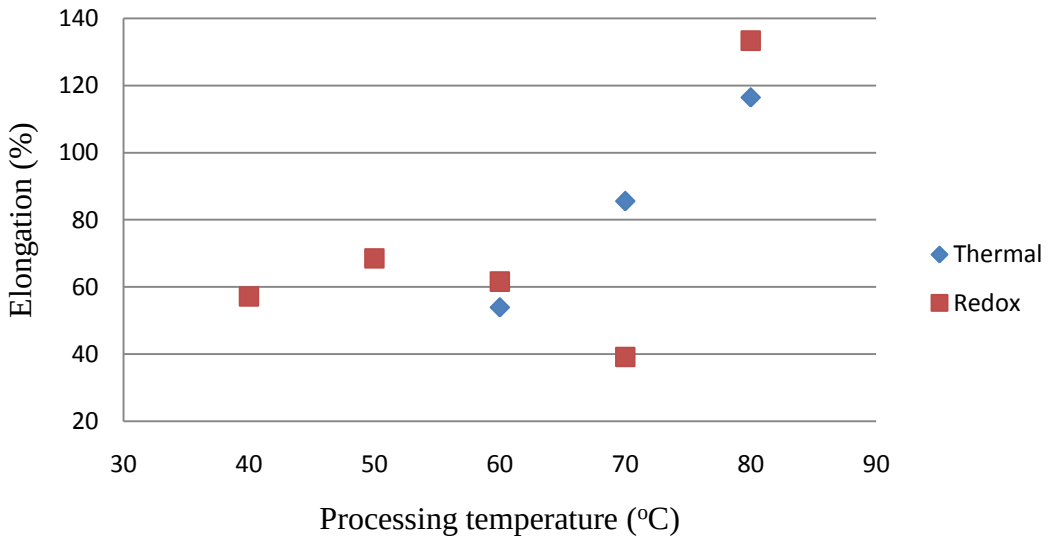


Figure 4.4: Percentage of elongation of polymers (without crosslinking)

Elongation of the polymer was affected by the flexibility of the polymer. If the polymer was flexible, this means that the bonding of polymer was not rigid. When the polymer was pulled, there was space available for the bonds to move or

extent to prevent it from breaking immediately. However, for a polymer that was less flexible, the bonding of polymer was rigid and hard. As a result, the polymer can break easily when force was applied on it and thus, it had lower percentage of elongation.

Table 4.4 shows that pure chitosan has the lowest percentage of elongation (28.8%). This is because pure chitosan is a semi-crystalline polymer with high crystallinity, and its chains are rigid and packed. However, when copolymer branches were grafted onto chitosan, the crystallinity of chitosan was altered and it became less crystalline. Consequently, the polymer chains became less rigid and less packed compared with just chitosan alone. Therefore, the grafted polymers gave higher percentage of elongation.

Figure 4.4 shows that most of the polymers produced by thermal initiator system were higher in the percentage of elongation compared with redox initiator polymer. Polymer films that were formed this way were softer and more flexible. This indicated that thermal initiator system produced polymer with less rigid chain packing which is more tolerance to the pulling force applied to it. On the other hand, the polymers produced by redox initiator system were mostly lower in the percentage of elongation while they had higher tensile strength (Figure 4.3). This can be concluded that the polymer films produced this way were less flexible but tougher due to more compact chain packing in the polymer system.

4.5 Differential Scanning Calorimetry (DSC)

Table 4.5: Melting temperature and enthalpy of polymers

	Types of initiator	Processing temperature (^oC)	T_m (^oC)	Enthalpy (J g^{-1})
Without crosslinking	Thermal	80	167.93	49.58
		70	161.92	47.55
		60	155.63	81.76
		50	*	*
		40	*	*
	Redox	80	165.64	56.85
		70	162.42	59.84
		60	161.97	44.32
		50	165.17	55.50
		40	164.75	52.68
With crosslinking	Thermal	70	167.11	58.44
	Redox	50	167.76	52.67
Pure Chitosan			151.32	261.31
Pure Copolymer			179.04	20.54

*No polymerization reaction

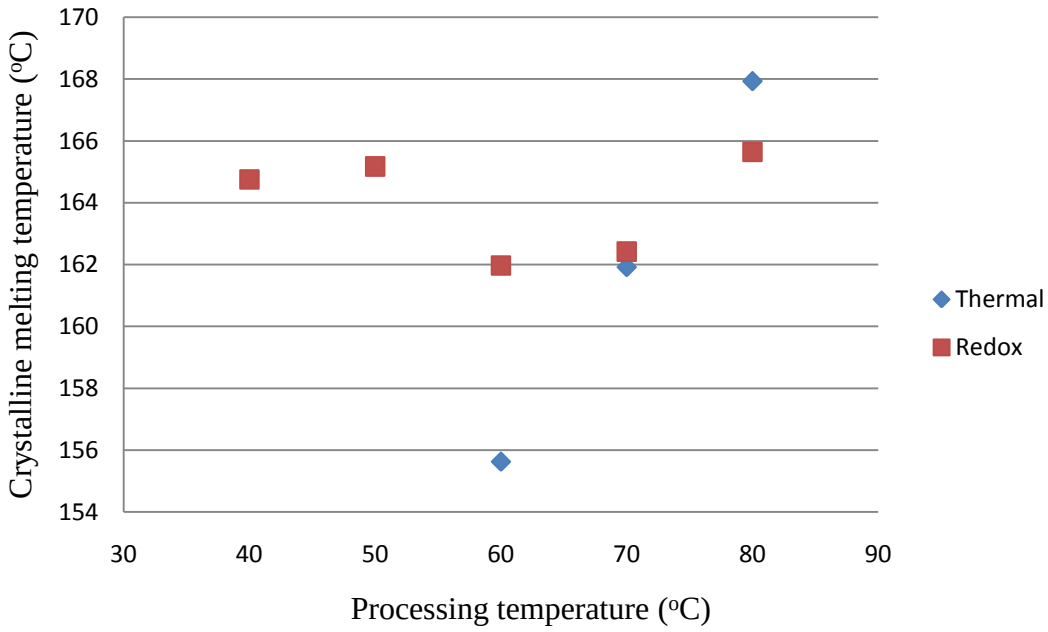


Figure 4.5: Crystalline melting temperature of polymers (without crosslinking)

Crystalline melting temperature, T_m is the melting temperature of the crystalline domains of a polymer sample. Table 4.5 shows that pure chitosan has the lowest T_m value (151.32^{o}C). However, when monomers were grafted onto chitosan, the melting temperature of the grafted polymer had increased. This means that the thermal stability of the grafted polymer had been enhanced when monomers were grafted onto chitosan. Higher temperature was needed in order to melt the grafted polymers. The crystalline melting point of the polymers was between the pure chitosan (151.32^{o}C) and the pure copolymer (179.04^{o}C). This suggests that the grafting process had been done successfully.

On the other hand, the pure copolymer had the lowest enthalpy (20.54 Jg^{-1}) while pure chitosan had the highest (261.31 Jg^{-1}). However, the grafted polymers had the enthalpy value between 20.54 and 261.31 Jg^{-1}. This indicates that when the monomers were grafted onto chitosan, the enthalpy value of the chitosan was decreased due to its crystalline structure was disrupted.

Figure 4.5 shows that most of the polymers produced by redox initiator system had similar melting point and higher melting temperature compared to the polymer produced by thermal initiator system except that at 80^{o}C. Similarly, due to ineffective crosslinking, the T_m values of the polymers incorporated with some crosslinker in both the initiator systems had shown little difference from polymers that was without crosslinker in both of the systems.

Redox initiator polymers had higher T_m value due to its more rigid chain. Polymers with rigid chains would be expected to have higher T_m value than polymers with less rigid chains. This was because if the chain was rigid, it was lower in entropy (S_m) and this will eventually increase the melting temperature of the polymer. The results in Figure 4.4 indeed show that redox initiator polymers have lower percentage of elongation due to its higher chain rigidity. For the thermal initiator system, the polymers chain was less rigid, thus higher in entropy.

$$T_m = H_m / S_m \text{ (if } S_m \text{ is smaller, then } T_m \text{ is larger)}$$

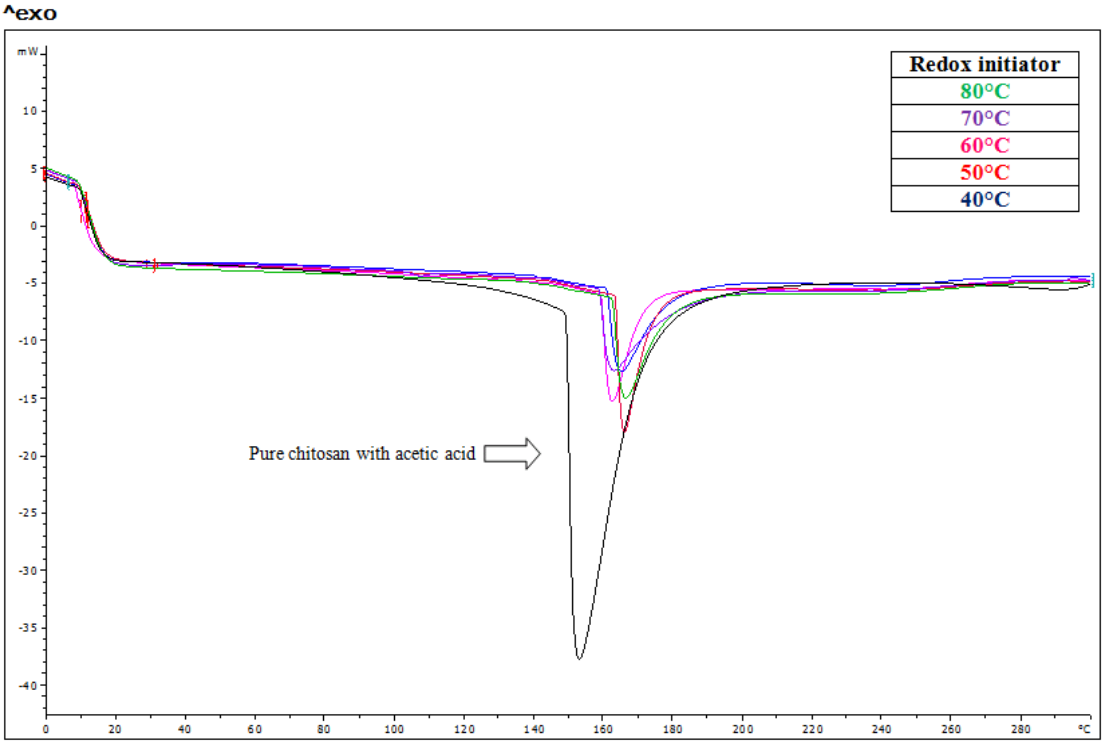


Figure 4.6: DSC curves of pure chitosan and redox initiator polymers (without crosslinking)

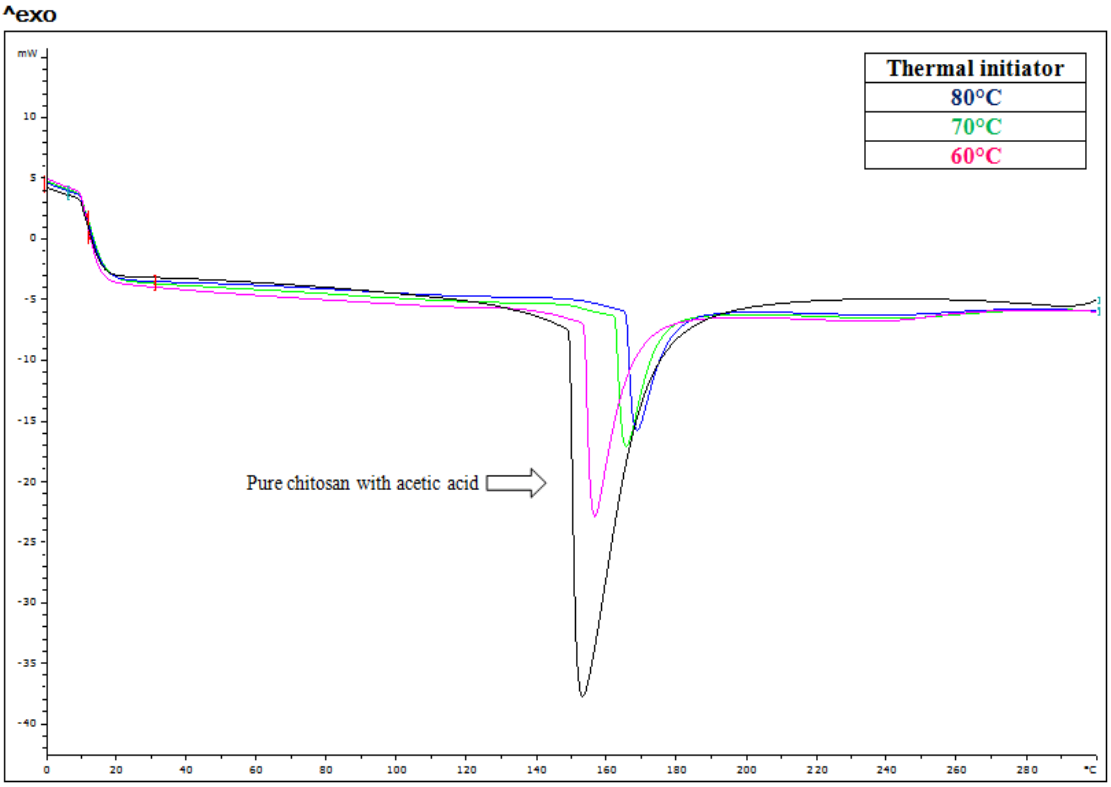


Figure 4.7: DSC curves of pure chitosan and thermal initiator polymers (without crosslinking)

4.6 Thermal gravimetric analysis (TGA)

During an overheating process, polymers undergo molecular deterioration which results in thermal degradation. At high temperature, components of polymer start to break down and react among each other. Consequently, it changes the properties of polymer. Thermal degradation can cause the polymer to loss its mechanical property. For this reason, TGA is used to determine the degradation temperature (T_d) of polymer and the percentage of residue left at a certain temperature. Degradation of polymer has very complex mechanism which

involves the processes such as dehydration, chain scission and deacetylation. (Don, Chuang and Chiu, 2002)

Table 4.6: Degradation temperature and percentage of residue of polymers

	Types of initiator	Processing temperature (^oC)	Degradation temperature (^oC)	Percentage of residue at 550 ^oC (%)
Without cross-linking	Thermal	80	378.13	8.11
		70	382.21	9.03
		60	382.26	8.17
		50	*	*
		40	*	*
	Redox	80	372.19	9.01
		70	372.83	8.55
		60	374.30	7.86
		50	376.00	9.87
		40	370.19	8.54
With cross-linking	Thermal	70	357.34	8.81
	Redox	50	356.77	8.84
Pure chitosan			299.61	28.9
Pure copolymer			378.47	8.34

*No polymerization reaction

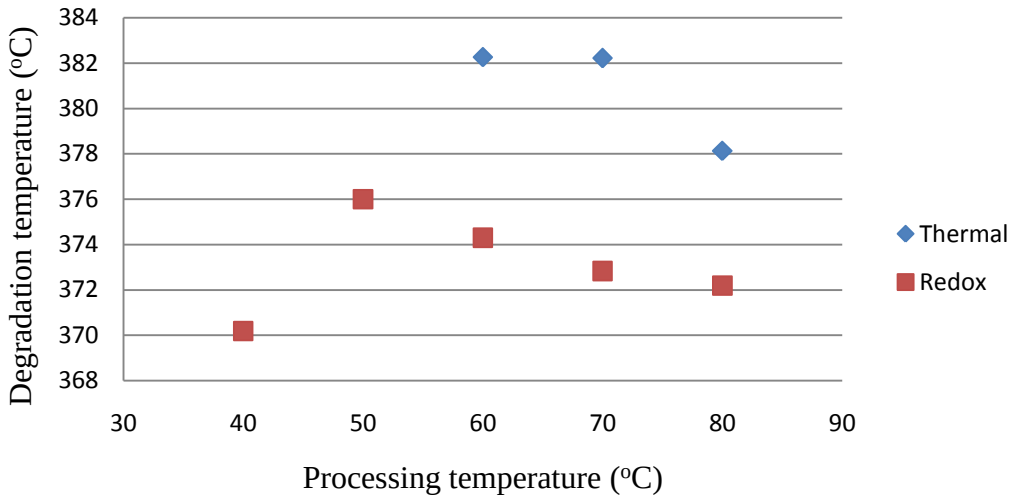


Figure 4.8: Degradation temperature of polymers (without crosslinking)

Pure chitosan was found to give the lowest thermal degradation temperature in this study (Table 4.6). In other words, chitosan was the easiest to undergo thermal degradation when heated. After the monomers were grafted onto chitosan, the thermal degradation temperature of the hybrid polymer was increased. This indicated that the grafted polymers became stronger and more resistant to thermal degradation.

It was found that the thermal initiated polymer produced at 70^{o}C had the highest thermal degradation temperature among all the grafted polymers produced whereas with the redox initiator system, the polymer produced at processing temperature of 50^{o}C had the highest thermal degradation temperature (Figure 4.8). Hybrid polymers produced via thermal initiator, generally have higher thermal degradation temperature.

In Figure 4.9, the thermogram of chitosan shows that degradation of the polymer started at 250°C with the inflection temperature at 280^{o}C. Before the temperature reached 280^{o}C, the residue left was about 88.0%. The mass loss may be due to the water content in the polymer. The thermogram shows a more gradual degradation after 300^{o}C which maybe contributed by the degradation of the chitosan main chain which gave a high char yield of 28.9% at 550^{o}C.

On the other hand, the thermogram of the copolymer shows that it had higher thermal degradation temperature where its main chain started to degrade at

350^{o}C and it ended at 400^{o}C. The thermogram shows a slight decrease in sample mass between 110^{o}C-350^{o}C and the residue left after this temperature range was 97.14%. This indicated that some side chains of the copolymer started to degrade. After 350^{o}C, the thermogram showed a more drastic drop in mass and the residue left after 400^{o}C was 8.34%. This indicates that the copolymer had almost been degraded completely at 400^{o}C.

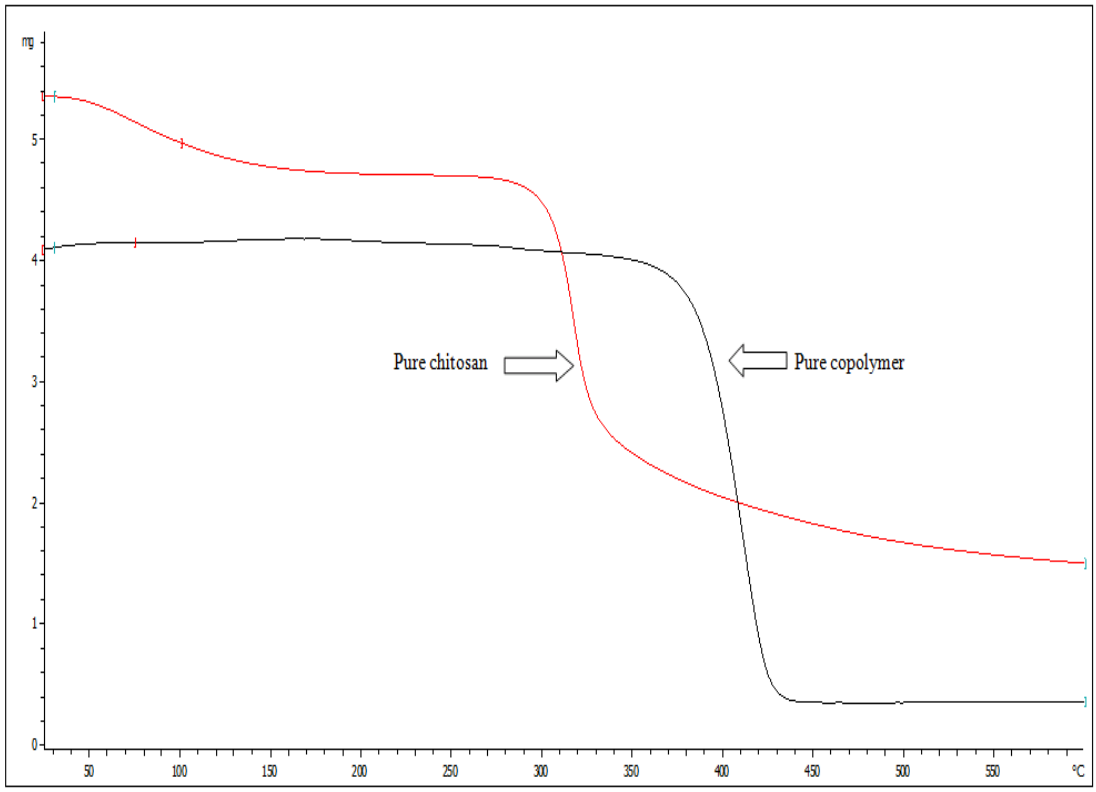


Figure 4.9: TGA curves of pure chitosan and pure copolymer

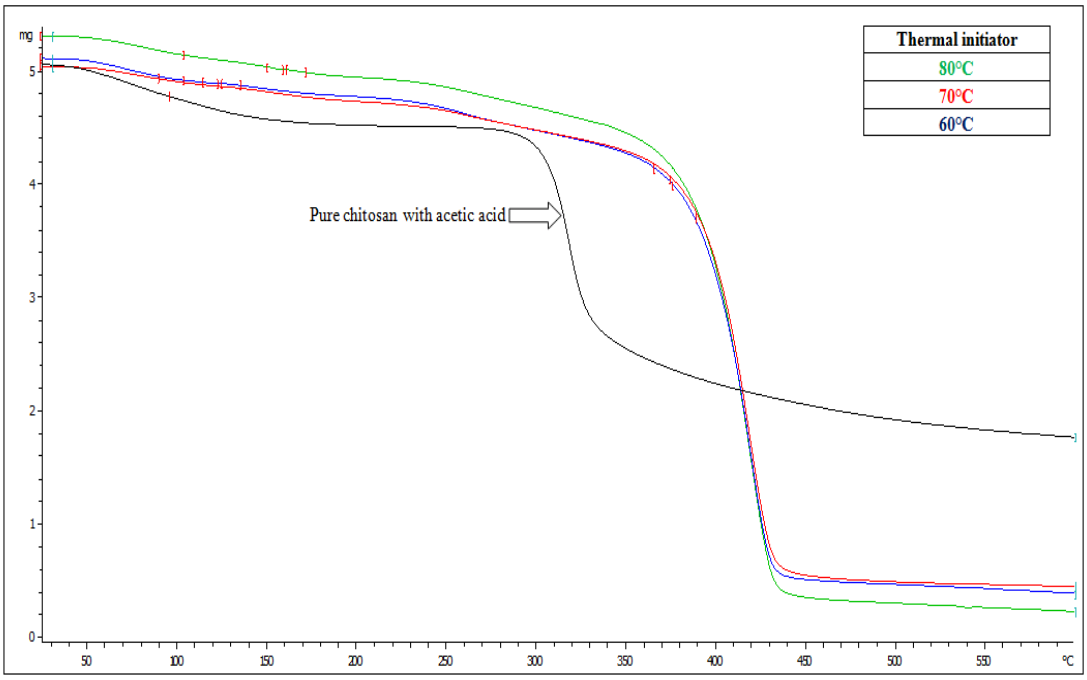


Figure 4.10: TGA curves of pure chitosan and thermal initiator polymers (without crosslinking)

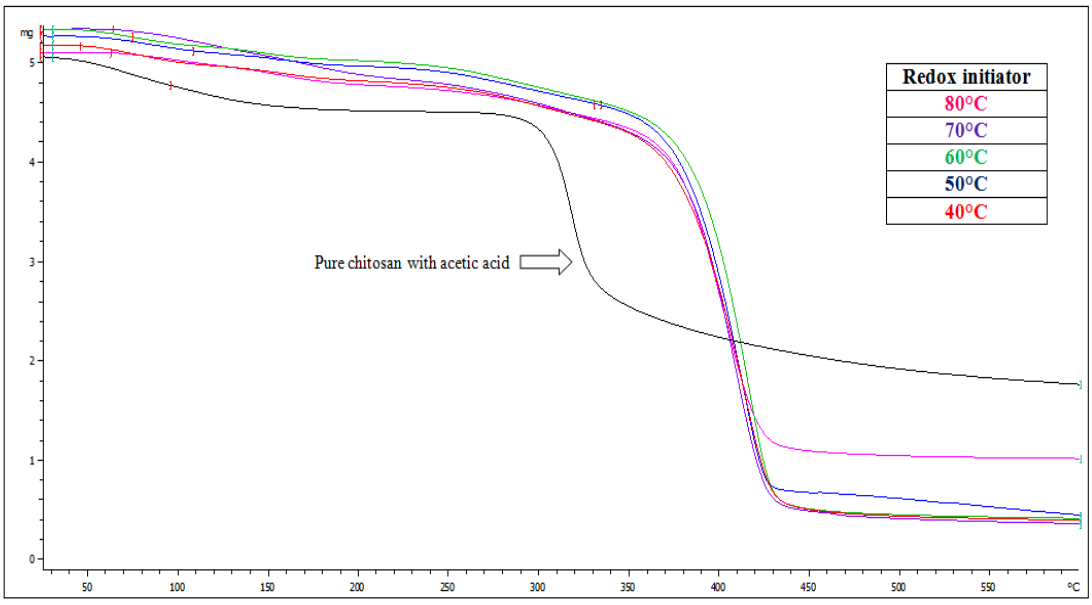


Figure 4.11: TGA curves of pure chitosan and redox initiator polymers (without crosslinking)

Table 4.7: Thermal event of grafted polymers at different temperature ranges

Type of initiator	Processing temperature (^{o}C)	Residue left (%)		
		25-110^{o}C	110-350^{o}C	550^{o}C
Thermal	80	97.08	83.06	8.11
	70	96.60	83.15	9.03
	60	95.58	83.06	8.17
	50	*	*	*
	40	*	*	*
Redox	80	97.48	83.87	9.01
	70	97.04	80.06	8.55
	60	96.57	83.56	7.86
	50	96.80	84.78	9.87
	40	96.55	81.69	8.54

*No polymerization reaction

According to the thermograms of grafted polymers (Figures 4.10-4.11), the thermal event of the grafted polymers can be divided into three parts. Table 4.7 shows that the first thermal event occurred at temperature between 25-110°C and it was accompanied by the weight loss of between 2.5% to 4.5%. This stage could be due to the loss of the excess water present in the samples. (Pieróg, Ostrowska-Czubenko and Gierszewska-Drużyńska, 2012)

The weight loss between 110^{o}C and 350^{o}C may be due to the degradation of some side chains or un-reacted chitosan. Besides that, the weight loss may be also contributed by the degradation of some homo-polymers or copolymers exist in the polymers film. When the temperature was further increased to above 350^{o}C, the main chain of the grafted polymer started to degrade and eventually the bonding was broken completely.

From the thermogram, it can be observed that chitosan started to undergo thermal degradation process at lower temperature (300^{o}C) compared with the grafted polymers. The main chain of chitosan polymer was degraded at 280^{o}C while that of the grafted polymers started to degrade at 350^{o}C. Table 4.6 shows that the pure copolymer had the highest thermal degradation temperature of 378.47^{o}C.

In this study, the ratio of chitosan and copolymer used was 1:7. Theoretically, almost 87.5% of the grafted polymers were made up by the synthetic part, if the polymerization process was done completely. Therefore, when large amount of copolymer (synthetic part of the grafted polymers) was grafted onto chitosan, it greatly increased the thermal degradation temperature of the latter. The residue left above 550°C was the polymer component that was more resistant to thermal degradation.

The grafted polymers (Figures 4.10-4.11) had showed a lower char yield at 550°C compared with chitosan alone. This indicated that the presence of copolymer enhances the thermal resistance of the grafted polymers. But once the temperature exceeds its degradation temperature, the synthetic part could serve as fuel and causes the hybrid polymer to degrade more completely.

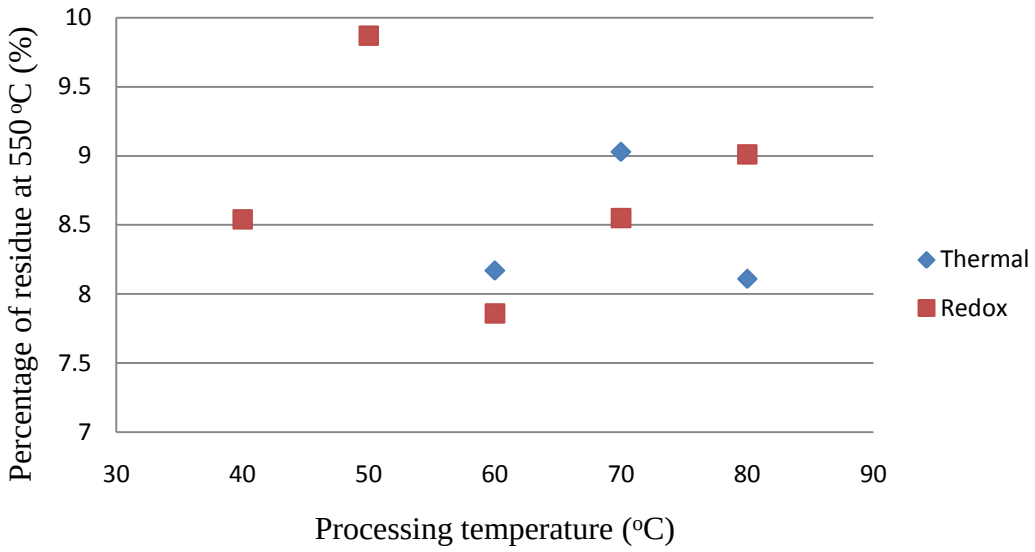


Figure 4.12: Percentage of residue of polymers at 550°C (without crosslinking)

Figure 4.12 shows that thermal initiator polymer produced at 70°C and redox initiator polymer produced at 50°C had higher percentage of residue at 550°C. This indicates that the polymers produced at these temperatures were more resistant to thermal degradation. These results proved that better grafting process and higher molecular weight had made the polymers stronger and more thermal stable. Theoretically, crosslinked polymers are expected to be more resistant to thermal degradation due to its strong network bondings. However, due to ineffective crosslinking in this study, the thermal stability of the crosslinked polymers has not been enhanced as expected.

In conclusion, the difference in degradation temperature of the grafted polymer compared with just chitosan alone indicates that, when monomers were grafted onto chitosan, some chemical changes had occurred in the structure of

chitosan. Therefore, the thermal behavior of the grafted polymers has been affected.

4.7 Fourier transform infrared spectroscopy (FTIR)

Table 4.8: Summarize data of spectrum of pure chitosan

Types of vibration	Wavenumber (cm^{-1})	
	Experimental	Literature
O-H stretching	3367	3356*
C=O stretching (amide I)	1651	1646*
N-H bending (amide II)	1560	1587*
CH_3 wagging	1420	1421*
C-C stretching	1349	1318*
C-O stretching	1030	1024*
C-O-C stretching	1080	1080#

Literature results were reported by

* Nazarudin, Shamsuri and Shamsudin (2011)

Prashanth and Tharanathan (2003)

Table 4.8 summarizes the IR peaks of pure chitosan. The IR spectrum of chitosan (Figure 4.14) shows a strong and broad peak at 3367 cm^{-1} which was due to the presence of OH group in the chitosan structure. On the other hand, the peak at 1651 cm^{-1} has been attributed to C=O stretching (amide I) of NH-CO-R. This

peak was contributed by the original structure of chitin that had not undergone deacetylation process completely to convert it into chitosan. In addition, the band at 1560 cm^{-1} was assigned for NH bending for the NH_2 groups on chitosan (amide II). (Nazarudin, Shamsuri and Shamsudin, 2011)

Table 4.9: Summarize data of spectrum of uncrosslinked grafted polymers

Types of vibration	Experimental wavenumber (cm^{-1})	
	Thermal polymer	Redox polymer
O-H stretching	3256	3289
C=O stretching (amide I)	1631	1651
C=O stretching (ester group)	1724	1728
N-H bending (amide II)	1544	Overlapped
C-O-C stretching	989	1063

In the case of grafted uncrosslinked chitosan polymers (Figures 4.15-4.16), there are several significant changes observed in the FTIR spectra.

First, the intensity of OH peak of the grafted polymers was reduced greatly. The initially broad OH peak observed in pure chitosan had become sharper and narrower in the grafted polymers. This was due to two factors: The amount of free OH groups in chitosan was reduced due to its involvement in the grafting process (Figure 4.25). Before the polymerization reaction was carried out,

the OH groups in chitosan were free which could contribute to high intensity of the OH peak.

In addition, pure chitosan film was able to absorb water molecules from the surrounding which form hydrogen bondings with its OH groups. This resulted in a broad and wide OH peak at 3367 cm^{-1} in pure chitosan spectrum. However, when the free hydroxyl groups in chitosan were converted into carbonyl groups, it can no longer absorb water molecules from the surrounding. Therefore, the intensity of the OH peak decreases.

Due to these two reasons, the frequency of the OH peak in the thermal and redox initiated grafted polymers was shifted to lower frequencies at 3256 cm^{-1} and 3289 cm^{-1}, respectively, with a decrease in intensity.

Second, a new peak was observed in the FTIR spectra of the grafted polymers, which is C=O stretching of the ester group at 1728-1724 cm^{-1}. Monomers used in this study such as MMA, BA and AA consists of ester groups R-COO-R' in their structure. Therefore, when the monomers were grafted onto chitosan, the ester group of these monomers had become one of the functional groups in the grafted polymer (Figure 4.25). As reported by Fares and Al-Ta'ani (2003), C=O stretching of the ester group has been observed at 1735 cm^{-1}. However, the frequency of this stretching had shifted to lower frequency at 1724 cm^{-1} and 1728 cm^{-1} for the thermal and redox initiated grafted polymers,

respectively. The presence of the ester functional group in the grafted polymers indicates that these monomers could have been grafted onto chitosan.

Third, the intensity of the CH, CH_2 and CH_3 groups have become more intense. From the proposed mechanism in Figure 4.26, it can be observed that large amount of alkyl groups were found in the grafted polymer as the side chains. After the polymerization process, large amount of monomers which consist of alkyl groups were introduced into the grafted polymers. Therefore, in the spectra of the grafted polymers (Figures 4.15-4.16), the intensity of the peak for CH stretching (around 3000-2850 cm^{-1}), CH_2 bending (around 1465 cm^{-1}) and CH_3 bending (around 1450 and 1375 cm^{-1}) had increased greatly compared to that of pure chitosan (Figure 4.14).

For the case of grafted crosslinked chitosan polymers (Figurea 4.17-4.18), significant changes were observed in the FTIR spectra besides those changes mentioned above.

In the spectra (Figures 4.17-4.18), it was observed that the intensity of the amide peak increases greatly compared with the grafted polymers that were without crosslinker. This is because the crosslinker added into the polymer was N, N'-methylenebis(acrylamide) which consists of amide groups (Figure 4.13). This had further increased the number of amide groups in the crosslinked grafted polymers. The C=O stretching of the amide at 1632 cm^{-1} (thermal hybrid polymer)

and at 1638 cm^{-1} (redox thermal polymer) had become more intense compared with uncrosslinked grafted polymers. Besides that, the NH stretching of the amide at 1560 cm^{-1} (thermal hybrid polymer) and at 1557 cm^{-1} (redox thermal polymer) had also increased its intensity in the spectra.

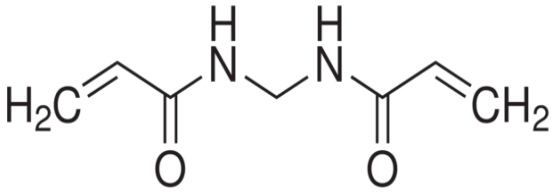


Figure 4.13: Molecular structure of N, N'-methylenebis(acrylamide)

Figure 4.14: FTIR spectrum of pure chitosan

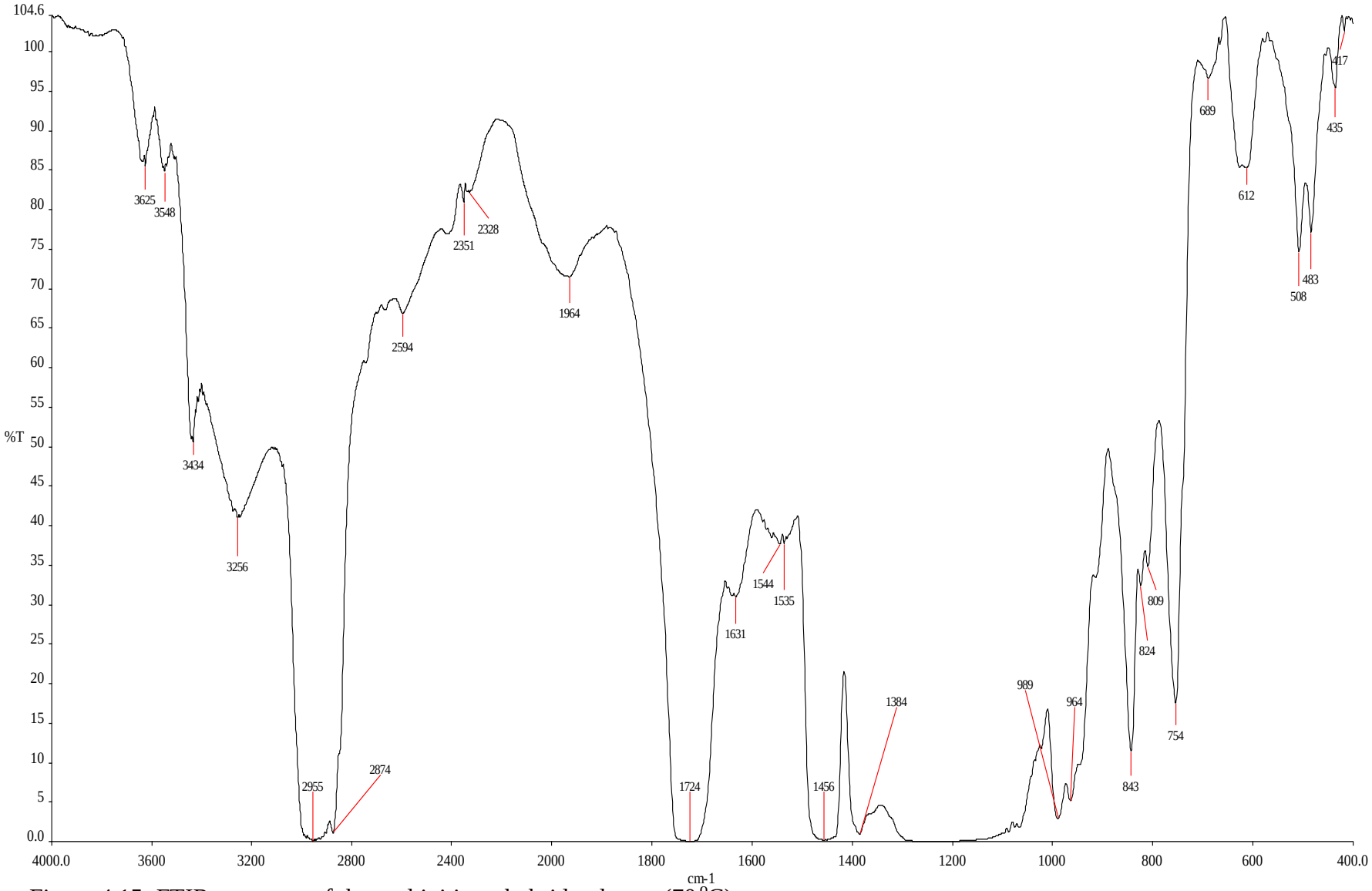


Figure 4.15: FTIR spectrum of thermal initiator hybrid polymer (70 ^{o}C)

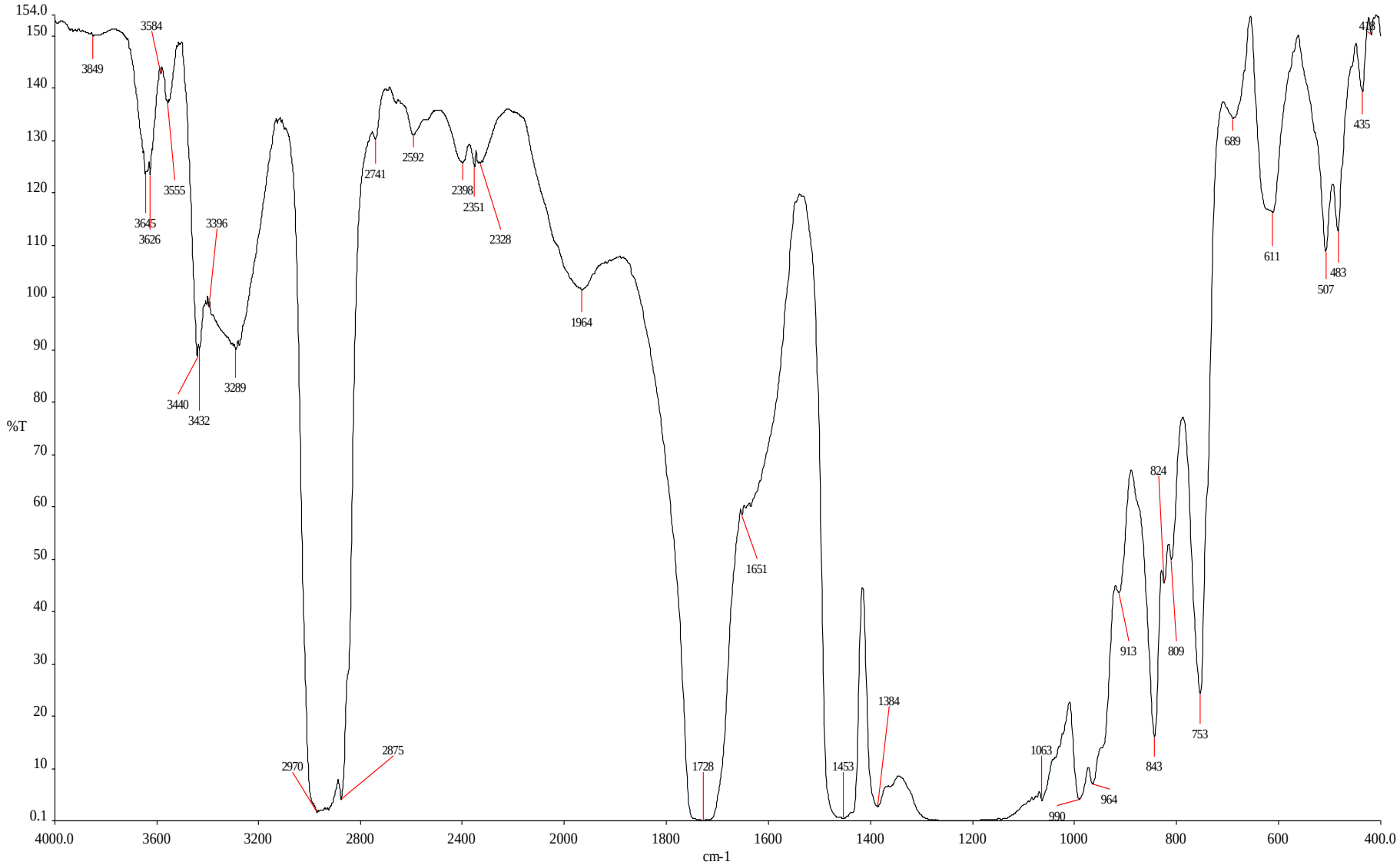


Figure 4.16: FTIR spectrum of redox initiator hybrid polymer (50 ^{o}C)

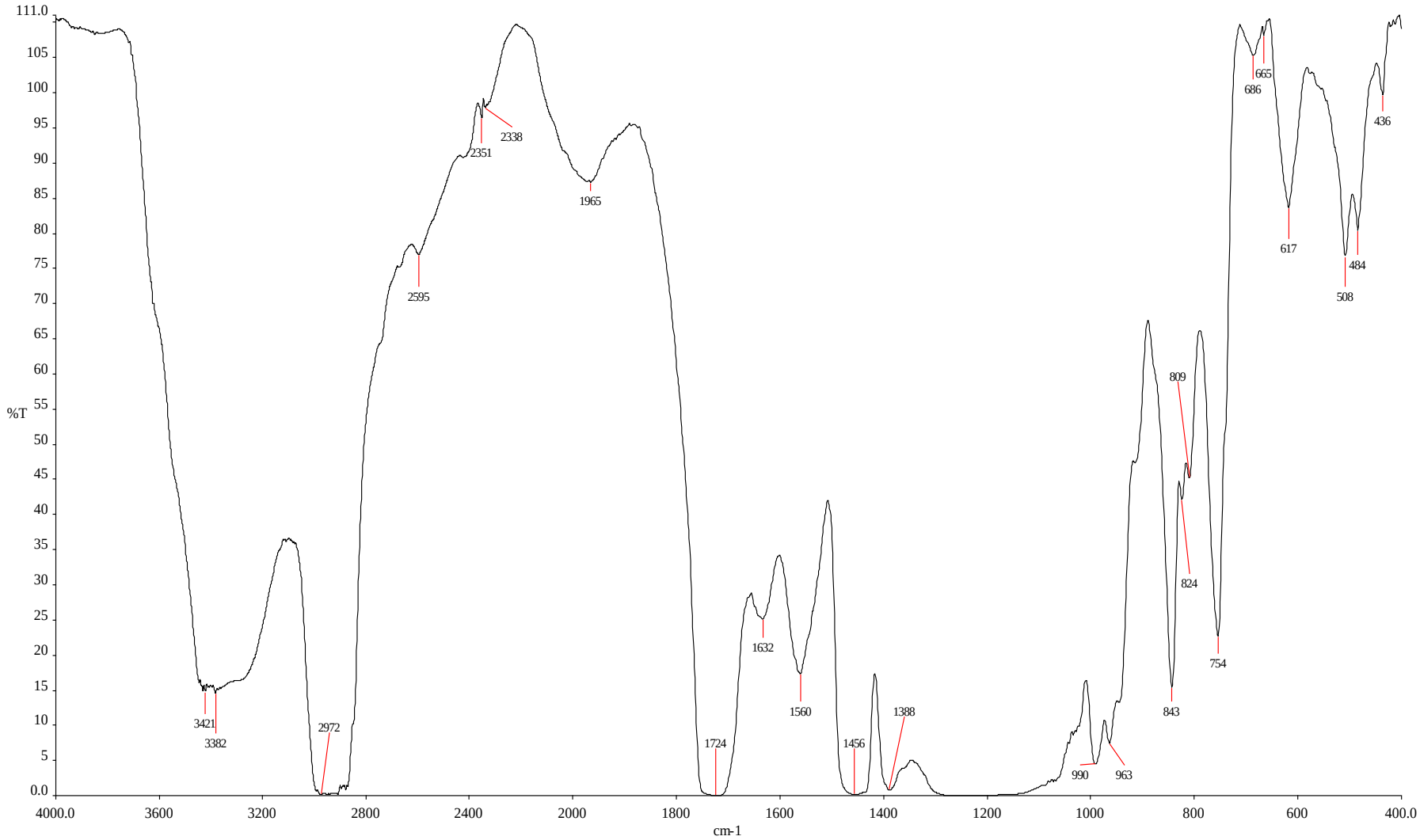


Figure 4.17: FTIR spectrum of thermal crosslinked hybrid polymer (70 ^{o}C)

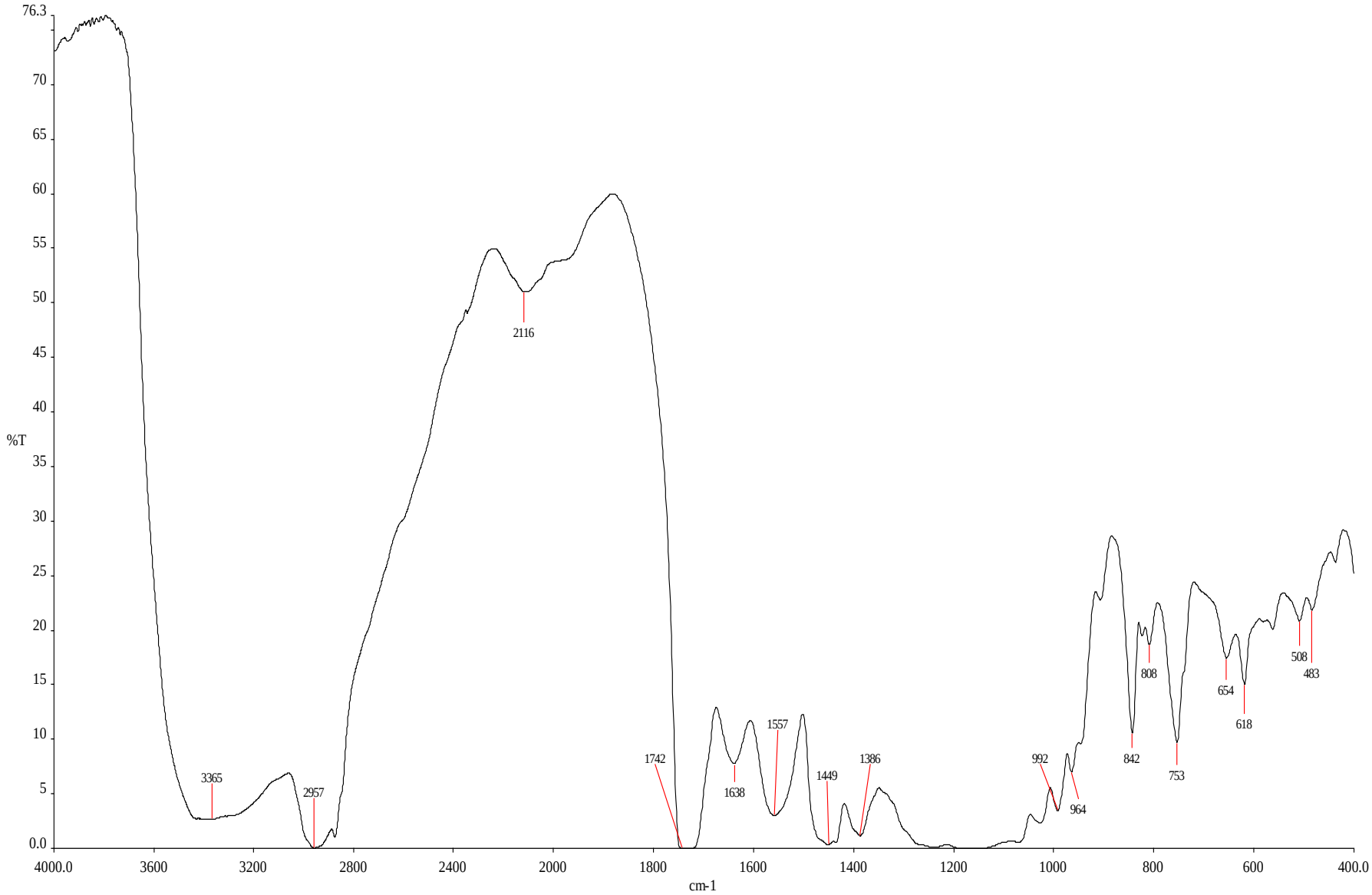


Figure 4.18: FTIR spectrum of redox crosslinked hybrid polymer (50 ^{o}C)

4.8 X-ray diffraction (XRD)

Chitosan is a partially crystalline natural polymer. Its crystallinity is due to the accumulation of linear chains in the structure. However, when monomers were grafted onto chitosan, certain crystalline chains of the polymer were distructed. (Mohammad and Bashar, 2003)

Wide angle XRD patterns of the chitosan and chitosan grafted polymers are shown in Figure 4.19 (a-e). The intensity of the crystalline peak of grafted polymers decreased or shifted with the extent of grafting (Table 4.10). (Acharyulu, Gomathi and Sudha, 2013)

Table 4.10: Three strongest peaks in X-ray diffractogram

	Three strongest peaks in X-ray diffractogram, 2θ (deg)		
Pure chitosan	23.02	24.02	38.30
Thermal polymer			
70°C	22.52	38.30	44.56
70°C (crosslinked)	22.48	38.38	44.62
Redox polymer			
50°C	22.20	38.40	44.66
50°C (crosslinked)	22.42	38.32	44.52

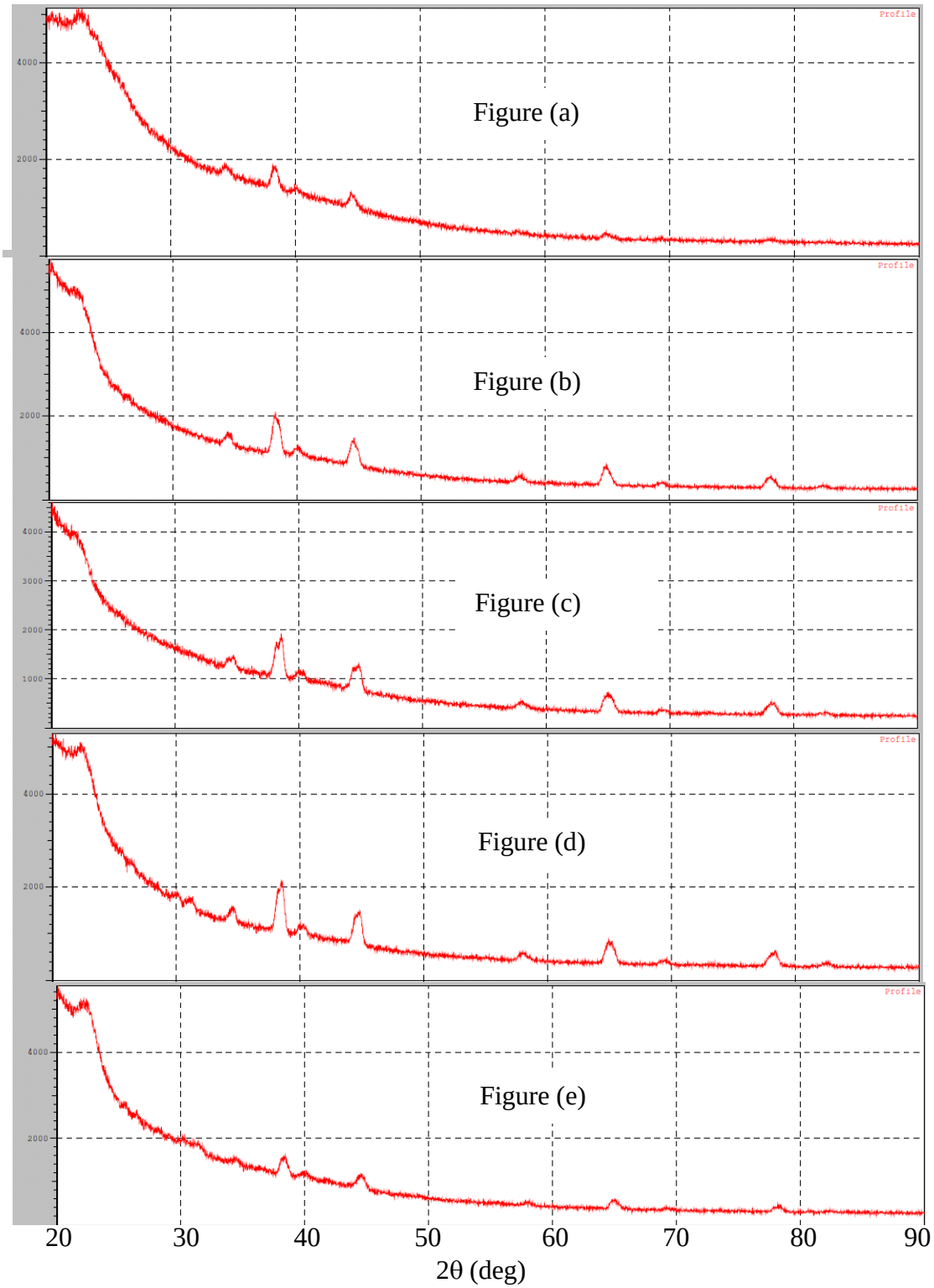


Figure 4.19: XRD of (a) pure chitosan and its hybrid polymers: (b) thermal polymer (70°C), (c) redox polymer (50°C), (d) crosslinked thermal polymer (70°C), (e) crosslinked redox polymer (50°C)

The XRD analysis was used to study the crystallinity of the polymer samples. The peaks at 2θ = 23.02°, 24.02° and 38.30° for pure chitosan indicated that it has the semi-crystalline structure. For the XRD spectra of grafted polymers, they have shown the shifted of 2θ values which indicated that the polymers was going from crystalline to amorphous nature. (Acharyulu, Gomathi and Sudha, 2013)

In addition, the shift of the 2θ values confirmed that grafting process has been taken place during the polymerization. Pure chitosan is a rigid crystalline structure that is stabilized by intra- and inter-molecular hydrogen bonding. When glucosamine units in chitosan long chain were protonated, the NH_2 groups were disrupted because hydrogen bonding involved the NH_2 groups. Thus, the crystalline structure had become weaken. (Acharyulu, Gomathi and Sudha, 2013)

Furthermore, after the monomers were grafted onto chitosan, the packing of the chitosan chains was disturbed and the crystalline regions were deformed. The deformation of the semi-crystallinity of chitosan caused the shifting of 2θ values of the grafted polymers. (Acharyulu, Gomathi and Sudha, 2013)

4.9 Flame test

Table 4.11: Heat capacity of the polymers

	Types of initiator	Processing temperature (^oC)	Heat capacity, C_p ($J\ g^{-1}\ ^oC^{-1}$)
Without crosslinking	Thermal	80	3.81
		70	3.66
		60	5.84
		50	*
		40	*
	Redox	80	3.34
		70	2.60
		60	3.55
		50	5.05
		40	2.77
With crosslinking	Thermal	70	2.54
	Redox	50	5.85
Pure Chitosan			11.36
Pure Copolymer			1.00

Figure 4.20 shows the chitosan polymer alone was flame retardant. However, it only works when the polymer was placed in open air environment with a relative humidity of 70%. The may be due to the chitosan film tends to absorb moisture from the surrounding easily due to the presence of hydroxyl groups which are able to form hydrogen bonding with water molecules.

When the polymer was placed in open air which has high moisture content, more water molecules were bonded to chitosan through hydrogen bonding and eventually the polymer will become flame retardant. When the polymer was placed into a dessicator which provides a less humid (~50% relative humidity) condition, the polymer was no longer flame resistant.

Table 4.11 shows that pure chitosan polymer had the highest heat capacity (11.36 J g^{-1} $^{o}C^{-1}$), therefore it can resist the heat from a flame to prevent itself from burning. However, all the grafted polymers had lower heat enthalpy, thus they can burn more easily compared with pure chitosan.

On the other hand, the grafted polymers showed no self extinguishing property even after being left in open air environment for some time. This is because once the monomers were grafted onto chitosan, the hydroxyl groups in the chitosan became less available to form hydrogen bonding with water molecules. Thus, the polymer can easily burn off. In order to introduce self extinguishing properties to the grafted polymer, some inorganic compound such as trimethoxyvinylsilane, TMVS could be incorporated.

Figure 4.20: Un-grafted chitosan polymer after flame test

4.10 Scanning electron microscopy (SEM)

Figure 4.21 shows the SEM micrograph of pure chitosan polymer in 20000× magnifications. The morphology shows a smooth surface because the sample was prepared in thin film form. The morphology shows some small

precipitate on the specimen which may be some un-dissolved chitosan or chitosan crystal.

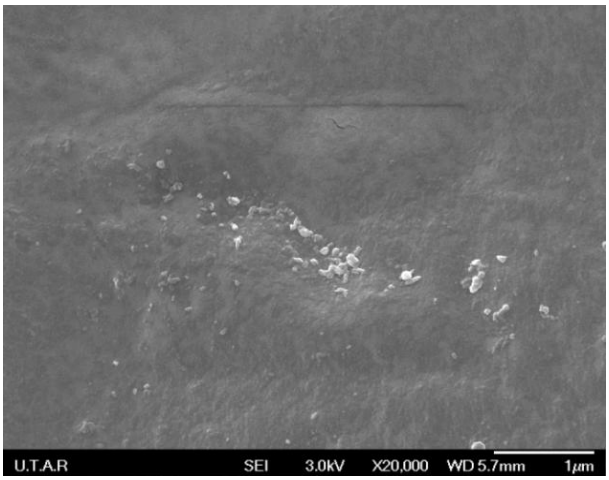


Figure 4.21: SEM micrograph of pure chitosan

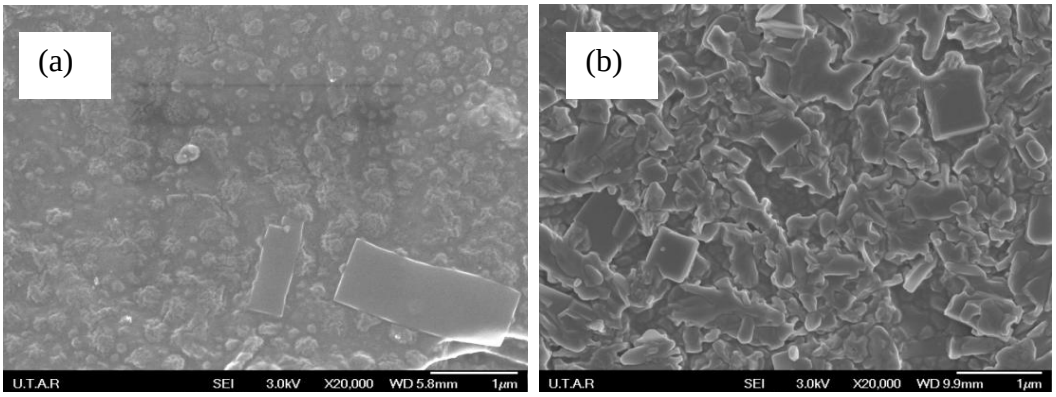


Figure 4.22: SEM micrographs of uncrosslinked (a) thermal hybrid polymer (70^{o}C) and (b) redox hybrid polymer (50^{o}C)

Figure 4.22 (a-b) shows the SEM micrographs of uncrosslinked grafted polymers in 20000× magnifications for the thermal and redox initiated polymers, respectively. The morphology of the thermal hybrid polymer shows a surface with uniform distributed particles of fine particle sizes. While, for the morphology of

the redox hybrid polymer has a rougher surface with particles of irregular shape and courser in size. This indicated that thermal initiated polymer was more homogeneous than the redox initiated polymer.

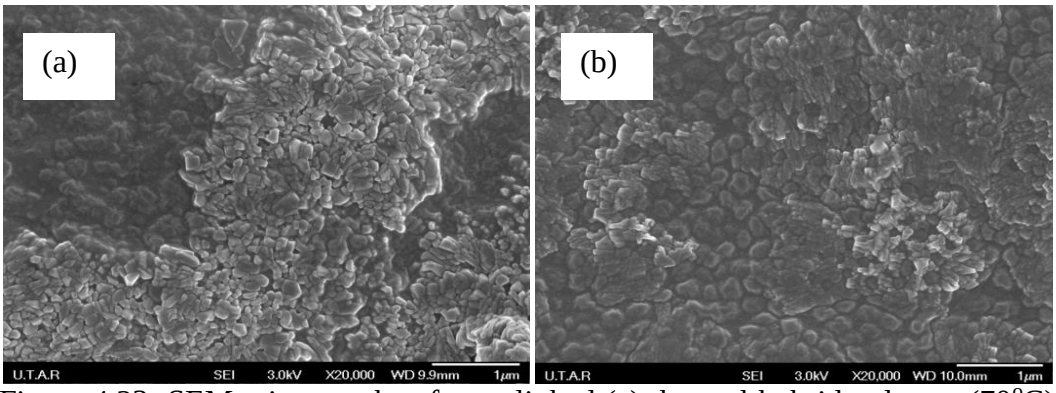


Figure 4.23: SEM micrographs of crosslinked (a) thermal hybrid polymer (70^{o}C) and (b) redox hybrid polymer (50^{o}C)

Figure 4.23 (a-b) shows the SEM micrographs of crosslinked grafted polymer in 20000× magnification for thermal and redox initiated polymers, respectively. The morphology of the thermal hybrid polymer shows the polymer had two different zones, one being more compact than the other. This may be due to non-homogeneity in the polymer mixture. This can be caused by an ineffective crosslinking process. On the other hand, the morphology of the redox hybrid polymer is arranged more uniformly and the particles size is more uniform in size.

4.11 Radical polymerization reaction

In this project, the mechanism involved was complicated and cannot be determined exactly. However, there are several proposed mechanisms that have been published by other authors.

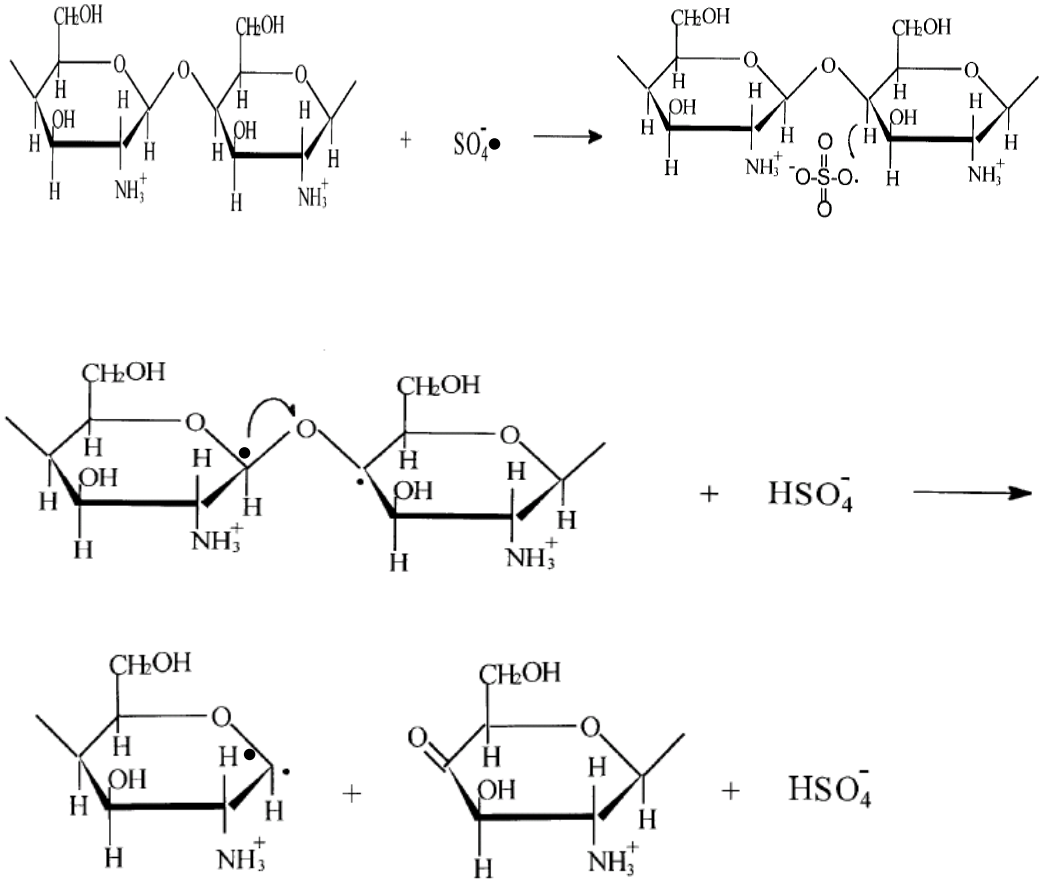
During polymerization, potassium persulfate acts as thermal initiator. It was a water soluble initiator which had weak peroxide bonds. It tended to form radicals in water and these radical initiated the chain reaction between the monomers in the solution. Once the peroxide bond of potassium persulfate was broken, the pair of electrons in the bonds separated into two fragments. Each fragment consists of one unpaired electron radical. Radicals formed by persulfate are shown as follows:

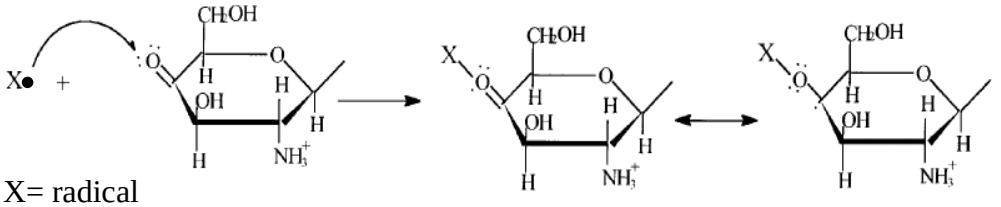
Figure 4.24: Potassium persulfate acts as initiator to form radicals

The unpaired electrons of initiators were reactive and readily reacted with the C=C double bonds in vinyl monomer. The unpaired electron of initiator obtained one of the electrons from C=C double bond. As a result, a new chemical bond was formed between the initiator and the monomer molecule with a new

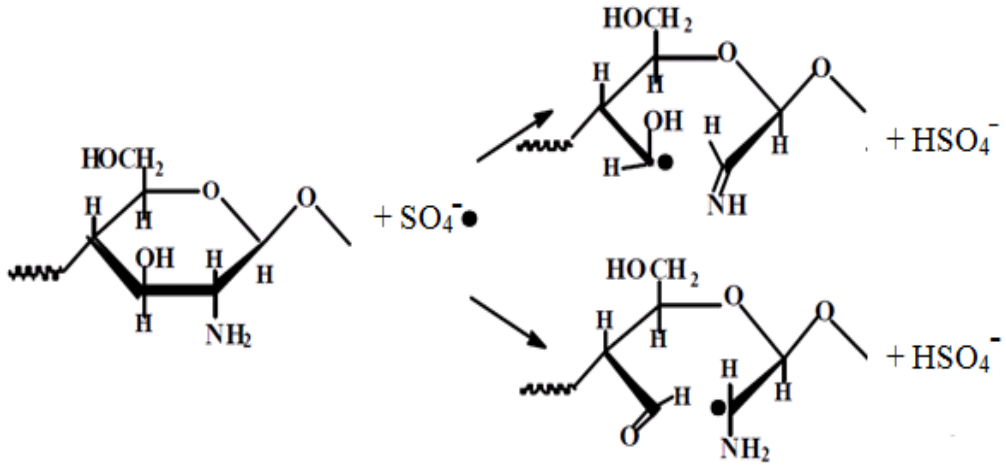
free radical formed. This process is known as initiation process. This newly formed radical will continue to grow by reacting with more monomer molecules in the mixture. Finally, a long radical chain was formed. (Grunlan, et al., 2001)

At the same time, under the action of potassium persulfate as radical initiator, there was a radical destruction of C_2-C_3 and C_1-O-C_4 links in chitosan macromolecule. This was results in the formation of macro radicals. These macro radicals then involve in radical reactions with vinyl monomers which result in the formation of grafted polymer chains (Figure 4.25). (Solomko, et al., 2009)

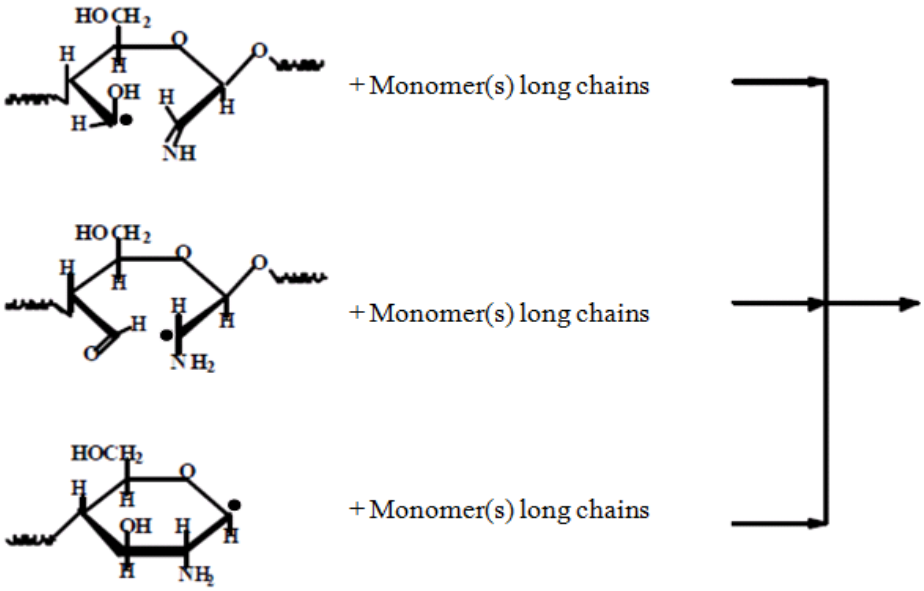


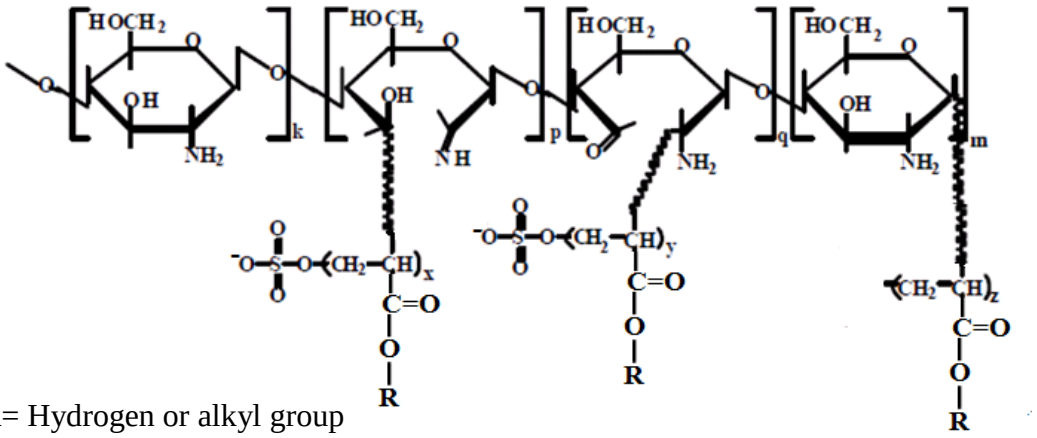


X= radical



The proposed structure for the chitosan grafted by monomers is shown as below:

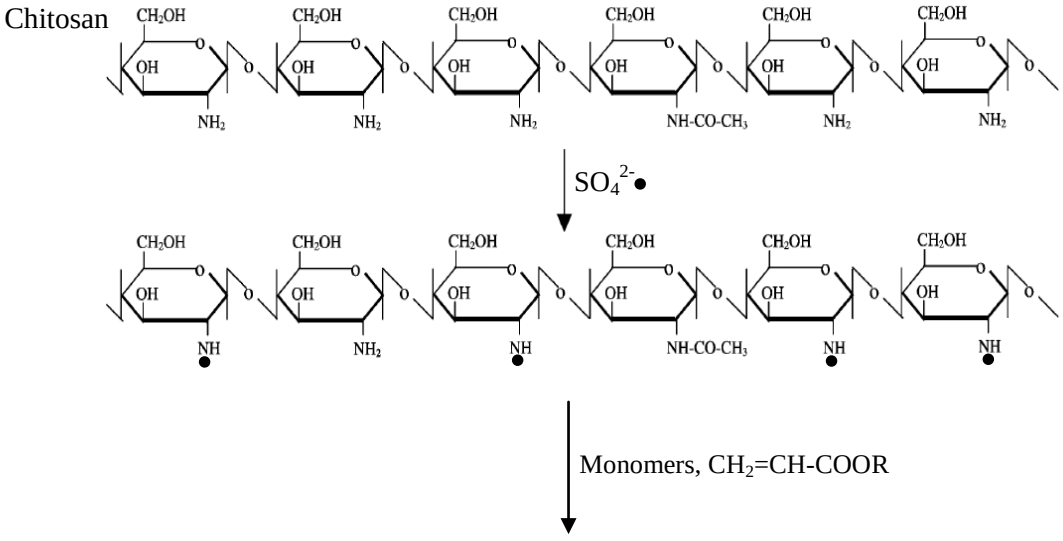




R= Hydrogen or alkyl group

Figure 4.25: Proposed mechanism of polymerization process by persulfate free radicals (Hsu, Don and Chiu, 2002) (Solomko, et al., 2009)

Another proposed mechanism which involved in this polymerization is shown below:



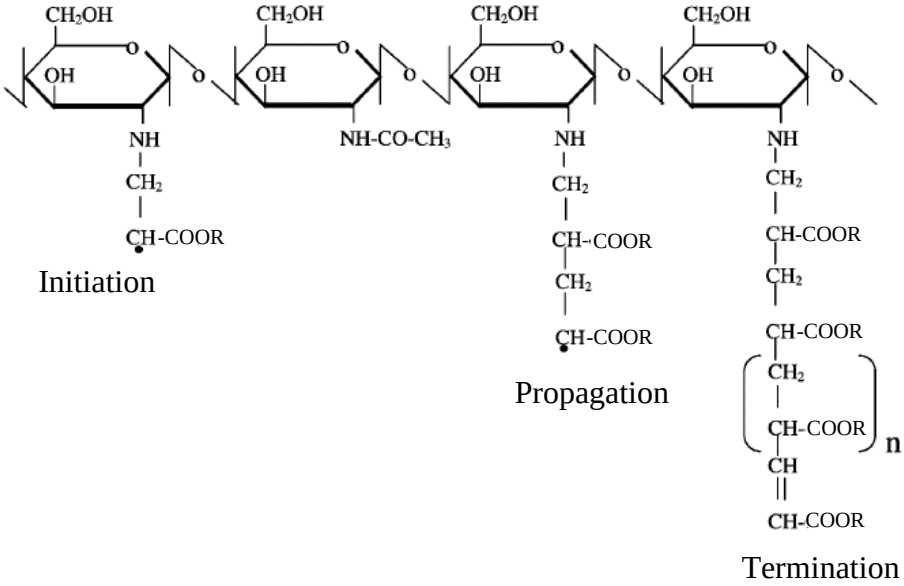


Figure 4.26: Proposed mechanism of the formation of chitosan grafted polymers (Prashanth and Tharanathan, 2003)

The radical was formed at the reactive amino group at carbon-2 in chitosan. The deprotonated amino group was a nucleophile which highly reactive and always readily reacted with electrophilic (monomers) that consists of radical sites. In this study, vinyl monomers were directly grafted onto chitosan via radical copolymerization. It was an easy and useful method to modify chitosan. Several stages of reactions were involved simultaneously during the polymerization, such as initiation, propagation and termination process. (Zohuriaan-Mehr, 2005)

However, this method has disadvantages. The complicated reaction system results in the formation of ill-defined structures and non-desirable homopolymers. The formation of such structures will eventually affect the grafting efficiency of

the polymers. This will result in the desired polymers being lower in molecular weight which will affect its chemical and mechanical properties.

Major efforts have been done by researches to reduce the formation homopolymer during polymerization; yet, it still has the problem of homopolymer formation during the process. However, this problem can be solved in some extent through activating the polymerization process by high-energy radiation, such as by using the pre-irradiation technique. (Zohuriaan-Mehr, 2005)

CHAPTER 5

CONCLUSION

5.1 Conclusions

Different initiator systems have its pros and cons. Therefore, it is important to choose a suitable initiator system in order to produce the desired polymers. For example, if the desired polymers are focused on tensile strength, thermal initiator system with 70^{o}C processing temperature will be a better choice to produce polymers with better tensile strength. On the other hand, redox initiator system will be a good choice to produce the polymers with better thermal stability.

One of the main important criteria for characterization of polymer is tensile test. From the result, it can be concluded that redox initiator system is able to produce the polymers with higher tensile strength compared with thermal initiator system. However, thermal polymers have higher elongation properties than redox polymers. In addition, it was found that thermal initiator has no function under low processing temperature (below 60^{o}C). On the other hand, redox initiator cannot function well in the polymerization process with high processing temperature (above 70^{o}C).

DSC test has shown that chitosan has the lowest melting temperature (T_m) which is about 151.32^{o}C, while the copolymer has T_m value of 179.04^{o}C. Based

on the results, the T_m value of the grafted polymers is between 151.32^oC and 179.04^oC. This indicated that the grafting process has been done successfully. Redox polymers have higher T_m value than thermal polymers because redox initiator system has provided a better grafting condition to produce polymer with higher resistant toward the heat energy.

Chitosan has the lowest degradation temperature (T_d) before it was grafted by monomers. After the grafting is done on chitosan, the polymer has an increase in T_d value. The difference of T_d between grafted polymers and chitosan indicated that chemical changes had occurred when the monomers were grafted onto chitosan and the thermal behavior of polymers was affected. Thus, the resulted polymers were more thermally stable toward degradation reaction.

Chitosan alone has the self extinguishing properties. However, this is only applicable when it was kept in open air surrounding which has higher relative humidity. Water molecules are bonded to chitosan through hydrogen bonding. After the chitosan has been grafted, less hydroxyl groups are available in the chain and thus the polymers are no longer flame resistant.

From this study, it can be concluded that different type of initiator system possesses its own uniqueness and excellent features. If the polymer is required for greater mechanical strength and higher melting temperature, redox initiator system should be applied. On the other hand, thermal initiator system was able to

produce polymers with higher resistance toward thermal degradation. Appropriate initiator system should be chosen in order to fulfill the specific requirements needed for a specific application.

The polymer samples were characterized by total solids content, tensile test (to determine tensile strength), differential scanning calorimetry, thermogravimetric analysis, fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and flame test. In order to find out the optimum condition to produce the polymer with better tensile strength, degradation temperature and melting temperature, different initiator system as well as different processing temperature were studied. Besides that, crosslinker was also added during polymerization with the intention to improve the mechanical strength of the hybrid polymer.

Polymer solutions produced by thermal initiated system were not stable. The polymers would be precipitated out from the solution after kept for 3 months and formed settlement. Redox initiated polymer solutions were more readily stable. However, the polymer film formed by these solutions would be lumpy and not smoothly.

5.2 Future perspective

In future, different concentration of initiator for both initiator systems should be carried out to determine the optimum condition to produce the polymer with better tensile strength, degradation temperature as well as melting temperature. In addition, grafting efficiency of the polymers should be determined. Moreover, inorganic compounds such as trimethoxyvinylsilane (TMVS) can be added to the polymer in order to produce a polymer with better flame retardant properties. Thus, the polymer can have more applications for the market. Furthermore, studies on the degradation of the chitosan based polymer should be carried out through either enzymatic or bacteria degradation.

Others physical tests that can be carried out on the grafted polymers are swelling properties, chemical control release process, water binding capacity, ash test, degree of acetylation as well as viscosity of polymeric solution. Besides that, grafted polymers can be tested using Gel Permeation Chromatography and ^{13}C Nuclear Magnetic Resonance to determine the molecular weight and the structure of the polymers.

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