

**STUDY OF POLYVINYL ALCOHOL-MONTMORILLONITE
COMPOSITES ENHANCED BY CARBON NANOTUBE**

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**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Hons.) Chemical Engineering**

**Lee Kong Chian Faculty of Engineering and Science
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Sept 2017

DECLARATION

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

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ABSTRACT

The purpose of this research was to investigate the effects of carbon nanotube and electron beam irradiation on enhancing the mechanical properties, morphology and chemical interactions of polyvinyl alcohol-montmorillonite composites. PVOH is a biodegradable and water soluble polymer. The Polyvinyl-alcohol-Montmorillonite-Carbon Nanotube (PVOH-MMT-CNT) nanocomposites were prepared using solution casting method. The cast samples were further electron beam irradiated to 10 kGy, 20 kGy and 30 kGy. The addition of carbon nanotube (CNT) into PVOH matrix has effectively enhanced the mechanical properties of PVOH nanocomposites. From XRD analysis, the addition of high loading level of monmorillonite (MMT) and CNT in PVOH matrix have induced the d-spacing and inter-chain separation value of deflection peak (002) when subjected to higher irradiation dosages. This indicates that the crosslinking network formed could promote the dispersion state of MMT and CNT particles in PVOH matrix. However, the addition of high loading level of CNT has reduced the mechanical properties due to the formation of agglomerated CNT particles as evidenced in SEM analysis. Besides, higher irradiation dosages could also decrease the mechanical properties of PVOH nanocomposites due to the occurrence of chain scissioning reaction. According to FTIR analysis, the addition of CNT into PVOH matrix could reduce the C-H stretching of PVOH nanocomposites. However, the C-H stretching was highly increased with the application of electron beam irradiation due to formation of crosslinking network within the polymer matrix.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Poly (vinyl alcohol) (PVOH) is a biodegradable, biocompatible, water-soluble, nontoxic and odourless polymer. PVOH is commonly used in paper coating, textile sizing and food due to its biodegradability characteristic. PVOH is produced through polyvinyl acetate. Moreover, PVOH can be divided into two groups which are fully hydrolysed and partially hydrolysed. Fully hydrolysed PVOH has higher crystalline material compared to partially hydrolysed PVOH due to the presence of strong hydrogen bonds that holds the polymer chains together. PVOH itself has the mechanical properties such as tensile strength, hardness and more flexibility. Moreover, the characteristics of PVOH with water-soluble, hydrophilic and biodegradable have almost similar physical properties with human tissues in resulting commonly used in biomedical applications. Biomedical applications such as wound dressing, artificial organs and drug delivery systems have been widely developed in current century (Kamoun et al., 2014)

Recently, many research and reports have been reported on the hybridization of polymer matrix with the clay platelets in enhancing the mechanical properties of polymer nanocomposite. This is due to some limitations of PVOH such as insufficient strength and low heat stability which has restricted the polymer nanocomposite for further applications (Zhao et al., 2009). Thus, addition of clay nano-filler into polymer matrix is very important for reinforcement purpose. The hydrophilic characteristics of clay platelets enable itself to form homogenous dispersion in polymer matrix (Gaaz et al., 2006). Montmorillonite (MMT) is the most commonly used clay nano-filler in reinforcing the properties of polymer due to their similar applications and water-soluble properties.

Carbon nanotube (CNT) has also been developed in the past few decades due to its high surface area, high aspect ratio and low density properties in order to improve the overall properties of polymer nanocomposite. CNTs can be described as graphite sheet in the form of rolled up tiny tube form with the carbon structures building up from sp^2 carbon units. CNTs can be mainly divided into two groups

which are single-walled carbon nanotube (SWCNTs) and multi-walled carbon nanotube (MWCNTs) (Ma et al., 2010). Moreover, there are few fabrication methods of CNTs into polymer matrix such as melt blending, in situ polymerization and solution mixing. The main reasons that CNTs are widely developed in reinforcing of polymer nanocomposite is mainly due to the enhancing effect on electrical properties, fire resistance and mechanical properties such as high Young's modulus, stiffness and tensile strength.

Nowadays, electron beam irradiation is widely applied on modifying polymer nanocomposite properties in order to expand their applications for more advance technology. Electron beam irradiation is a form of ionization energy which characterizes with low penetration and high dosage rates. Two principal changes would occur when undergo radiation which are crosslinking and chain scissioning reaction (degradation). The molecular weight is highly depends on the two principal changes where crosslinking increases the molecular weight and chain scission decreases the molecular weight. The discoloration application of radiation could cause and reduce of the properties of polymer such as PVOH has turned radiation to be noticeably famous in the biomedical field. This function is suitable in the invention of implantable surgical devices technology (Robert, 1997).

In summary, there are few researches on the mechanical properties of PVOH/MMT with the enhancement of carbon nanotube and electron beam irradiation, thus deeper investigate on these topics is to be expected. Therefore, the investigations on how mechanical properties can be enhanced by electron beam radiation and carbon nanotube are reported in this study. The purpose of this study is to determine the characteristic and properties of PVOH on different loading of MMT and CNTs with various irradiation dosages. The understanding of how carbon nanotube and radiation can control the properties is very important through this research in order to improve the PVOH modification in different applications especially biomedical fields.

1.2 Problem Statement

PVOH is a hydrophilic and biodegradability polymer which is widely used in biomedical applications. However, the propertie of PVOH has been restricted for further advance application nowadays. Thus, the properties of PVOH can be further improved by adding clay nanofiller such as MMT and CNT. Addition of CNT can

highly enhanced the mechanical properties of PVOH matrix. However, the limitations of PVOH-CNT nanocomposites such as structure control of CNTs, dispersion of CNTs within the polymer and interfacial interaction between CNTs and polymer matrix. Thus, this problem had been further investigated in this report. Furthermore, many researches had been carried out to investigate the properties of PVOH-MMT nanocomposites can be further improved by application of electron beam irradiation by forming crosslinking structure within the matrix.

The following problems of this study have been identified:

1. What are the effects of addition of carbon nanotube in polyvinyl alcohol-montmorillonite composites in terms of mechanical properties, morphology and chemical interactions?
2. What are the effects of electron beam irradiation on polyvinyl alcohol-montmorillonite composites in terms of mechanical properties, morphology and chemical interactions?

1.3 Aims and Objectives

The main objective of this report was to investigate the effect of carbon nanotube added to PVOH/MMT with irradiation under electron beam radiation.

In order to achieve the main objective of this study, the following sub-objective was required:

1. To find out the effects of carbon nanotube to enhance the mechanical properties, morphology and chemical interactions of polyvinyl alcohol-montmorillonite composites.
2. To investigate the effects of electron beam irradiation on enhancing the mechanical properties, morphology and chemical interactions of polyvinyl alcohol-montmorillonite composites.

1.4 Scope of the Study

Based on the objectives of this study, several technical tasks and analysis jobs were performed. The scopes were separated into two main parts, which were sample preparation and sample evaluation as shown below:

- a) Sample Preparation

PVOH, MMT and CNTs were compounded by using solution casting method. The samples were irradiated using electron beam irradiator, after dried in the oven.

b) Sample Characterization

Mechanical, physical and chemical properties of irradiated polymer were investigated as shown in the following:

I. Mechanical Properties

Tensile properties were measured by using Instron Universal Testing Machine in accordance to ASTM D638.

II. Physical Properties

Physical properties were investigated by using XRD and SEM as shown in the following:

1. XRD was conducted by model Shimadzu XRD 6000 Diffractometer.
2. SEM was conducted by model Hitachi Scanning Electronic Microscopy of BS 340 TESLA.

III. Spectroscopy Properties

FTIR spectroscopy was investigated by machine model Nicolet iS10 FT-IR Spectrometer.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of Poly (Vinyl alcohol)

Poly (vinyl alcohol) (PVOH) is a biodegradable, non-toxicity, water-soluble polymer which commonly used in application of paper textile coating and textile sizing. There are many research studies have been carried out on the theoretical and applied studied of PVOH these few decades. The synthesis, properties, applications of PVOH have been discussed and summarized in the following parts.

2.1.1 Synthesis

PVOH is produced from the method of hydrolysis of polyvinyl acetate through saponification process. This is because PVOH particles unable to produce by direct polymerization of vinyl alcohol. Polyvinyl acetate is dissolved in methanol by adding anhydrous sodium methylate or aqueous sodium hydroxide in order to hydrolyse the acetate groups into hydroxyl groups. Degree of polymerization and degree of hydrolysis could be highly affected on the physical characteristic and functional uses of PVOH (Saxena, 2004).

2.1.2 Types

There are two types of PVOH which are partially hydrolysed and fully hydrolysed PVOH. The melting point of fully hydrolysed PVOH is at the range of $\sim 228^{\circ}\text{C}$ and for partially hydrolysed is at the range of $180 - 190^{\circ}\text{C}$. Partially hydrolysed PVOH is commonly used in foods which acts as a moisture barrier film in food supplement tablets and dry food (Saxena, 2004). The chemical structure of fully and partially hydrolysed PVOH is shown in Figure 2.1 (Gaaz et al., 2015).

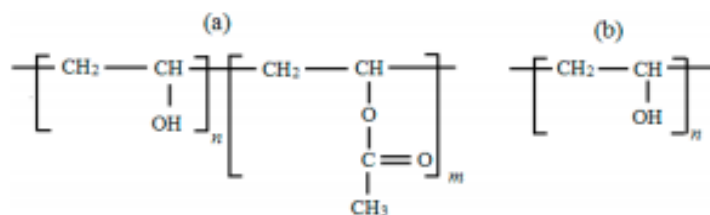


Figure 2.1: Chemical structure of fully and partially hydrolyzed PVOH

a) partially hydrolysed PVOH; b) fully hydrolysed PVOH (Gaaz et al., 2015)

2.1.3 Properties

The chemical, physical properties and water solubility of PVOH are highly depends on the percentage of hydrolysis, molecular weight and crystal precipitation. PVOH itself has good tensile strength, hardness, flexibility and gas barrier characteristics. The biodegradability and water solubility characteristics of PVOH are commonly used in biomedical applications due to similar physical properties with human tissues. This is due the biocompatible structure of PVOH which able to attract the protein molecules and binds with the human cell without producing toxic effects.

2.2 Background of Montmoriillonite

Montmoriillonite (MMT) is a nanoscale filler which used to reinforce the properties of polymer in hydrophilic and hydrophobic polymer matrix (Gaidukov, Danilenko and Gaidukova, 2015). MMT is a 2:1 phyllosilicate clay which has a sandwiched layered structure consists of two silica tetrahedron as external part and a octahedral sheet of alumina in between the two silica tetrahedron. The layered thickness is approximately 1nm with the properties of high stiffness and high strength. Polymer molecules can intercalate into the layered structures in order to create a nanocomposite with high aspect ratio. The molecular structure of MMT is shown in Figure 2.2 (Motawie et al., 2014).

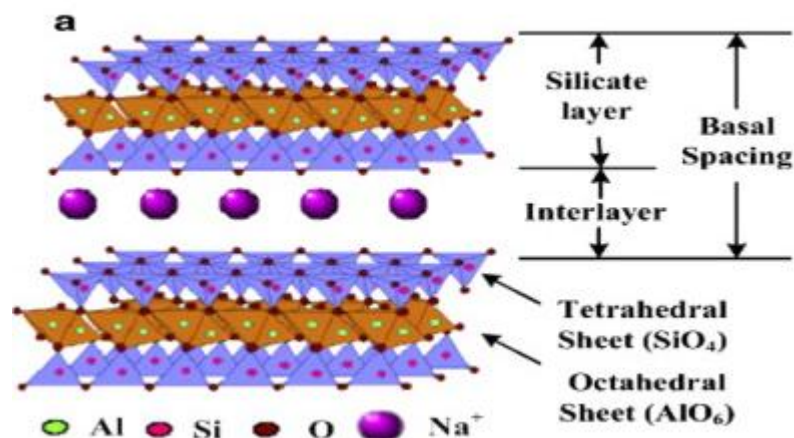


Figure 2.2: Molecular Structure of MMT (Motawie et al., 2014)

2.3 Background of Poly (vinyl alcohol)-Montmorillonite

Poly (vinyl alcohol)-montmorillonite (PVOH-MMT) is a structure of adding MMT into PVOH matrix so as to enforce mechanical and thermal properties without reduction in optical clarity of PVOH. The summary of research studies such as synthesis, properties, advantages and applications are discussed in the following part.

2.3.1 Synthesis

PVOH-MMT can be synthesised through Layer-by-Layer (LBL), simple vacuum filtration, doctor blading and solution casting method. Addition of MMT into PVOH matrix has large improvement and highly increased on mechanical properties compared to pristine PVOH. Other than improvement on mechanical properties, excellent properties have also been exhibit such as flame resistance, barrier, and optical clarity (Allison et al., 2015). The overall properties of PVOH nanocomposites are strongly depend on the degree of dispersion of MMT platelets into the PVOH matrix during the synthesis process. In this synthesis process, MMT interact with PVOH matrix by developing three types of nanocomposites which are phase separated, intercalated and exfoliated nanocomposites. The molecular structure of PVOH and sodium MMT is shown in Figure 2.3 (Mondal et al., 2013).

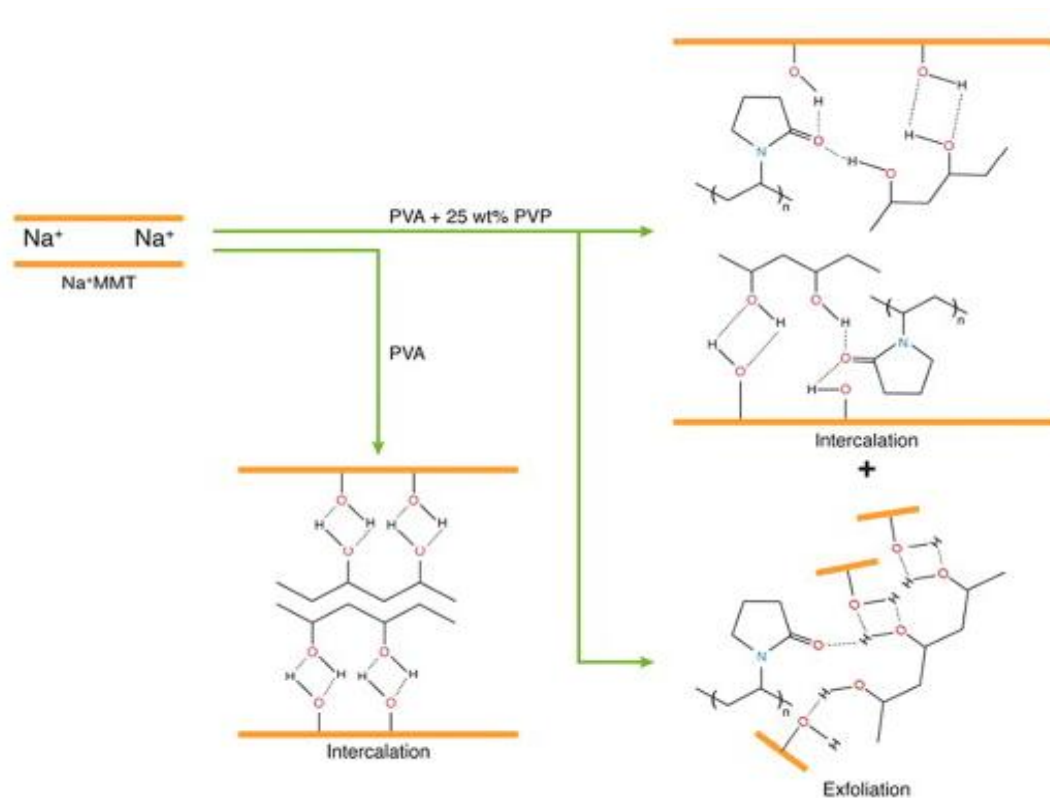


Figure 2.3: The molecular structure of PVOH and sodium MMT (Mondal et al., 2013)

2.3.2 Types

There are three types of structure for PVOH-MMT nanocomposites which are phase separated, intercalated nanocomposites and exfoliated nanocomposites. The interactions between silicate layers and polymer matrix in phase separated systems are very weak, resulting relatively poor mechanical properties. Meanwhile, for intercalated nanocomposites, the polymer chains and silicate structure are attached and stacked in a well ordered multilayer form. The properties of intercalated nanocomposite are similar to ceramic materials. On the other hand, the silicate structures in exfoliated nanocomposite are separated from one another and in the form of individually dispersed in polymer matrix. Therefore, the mechanical and physical properties of exfoliated system have been maximized compared to intercalated systems (Andreas, Fotios and Nick, 2011). Furthermore, exfoliated nanocomposites are generally used due to its high aspect ratio. The schematic illustrations of the three types of nanocomposite are shown in Figure 2.4 (Andreas, Fotios and Nick, 2011).

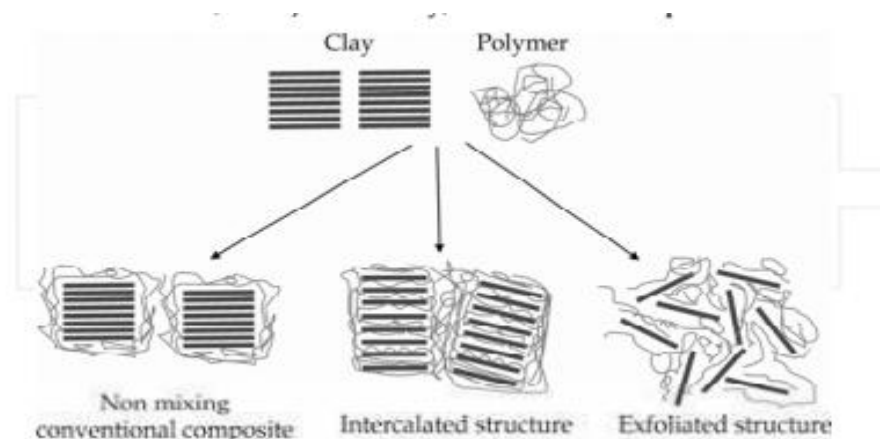


Figure 2.4: Schematic illustrations of the three types of structure of nanocomposites (Andreas, Fotios and Nick, 2011)

2.3.3 Properties

Dispersing of MMT into PVOH has large improvement in overall properties such as mechanical properties, thermal properties and fire retardancy. Mechanical properties such as toughness, tensile strength and high young modulus have been highly improved on PVOH-MMT nanocomposites. The lamina structure between the PVOH matrix and MMT layers could enhance the mechanical properties such as strength and stiffness (Gaidukov, Danilenko and Gaidukova, 2015). Moreover, the development of intercalated or exfoliated structure of PVOH-MMT has highly enhanced in the tensile property. From the report of Strawhecker and Manias (2001), they had stated that the tensile strength of PVOH-MMT increases by 62% compared to pure PVOH. This is due to the good dispersion of MMT layers in the PVOH matrix in formatting a strong interaction which is hydrogen bonds. This interaction can be explained in creating the process of exfoliated structure where the OH groups of PVOH binds with the OH groups of MMT. Furthermore, according to Soundararajah and Karunaratne (2009), the Young modulus had increased by 61% for PVOH-MMT nanocomposites. This is mainly due the clay layers are highly affected by the polymer on its surface. MMT clay with only one dimension can exposed large area to the polymer matrix, resulting increase in the modulus. According to Soundararajah and Karunaratne (2009), the tearing energy in toughness was twice compared to neat PVOH in 4wt% of PVOH-MMT nanocomposites. This is because microvoids which released from plastic constraint in the polymer matrix

have precipitated large amount of plastic deformation, resulting tearing effect of matrix ligaments between microvoids. On the other hand, the toughness of neat PVOH is low compared to PVOH-MMT nanocomposites due to only contributes to energy absorption.

PVOH-MMT has also exhibits excellent properties in flame resistance. MMT platelets which accumulated with small amount of char act as a protective surface barrier/insulation layer in reducing the peak heat release rate (PHRR) of polymer and spreading speed of flames. The char is developed on the outer surface during combustion. Moreover, the char on the outer surface functioned as insulator barrier for O₂ and combustion products generated during decomposition so as to prevent further burning (Tomasz, 2016).

Andreas, Fotios and Nick (2011) had stated that the heat resistance is important aspect for nanocomposites in application. They had investigated that there is 40% less of weight loss in PVOH-MMT nanocomposites compared to pristine PVOH. MMT acts as a barrier in maximizing the heat insulation and minimizing the permeability of volatile degradation products in the material so as to enhance the thermal stability of PVOH-MMT matrix.

The properties of optical clarity is depends on the dispersion rate within clay platelets and polymer matrix. Scattering effects could be eliminated by good interfacial interaction between polymer matrix and particles, resulting reduce of light transmittance of nanocomposites (Andreas, Fotios and Nick, 2011). In addition, a strong and transparent films, coating and membranes could formed based on the interfacial interaction effect between MMT particles and PVOH matrix.

2.3.4 Advantages

PVOH provides various advantages and benefits but the most attractive advantage is green eco-friendly. PVOH-MMT nanocomposites play a role to solve the problem of disposable plastic packaging wastes with reducing the usage of landfill and safe environment. The final degradative products from PVOH-MMT are carbon dioxide and water which can easily dispose out to the environment with no pollution (Guo and Zhang, 2011). Furthermore, PVOH can be disposed of properly and break down to harmless natural products for single-use food packaging. In addition, PVOH can reduce the usage of fossil resources by producing conventional plastics.

The biocompatible and biodegradable of PVOH-MMT is also another important advantage with high surface area, eco-friendly and low cost. The PVOH-MMT nanocomposite hydrogels are non-toxic, highly elastic, durable and no carcinogenic effects which is very important for biomedical applications. Another advantage is increasing the viscosity and shortening the curing and cooling time process in the application of plywood, artificial board and timber processing. PVOH acts as a de-characterizing agent of thermosetting resin in order to enhance the initial cohesion of the products. Furthermore, PVOH can be easily processed through injection molding, film extrusion and others casting method with the presence of PVOH resins. This is mainly depends on the high processibility and stability properties of PVOH.

2.3.5 Applications

Various reports have been discussed on the characteristics and good performance properties of PVOH-MMT nanocomposites in applying on different applications.

PVOH-MMT nanocomposites have been found out increasing usage on the packaging applications due to its good biodegradability, transparency, easy processibility, compatibility, and mechanical and thermal properties. The mechanical properties of high strength and high modulus of PVOH-MMT can be easily manufactured on standard plastics by yielding the molded parts, film or fibers. Moreover, PVOH-MMT nanocomposite is used in the textile, paper industry and food packaging industry due to its high chemical and thermal stability. The main reason of using PVOH-MMT nanocomposites in food packaging industry is because to improve the food quality by increasing the shelf-life of food and low manufacturing cost from the transportation and area for storage purpose (Gaaz et al., 2015).

Nowadays, PVOH-MMT is becoming noticeably popular in biomedical applications. The properties of biocompatibility in the polymer gel are mainly used in several applications such as organ replacement, drug delivery devices and wound dressing management. PVOH acts as a water soluble polymer in water solution in order to produce as protective agents, so as to abundant the OH groups and absorb metal ions in forming complex products (Gaaz et al., 2015).

2.4 Reviews on Effects of Carbon Nanotubes on PVOH-MMT

There are recent reports on the developing of new technologies by using carbon nanotubes (CNTs) as filler material in polymer nanocomposites so as to explore more advance applications. CNTs are fabricated into polymer through solution mixing, melt blending and *in situ* polymerization method. There are two types of CNTs produced through synthesis which are single-walled carbon nanotubes and multi-walled carbon nanotubes. Single-walled carbon nanotubes usually used for enhancing the electronic properties with changing their chiral vector. In other hand, multi-walled carbon nanotubes are used in enhancing mechanical, thermal and electrical properties of polymer. The two types of CNTs structure and the structural formula of PVOH-CNTs are shown in Figure 2.5 and Figure 2.6 (Wang, 2007) and (Dai and Sun, 2016). The adding of CNTs is very important for enhancing the performance properties of PVOH-MMT. Therefore, the effect of CNTs in degree of crystallinity, properties and morphology of PVOH-MMT nanocomposites will be discussed in the following parts.

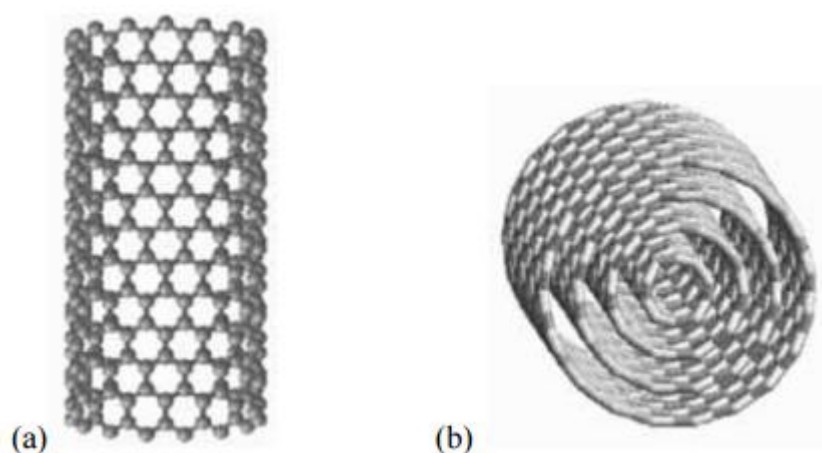


Figure 2.5: Two types of CNTs structure a) single-walled carbon nanotubes, b) multi-walled carbon nanotubes (Wang, 2007)

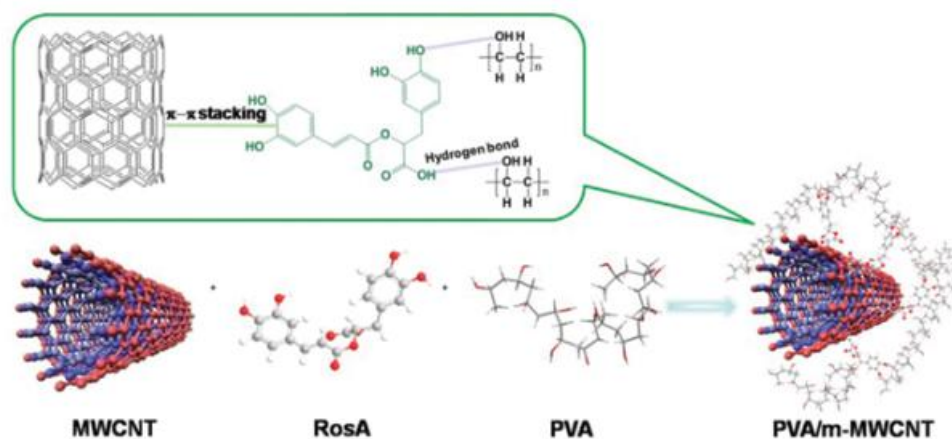


Figure 2.6: Structural formula and schematic diagram of PVOH-CNTs (Dai and Sun, 2016)

2.4.1 Degree of Crystallinity

The presence of CNTs acts as a nucleating agents, in order to increase the rate of crystallization of PVOH. CNTs affect the growth of crystals by altering their chain mobility with providing impediment to growth. Cadek, Coleman and Barron (2002) had investigated out that the crystallinity of pure PVOH and PVOH/CNTs was increased from 24% to 27% with 1wt% of CNTs loading.

Furthermore, according to Dassios and Galiotis (2012), the crystallinity of pristine PVOH and PVOH/MWNTs composite mats was used in the experiments at same heating rate. This result showed that the pure PVOH had a relatively low crystallinity of 19% compared to PVOH/MWNTs. On the other hand, the crystallinity of PVOH/MWNTs increased to 37% with the presence of MCNTs.

2.4.2 Properties

The main purpose of adding CNTs into PVOH matrix is to improve the performance properties with demand characteristic for desired applications.

CNTs itself have excellent mechanical properties with highest Young's modulus of 1.2 TPa and tensile strength of 50-200 GPa (Ma et al., 2010). Thus, these combine properties with the characteristics of high aspect ratio, large surface area and low density make CNTs as an ideal nanofiller for reinforcement on the PVOH-MMT nanocomposite. Mechanical properties are highly depends on few factors which are dispersion rate of CNTs, alignment, high aspect ratio and interfacial stress transfer between CNTs filler and polymer matrix (Coleman et al., 2006). The aspect

ratio has to be sufficiently large so as to increase the load transfer between the CNTs and PVOH-MMT matrix. From the investigation of Wong, et al (2009), the elastic modulus of PVOH was increased from 4 to 8 GPa by increasing the aspect ratio of CNTs from 24 to 43.

Good dispersibility of CNTs into PVOH-MMT matrix is very important in increasing the elastic modulus and yield strength of nanocomposites. Good dispersion of CNTs into PVOH-MMT matrix is not only to form bonding with matrix, but to prevent aggregation begins when the CNTs loading level is increased beyond the point. Therefore, CNTs has to be uniformly dispersed in the form of individually coated with polymer, so as to achieve uniform stress distribution in minimising accumulation of stress concentration (Coleman et al., 2006).

Alignment such as diameter of CNTs and CNTs content is another factor that affects the final mechanical properties of nanocomposites. A higher CNTs content will tend to decrease the tensile strength and strain stress curve of polymer nanocomposites. Dai and Sun (2016) have reported that the tensile strength of MWCNTs/PVOH was decreased from 926 MPa to 805 MPa with increasing of MWCNTs from 2 wt% to 3 wt%. However, the Young's modulus keeps increasing with increase amount of MWCTs content. Furthermore, smaller diameter is more beneficial in the structures because of greater extensional flow in polymer matrix.

Furthermore, interfacial interaction is an important factor which influenced the mechanical properties such as stiffness. According to Dai and Sun (2016) report, a neat PVOH was compared with PVOH/MWCTs in an experiment of stiffness test. Pure PVOH was evidently ductile fracture, whereas PVOH/MWCTs was resulted an expected feature of stiff and rigid fracture behaviour and a clear-cut fracture cross section.

Other than improvement on mechanical properties, electrical conductivity has also been improved and proved in some reports. From the report of Alghunaim (2016), the electrical conductivity of pure PVOH and PVOH/CNTs was in frequencies ranging from 100 Hz to 5MHz at room temperature. Electrical conductivity behaviour can be explained by percolation theory. Polymer nanocomposite tended to undergo an insulator-to-conductor transition with increasing of CNTs content, thus this critical CNTs content known as percolation threshold. It is known that the concentration of CNTs filler has to be higher than

percolation threshold so as to achieve conducting networks in the polymer nanocomposite (Ma et al., 2010).

Some reports have stated that the thermal conductivity of SWNT and MWNT can as high as 6600 W/mK and 3000 W/mK at room temperature (Du, Bai and Cheng, 2007). Therefore, CNTs are known as a best heat-conducting material where largely used in enhancing the thermal stability and thermal conductivity of polymer nanocomposite at high temperature. Lin, et al (2016) had reported that the initial decomposition temperature of pure PVOH and PVOH/CNTs was increased from 220°C to 240°C with 1.5 wt% CNTs loading. Moreover, the thermal resistance has been increased due to the high resistance at the CNTs/PVOH matrix interfaces which limits thermal transport along the percolation networks (Du, Bai and Cheng, 2007).

2.4.3 Morphology

Lin, et al (2016) had pointed out that high CNTs content could decrease the tensile strength due to the high aspect ratio of CNTs which easily induces van der Waals force. Van der Waals force tends to attract to each other when higher amount content of CNTs added, resulting formation of bundles and entanglements of CNTs network. This formation is known as agglomeration which prevents the mobility of PVOH molecular chains, thus decreased the tensile strength of nanocomposite. It can be observed from Figure 2.7 (b), the van der Waals force tends to agglomerate together and form bundle. The comparison of SEM images of 1.5wt% and 2.0wt% CNTs loadings are shown in Figure 2.7 (Lin et al., 2016).

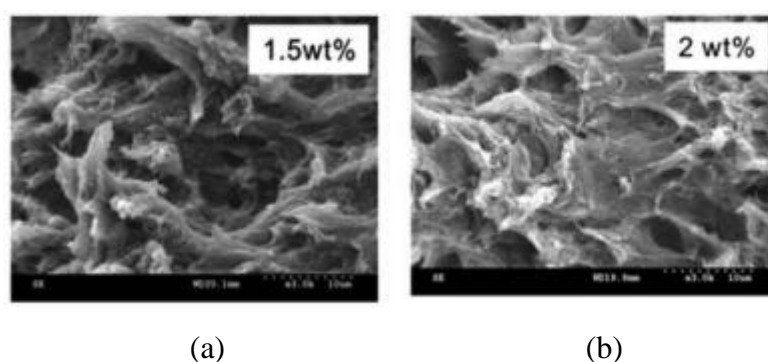


Figure 2.7: SEM images (3000X) a) 1.5wt% of CNTs loadings, b) 2.0wt% of CNTs loadings (Lin et al., 2016)

Addition of CNTs into PVOH-MMT has increased the stiffness compared to pure PVOH. This can be explained that the interfacial hydrogen bonding speed up the stress transfer and reduces the density of hydrogen bonding of PVOH, in order to enhance the plastic deformation of the polymer nanocomposite. (Dai and Sun, 2016)

2.5 Review on the Effect of Irradiation on PVOH-MMT-CNT

Radiation chemistry dealing with polymers has dramatically applied so as to modify the properties in order to expand the applications by forming crosslinking structure. As a result of absorption of high and large energy irradiation by ionizing radiation, chemical bonding of PVOH-MMT can be often broken or recombined in resulting large influence on the properties. Radiation energy can be transferred to a polymer by a process of ejecting of electrons from molecular orbitals and by subionizing excitation of the orbital electrons (Adolphe, 1964). Two principal changes which are chain scissioning and crosslinking can be occurred when subjected to irradiation. There are some decomposition products such as hydrogen, carbon dioxide and carbon monoxide from the process of irradiation (Robert, 1997). Chain scissioning and crosslinking effect can be affected by temperature and crystallinity.

Crosslinking reaction can caused an increase in molecular weight where higher molecular weight is more sensitive to radiation compared to lower molecular weight polymers. Crosslinking reaction occurs when a free radical abstract to a molecule. Free radicals can be produced by two processes which are releasing of hydrogen atom from irradiated polymer and addition of hydrogen atom into an unsaturated group (Robert, 1997). The mechanism of crosslinking reaction by irradiation can be referred as shown in Figure 2.8 (Robert, 1997). The hydrogen atom produced from cleavage of a C-H bond of one polymer chain may abstract another hydrogen atom from a neighbouring polymer chain to produce hydrogen, thus this two polymeric radicals combine to form a crosslink.

Somehow, crosslinking reaction is often accompanied by degradation reaction. Furthermore, crosslinking reaction in polymers has a “memory effect” where the polymer remains the stretched size or shape after cooled. However, any addition heating above the softening point can caused shrinkage to the original dimensions which is usually applied in poly (ethylene) film and tube (Malcolm, 1991). The mechanical properties of PVOH-MMT are highly depends on the density of crosslinking. Therefore, mechanical properties can be enhanced by increasing

radiation dose in order to produce more radicals by intensive excitation, resulting more crosslinking reaction (Tran et al., 2007).

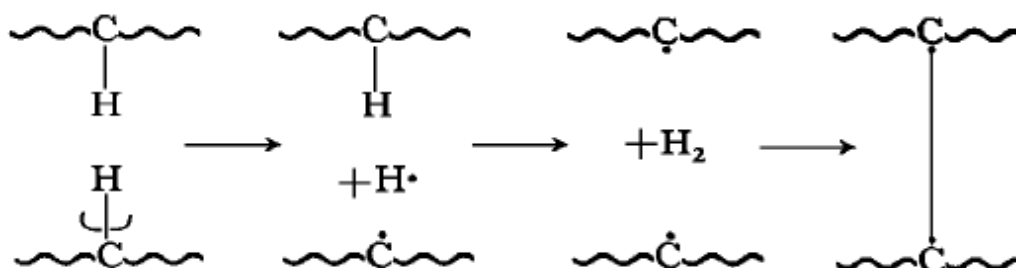


Figure 2.8: Mechanisms of crosslinking reaction (Robert, 1997)

On the other hand, chain scission process take place with crosslinking as an effect of irradiation in the amorphous regions. Polymer molecules in solid state tend to form two free radicals so that the resultant chain must mitigate against the permanent scission. This concept can be explained by the increasing yields in amorphous phase compared to crystalline polymers. The plasticity and structural strength has been decreased during the chain scission reaction. This is because carbon dioxide may be trapped in the polymer which leads to cracking due to high accumulation of local stresses (Robert, 1997). Free radicals will be formed by exciting the macromolecules of polymer during the ionization radiation. These free radicals may affect the behaviour of polymer chain by combining with the presence of oxygen, resulting formation of peroxides (Robert, 1997).

Electron beam and gamma rays are widely used processing type of ionization radiations for improving the mechanical properties of polymer nanocomposite. E-beam radiation is a form of ionizing energy which is generally characterized as low penetration and high dosage rates. The beam which consists of highly charged electrons are produced by the conversion of electricity. The energy that is absorbed is known as absorbed dose. This absorption energy is for altering the chemical bonds of the polymer (Sterigenics.com, 2015). In fact, the principal function of E-beam radiation is similar to gamma processing.

2.5.1 Degree of Crystallinity

The degree of crystallinity would be increased with increasing radiation dosages due to more amorphous chains are scissioned by crosslinking effect so as to promote

recrystallization. The crystallization region which consists of more chains are more oriented and tightly packed order compared to the amorphous regions. The polymer chains in the crystalline structures are tends to trap free radicals and recombine, thus reducing the number of chain scission. This effect is known as ‘cage effect’.

From the study of Nouh and Bahareth (2012), the degree of crystallinity increases up to a maximum value of 95 kGy electron beam dose, followed by decrease with increasing electron beam dose up to 210 kGy. The number of entanglements has been reduced by crosslinking in order to increase the chain mobility, resulting recrystallization. On the other hand, crystallinity decreased by increasing the electron beam dose is due to the highly ordered crystalline structure has been destroyed by occurrence of chain scissioning. Furthermore, presence of strain on the crystals has been implied by the increasing of crosslinking in the polymer network, resulting formation of three-dimensional network of chains (Ali, Ali and Hosam, 2008).

The similar results of Nouh and Bahareth also can be found in the report by Bee et al (2014), the crystallinity and crystallite size increase up to a maximum electron beam dose of 16k Gy of 0 MMT loading level, followed by decrease in increasing electron beam dose. Moreover, adding of MMT into PVOH matrix also increased the crystallinity due to the formation of crosslinking which have caused the PVOH chains arranged in an ordered arrangement in the amorphous region of PVOH matrix. Therefore, the highly ordered crystallite structures have formed. Increasing of MMT into PVOH matrix would cause decrease of crystallinity due to the MMT tend to agglomerate together to form larger aggregates particle, thus slow down the kinetics of crystallization. (Ali, Ali and Hosam, 2008)

2.5.2 Properties

The mechanical properties such as tensile strength, elongation and thermal properties are mainly depend on molecular weight and intermolecular interaction bonding forces of crosslinks. The changes of molecular weight are highly related to chain scission or crosslinking reaction which induced by irradiation. Crosslinking will result increase of molecular weight whereas chain scission will result decrease in molecular weight.

From the report of Bee et al (2004), electron irradiation induced the chains into the polymer matrix to form crosslinking network. It was found that the tensile

strength has been improved at the irradiation dosage of 16Gky, whereas the tensile strength was decreased with further increased of irradiation dosage. This can be explained that the entanglement chains are arranged in ordered form with the presence of crosslinking network, thus the tensile strength has been enhanced. On the other hand, increasing of irradiation dosage will cause rupture of PVOH due to the 'attack' by excessive free radicals. Moreover, amount of MMT loading is another factor which affects the tensile strength of PVOH-MMT. MMT content which exceeded 2.5 phr according to Bee et al had resulted in decreasing of tensile strength. This is because the free movement for the irradiation to attack the polymer chain for forming crosslinking network has been restricted by the high amount of MMT.

Meanwhile, some of the reports have investigated that the elongation of pure PVOH is highest compared to polymer nanocomposite. This is mainly due to absent of entangles polymer chains which causes restriction movement of sliding freely during extension. From the study of Bee et al (2004), the formation of crosslinking network induced by electron irradiation has caused restriction movement chains sliding capability, resulting decrease of elongation. However, the elongation was found that has higher value with increasing of irradiation dose. This is due to the chain scission process produce low molecular weight compound which turns the polymer chains become shorter in amorphous phase. Therefore, the short polymer chains act as the chain slider for providing easier movement of the polymer matrix under restricted free condition.

Thermal properties is mainly depends on the molecular weight by the crosslinking process. Increasing of irradiation dosage results decreasing of molecular weight which provides more flexible and movable movements of the polymer matrix, thus the thermal is unstable resulting in low melting point (Milicevic et al., 2007). According to Milicevic et al (2007), the annealing treatment has affected decrease the concentration of free radicals and chain scissions on irradiated polymer, thus it had a great impact on thermal properties.

Thermal properties were also affected by the degree of crystallinity where the melting point is decreased due to decrease of crystal size with high irradiation dosage. Decreasing in crystal size is mainly due to the crystallinity damage which has been attacked and destroyed by the peroxy free radicals with restricting the crystal interface moving towards to the core of crystal (Loo, Ooi and Boey, 2005). This theory can be proved by Ali, Ali and Hosam (2008) report, the melting point of

PVOH/VXG was decreased from 226°C to 261°C compared to unirradiated polymer with increasing of irradiation dosage.

2.5.3 Morphology

The morphological properties of polymer nanocomposites are highly influenced by the changes of molecular weight when subjected to irradiation. There are some factor that affects the surface morphology which is the degree of crystallinity between amorphous phase and crystalline region of PVOH-MMT-CNT. According to Milicevic et al (2007), decreasing of degree of crystallinity leads to decrease of crystal size, which due to the introduction of crystal defects. Introduction of crystal defects state that increasing in crystallinity can attribute scission of strained molecules and increase in lamellar thickness on the surface of crystalline phase. The degree of crystallinity can be altered by the radiation dosage and the structure of chains (Milicevic et al., 2007).

The decrease of molecular weight is due to the backbone main chain scission in the amorphous region. The long backbone breaks into shorter chains due to the radiation energy has exceeded the attractive forces between the atoms. Moreover, molecular weight decreases with increasing of dosage number which is caused by chain scission due to formation of radical. Chain scission is a dominant effect of irradiation which has a consequence of growing new thin crystal lamellae due to higher absorbed doses (Milicevic et al., 2007).

From the report of Bee et al (2004), the width of fibrils was found to be increased and orientated straightly and parallel to each other with increasing irradiation dosage from 6kGy to 16kGy. On the other hand, the fibrils with was decreased with further high irradiation dosage due to the formation of crosslinking in PVOH which leads to increase the matrix continuities. Moreover, the intercalation and dispersion effect of MMT in PVOH matrix can be enhanced by the crosslinking network from radiation by reducing the agglomeration effect of MMT particles.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Materials

Polyvinyl alcohol (PVOH) grade 325 manufactured by Sekisui Chemical Co. Ltd and Nanoclay Montmorillonite (MMT) was purchased from Timlewis (M) Sdn. Bhd. PVOH-MMT was used as base polymer in this study. Multi-walled carbon nanotube (MCNTs) with diameter of 50 nm was supplied from Ant Spirits Sdn Bhd and used as enforcing agent in this study.

3.2 Formulation

There were 12 samples prepared in this study with varies of CNTs and MMT in constant amount of PVOH as shown in Table 3.1. The constant amount of PVOH used was 100 phr. In other hand, MMT varied from 0, 2 and 4 phr and CNTs varied from 0.5, 1, 1.5 and 2 phr.

Table 3.1: Formulation of PVOH, MMT and CNTs

Polyvinyl alcohol (phr)	Montmorillonite (phr)	Carbon nanotube (phr)
100	0	0.5
100	0	1
100	0	1.5
100	0	2
100	2	0.5
100	2	1
100	2	1.5
100	2	2
100	4	0.5
100	4	1
100	4	1.5
100	4	2

3.3 Samples preparation

Solution casting method was used to prepare polyvinyl alcohol (PVOH) with montmorillonite (MMT) and carbon nanotube (CNTs) composite. During the preparation, 200 ml of distilled water was added into 20 g of PVOH as shown in Table 3.1 by stirring at the speed of 350 rpm with magnetic stirrer for 1 hour at room temperature, so as to form suspension solution. Next, 0.4 g of MMT sample was added slowly and continuously into the suspension solution. This process was stirred and heated to 90-95 °C with hot water bath for 1 hour until the homogenous mixture was formed. Furthermore, 0.1 g of CNTs was added slowly and continuously into the homogeneous solution. The mixture was then poured into 5 petri dishes and dried it to become porous scaffolds in the oven with temperature of 60°C for 1 day. The following different formulation samples were prepared by repeating the same steps. The samples were then sealed for storage at room temperature for conditioning purpose. Lastly, samples were irradiated by using electron beam irradiation with the irradiation dosages of 10 kGy, 20 kGy and 30 kGy at room temperature.

3.4 X-ray diffraction (XRD) Test

XRD test was performed to investigate the crystalline structure and morphology of samples. X-ray spectra was collected by using XRD-6000 Shimadzu X-ray diffractometer with Cu-K α radiation ($\lambda=1.5404$ Å) at 40 kV and 30 mA with the scanning rate of $1^\circ/min$. The range of samples scattering angles were $2\theta(0^\circ < \theta < 3^\circ)$. The d-spacing and inter-chain separation of CNT and CNT added PVOH-MMT were calculated according to the Bragg's formula ($=2d\sin\theta$). Samples were cut into 1cm x 1cm x 1cm and prepared in the form of thin films in order proceed to XRD scanning.

3.5 Scanning Electron Microscopy (SEM) test

SEM test was performed to observe the surface morphologies of the fractured samples by using the model of Hitachi Scanning Electronic Microscopy of BS 340 TESLA with a voltage of 20. Samples were cut into small portion with the length not more than 3 mm. The cut samples were placed and pasted on the copper stub with the fractured surface facing up. Moreover, these samples were coated with a thin layer of gold in order to proceed for scanning. The SEM photographs were observed and recorded under the microscopy at magnification of 500X, 1000X and 3000X.

3.6 Tensile Test

Mechanical properties were investigated by using Instron tensile machine. Samples were cut into 8cm X 0.6cm size. The tensile test was performed at the speed of 50mm/s, room temperature (25°C). The tensile strength and Young's modulus were recorded by using Bluehill software. The final value of tensile property strength and Young's Modulus for each sample were measured from the average of 5 specimens.

3.7 Fourier transformed infrared spectroscopy (FTIR)

The samples were investigated by using Nicolet iS10 FT-IR Spectrometer. The wavenumber range of the instruments is 400 - 4000 cm^{-1} , with the accuracy better than $\pm 4 cm^{-1}$.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Mechanical Properties Analysis

The mechanical properties of samples are mainly depends on the dispersion of filler with the matrix and distance between the crosslinking points and crosslinking structure. The presence of CNTs and EB-irradiation had highly effected on the mechanical properties such as tensile strength and Young's modulus.

4.1.1 Tensile Strength

By referring to *Figure 4.1*, the tensile test for non-irradiated PVOH-MMT-CNT nanocomposites has gradually increased with increasing of MMT up to 2 phr. This might be due to the presence of O-H functional group with hydrophilic behaviour in PVOH matrix which could well interact with the hydrophilic end of MMT particles. This also indicates that the addition of low amount of MMT particles with hydrophilic characteristics in PVOH matrix could effectively interact with O-H functional group by forming strong hydrogen bond in PVOH matrix. Besides, the increment of tensile strength is also attributed to the good dispersion and intercalation effect of MMT particles in PVOH matrix. This is because the PVOH matrix could effectively intercalate into the interlayer spacing of MMT particles as observed in XRD observation. The good intercalation effect of MMT in PVOH matrix could enable the stress acted on polymer matrix to be effectively transferred throughout whole polymer matrix. Thus, the tensile strength also significantly increased. However, when the loading level of MMT increased from 2 phr to 4 phr, the tensile strength decreased rapidly as shown in *Figure 4.1*. This is because of the particles of MMT tended to agglomerate with higher loading level due to poor dispersion and intercalation effect MMT particles in PVOH matrix. The agglomerate particles could reduce the tensile strength of PVOH nanocomposites by acting as stress concentration point in PVOH matrix when subjected to straining, subsequently weaken the tensile strength of PVOH matrix.

The increasing of CNT loading level from 0.5 to 1.5 phr into PVOH matrix has gradually increased of tensile strength of PVOH nanocomposites as shown in *Figure 4.1*. This is because the good dispersion effect of CNT particles could provide

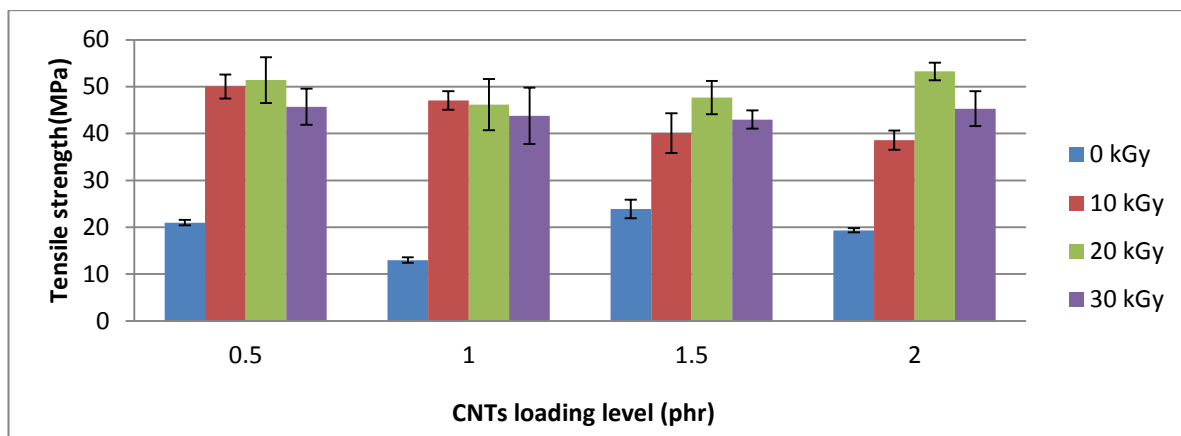
reinforcement effect to PVOH matrix by strengthening the structure of PVOH matrix. Thus, this can be further proved by the reduction wavenumber of C-H stretching as discussed in FTIR analysis. Besides, the good dispersion between CNT particles and polymer matrix has significantly induced the stress applied to PVOH matrix to be effectively and evenly transferred to whole polymer matrix when subjected to drawing and thus induce the resistant ability of PVOH matrix during drawing. By referring to *Figure 4.1*, the tensile strength rapidly decreased when higher amount of CNT added into PVOH-MMT matrix. The decrement was mainly due to agglomeration of CNT particles tended to reduce the interfacial adhesion effect within PVOH-MMT matrix. The agglomerated CNT particles could hinder the transfer of the stress acted on PVOH matrix from CNT particles to whole polymer matrix and weaken the strength of polymer matrix.

On the other hand, the application of electron beam irradiation up to 10 kGy has highly improved the tensile strength in *Figure 4.1*. This also indicates that the application of low irradiation dosage (≤ 10 kGy) could significantly induce the tensile strength of all PVOH-MMT-CNT nanocomposites by introducing the formation of crosslinking. This is due to the crosslinking networks formed by low electron beam irradiation could further improve the interaction effect between the MMT and CNT particles with PVOH matrix. The crosslinking networks could enable the applied straining stress to be evenly and effectively transferred from PVOH matrix to the particles and thus increase the tensile strength of PVOH-MMT-CNT nanocomposites (Bee et al., 2014). From Bee et al, 2017, the formation of crosslinking network within PVOH matrix could resist the chain movement when subjected to extension, resulting improvement of mechanical properties. Furthermore, the structure of the PVOH entangled chains tended to rearrange in sequential form by the formation of crosslinking network at lower irradiation dosage. Whereas, the long polymer chain of PVOH tended to breakdown into shorter chains when subjected to higher irradiation dosage (<30 kGy). The deterioration of tensile strength for PVOH-MMT-CNT nanocomposites might be due to the occurrence of chain scissioning reaction in PVOH matrix. This is because the available amounts of O-H groups in PVOH matrix to generate free radicals was significantly reduced and caused the electrons (released by accelerator) tended to attack the C-H bonds to generate free radicals. Thus, the tensile strength has gradually decreased at higher irradiation dosage.

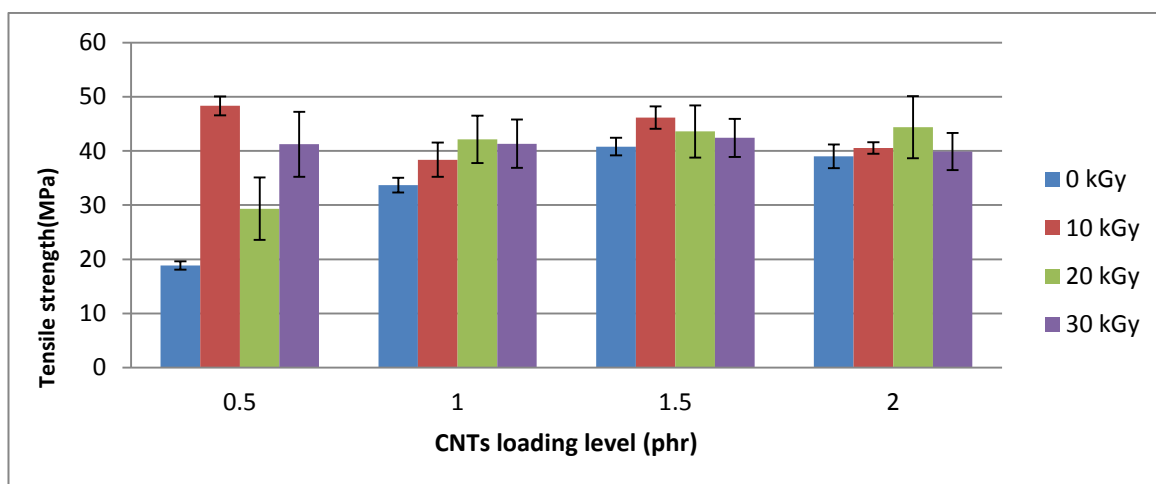
4.1.2 Young's Modulus

For non-irradiated PVOH-MMT-CNT nanocomposites, the Young's modulus has gradually increased when loading level of MMT increased from 0 to 2 phr as shown in *Figure 4.2 (a) to (c)*. This might be due to the presence of MMT with hydrophilic characteristics could form hydrogen bonding with the hydrophilic O-H functional group of PVOH chains within the polymer matrix. Moreover, the low loading level of MMT particles in PVOH matrix could further induce the rigidity of PVOH matrix due to its good dispersion and intercalation effect in PVOH matrix. The good dispersion of MMT particles could induce the interfacial adhesion between MMT and PVOH matrix which the PVOH matrix could effectively intercalate into interlayer galleries of MMT particles. As results, the stress acted on PVOH matrix can be effectively transferred and absorbed by. The MMT particles in PVOH matrix and thus induced the rigidity of PVOH-MMT-CNT. On the other hand, it can also be observed that the Young's Modulus of PVOH-MMT-CNT nanocomposites posed similar pattern to tensile strength when added with higher loading level of MMT.

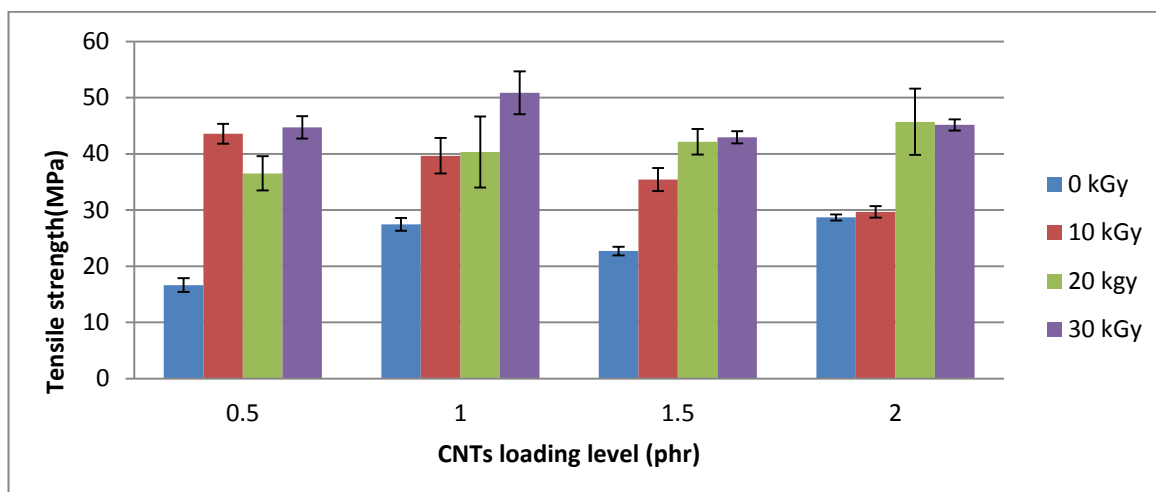
By referring to *Figure 4.2*, it was found that the Young's Modulus of 4 phr MMT added PVOH-MMT-CNT nanocomposites (0.5 phr CNT and 2 phr CNT) have gradually increased with increasing of irradiation dosage up to 30 kGy. The increment of Young's modulus indicates that the formation of crosslinking by electron beam irradiation could induce the structural rearrangement of polymer chain, resulting formation of highly rigid crystal structure in PVOH matrix. Hence, the rigidity of PVOH-MMT-CNT nanocomposites has been highly enhanced by the formation of rigid crystal structure.



(a)

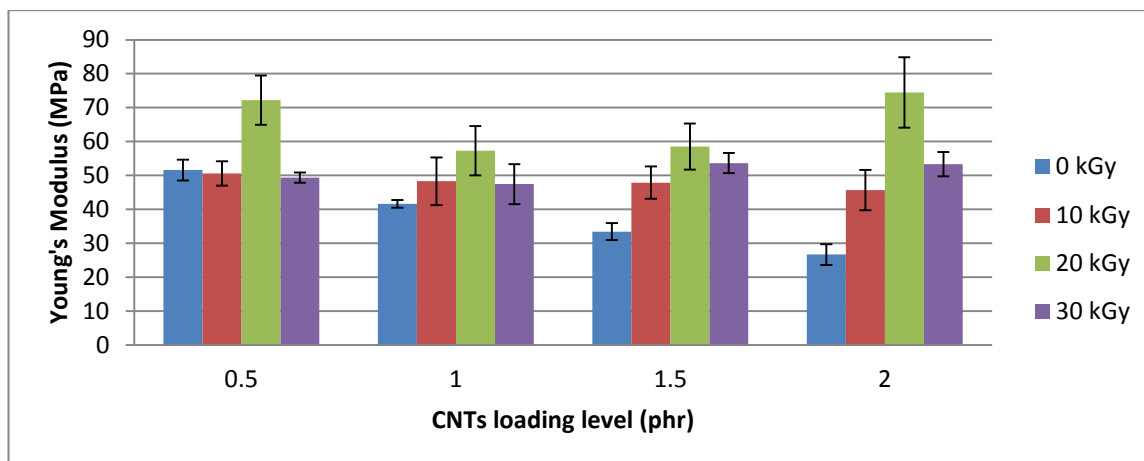


(b)

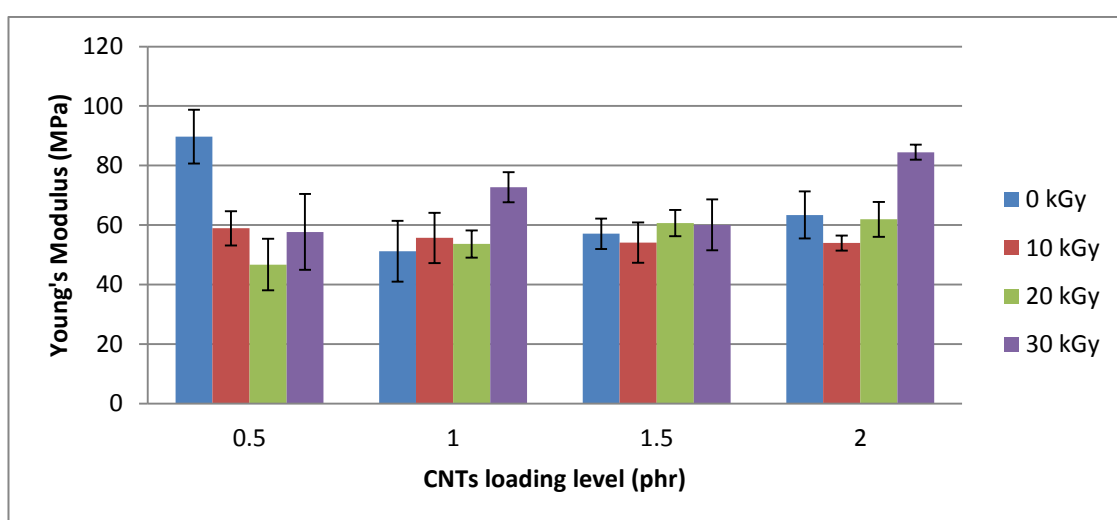


(c)

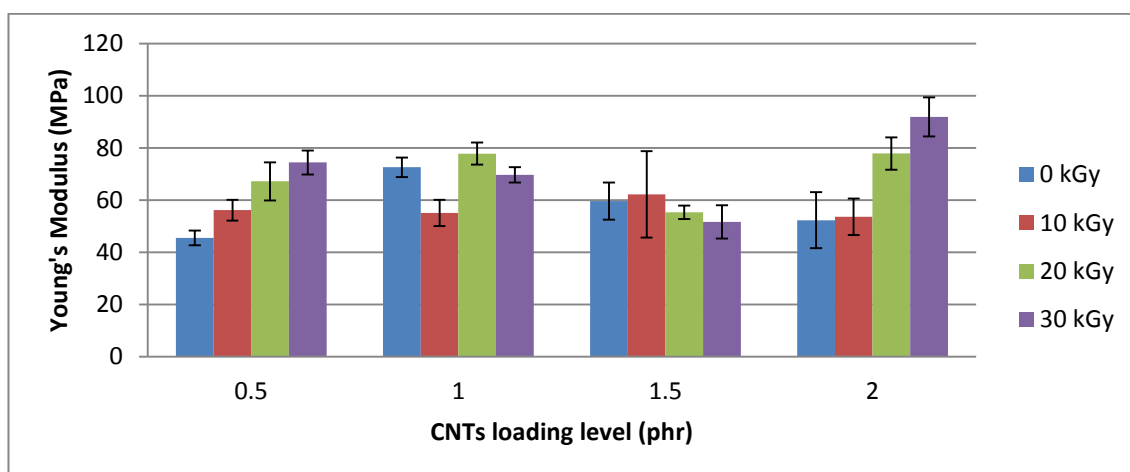
Figure 4.1: Tensile strength of PVOH nanocomposites with different CNT loading level under various irradiation dosages: (a) 0MMT, (b) 2 MMT, (c) 4 MMT



(a)



(b)



(c)

Figure 4.2: Young's modulus of PVOH nanocomposites with different CNT loading level under various irradiation dosages: (a) 0MMT, (b) 2 MMT, (c) 4 MMT

4.2 Scanning Electron Microscopy (SEM)

Figures 4.3 and *4.4* show the SEM micrographs of various loading levels of MMT and CNT added PVOH nanocomposites. Fibrils were found in the fractured surface of PVOH matrix for all non-irradiated and irradiated PVOH nanocomposites. Formation of fibrils was mainly due to the straining stress applied on PVOH matrix during tensile test. By referring to *Figure 4.3 (a)*, it was observed that the tearing effect on the polymer matrix of non-MMT added PVOH-CNT nanocomposites was elongated continuously when subjected to extension. However, from *Figure 4.3 (b)* the morphology with presence of MMT in PVOH-CNT matrix was observed to have no elongation effect when subjected to straining stress. This also indicates that the rigidity behaviour of PVOH nanocomposites when added with MMT particles. Meanwhile, the agglomeration of MMT particles can be significantly seen in PVOH matrix when the MMT loading level increased from 2 phr to 4 phr. This is mainly due to the poor dispersion and poor intercalation effect between MMT particles with PVOH matrix. This observation can be proved by the severe decrement in tensile strength as shown in tensile analysis. By referring to *Figure 4.3 (d-f)*, more fibrils can be seen with high loading level of CNT compared to low loading level of CNT. The structure with high loading level of CNT and 2 phr MMT was observed to have a smoother surface and thicker width of fibrils as shown in *Figure 4.3 (e)*. This is because the hydrophilic characteristic of MMT could enhance the dispersion of CNT particles by promoting double reinforcement effect on the properties of PVOH-MMT-CNT nanocomposites. Besides, the fracture surface from *Figure 4.3 (f)* was found not as smooth as compared to *Figure 4.3 (e)* when loading level of MMT and CNT increased. This was mainly due to excess of MMT particles could not interact effectively with CNT particles, resulting formation of agglomeration. The agglomerate particles would act as a weak point by reducing the tensile strength as discussed earlier in tensile analysis.

The fracture surface morphology of PVOH-MMT-CNT nanocomposites at various irradiation dosages are shown in *Figure 4.4*. By referring to *Figure 4.4 (a-b)*, the fibrils were seen to be in orientated form and parallel to each other when subjected to low irradiation dosage. Furthermore, the width of fibrils for irradiated PVOH nanocomposites was thicker compared to non-irradiated PVOH nanocomposites. This indicates the application of electron beam irradiation could induce the formation of crosslinking network in PVOH matrix. Besides, the

dispersion and intercalation effect of CNT could highly enhance by the formation of crosslinking network, resulting increment effect in mechanical properties as discussed in tensile analysis. However, the fracture surface morphology of PVOH matrix was seen to degrade when higher irradiation dosage is applied as shown in *Figure 4.4(c-d)*. This might be due to the occurrence of chain scissioning effect by the application of electron beam irradiation. The agglomeration of CNT particles in PVOH matrix was observed in *Figure 4.4 (b)*. This observation is similar to the result for non-irradiated samples as discuss earlier (*Figure 4.3 (d-f)*). However, the size of CNT agglomerated particles in *Figure 4.4 (c)* and *(d)* is found to be smaller when subjected to irradiation. This is because formation of crosslinking network could enhance the intercalation and dispersion effect within PVOH matrix and CNT particles. Thus, the agglomeration effect of CNT particles in PVOH matrix has highly reduced by application of electron beam irradiation.

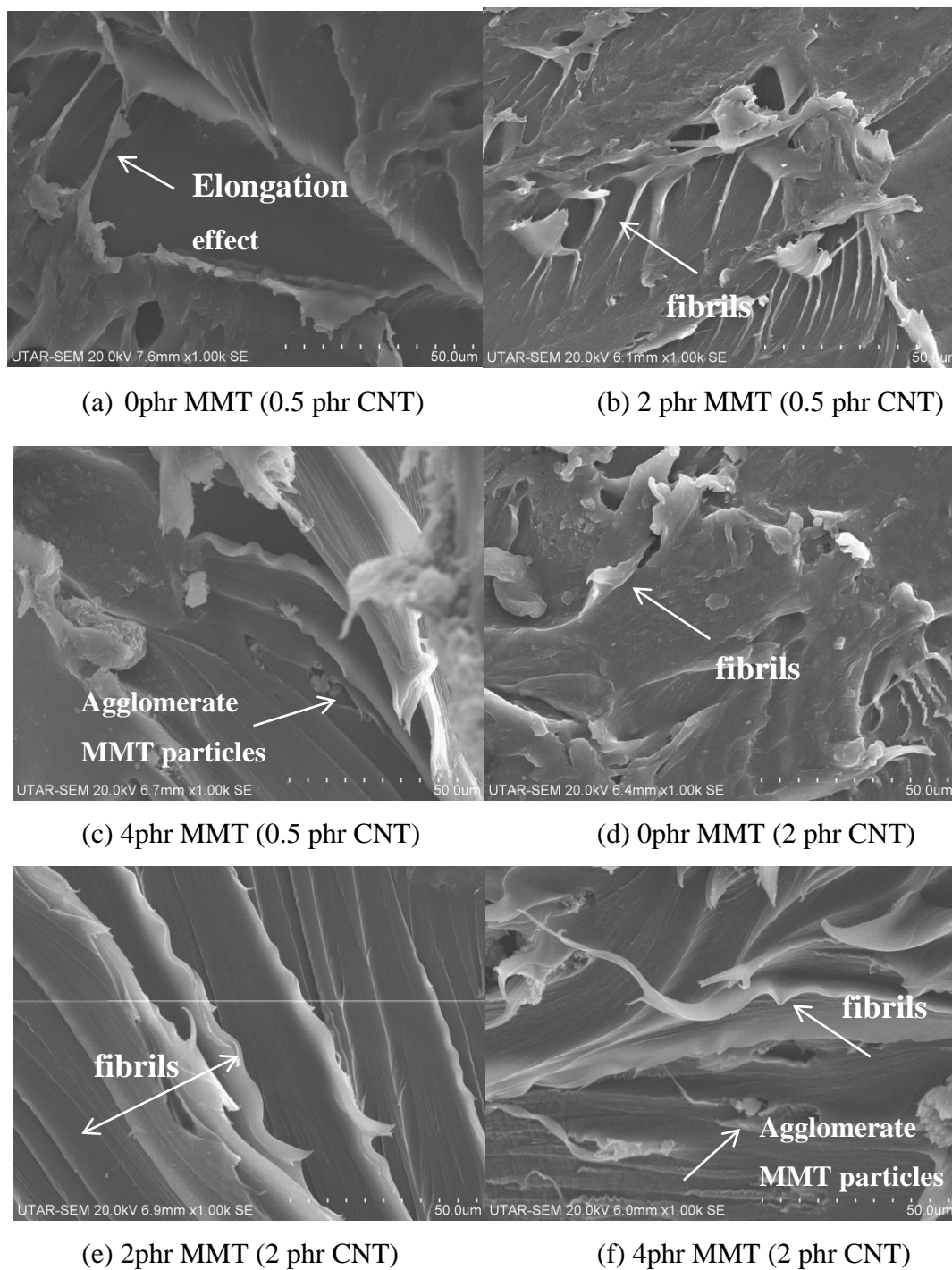
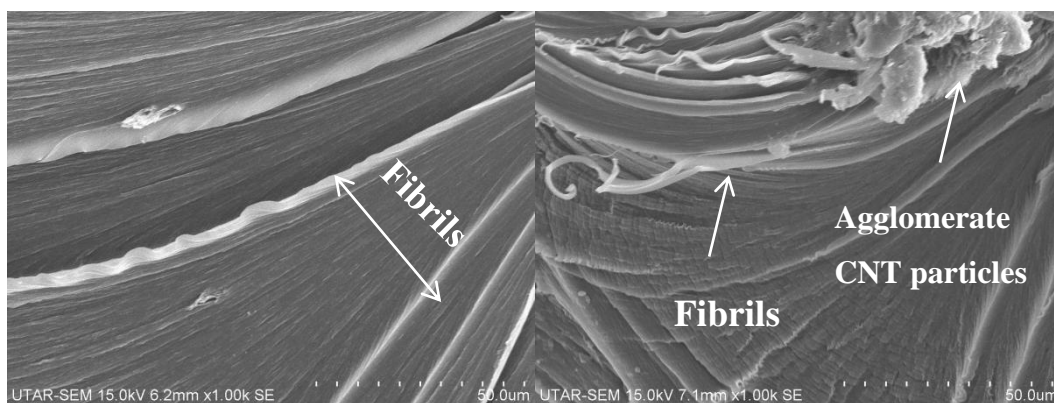
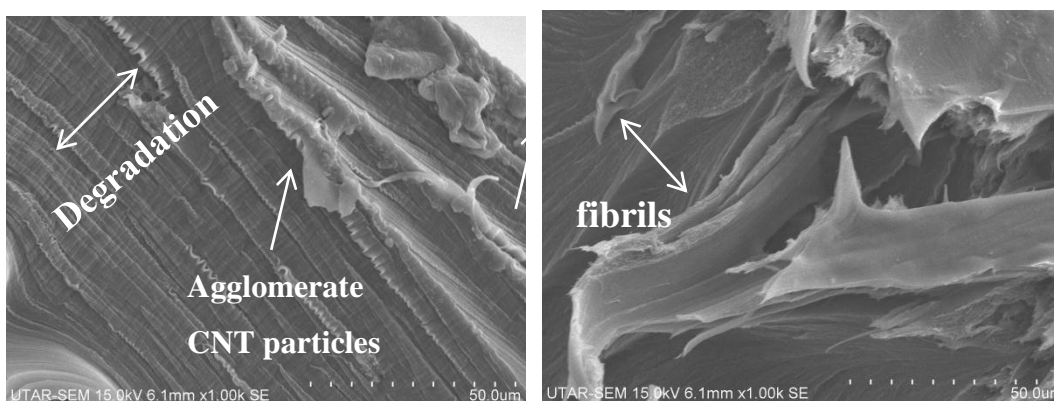


Figure 4.3: SEM morphologies of non-irradiated PVOH nanocomposites: (a-c) various loading level of MMT at low loading level of CNT and (d-e) Various loading level of MMT at high loading level of CNT



(a) 10 kGy (0phr MMT and 0.5phr CNT) (b) 10 kGy (0phr MMT and 2phr CNT)



(c) 30 kGy (0phr MMT and 0.5phr CNT) (d) 30 kGy (0phr MMT and 2phr CNT)

Figure 4.4: SEM morphologies of irradiated PVOH nanocomposites with different loading level of CNT: (a-b) 10 kGy and (c-d) 30 kGy

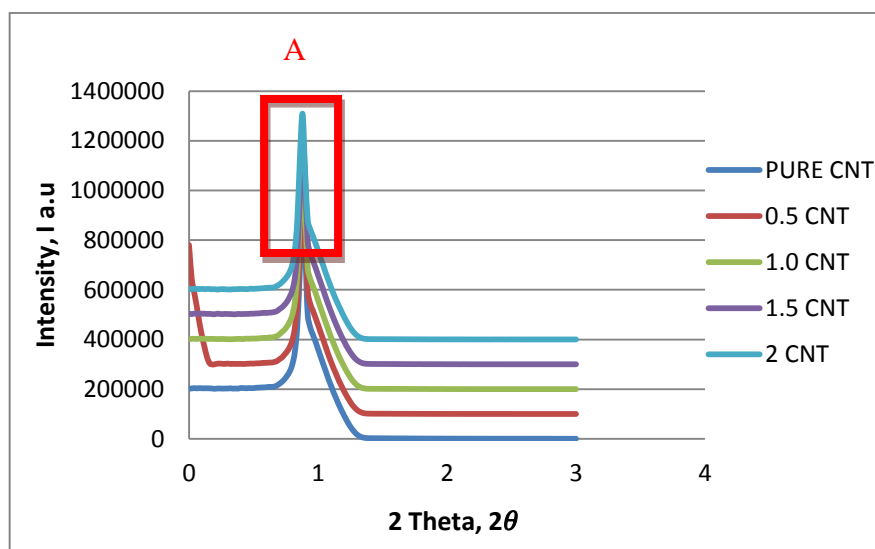
4.3 X-Ray Diffraction (XRD) Study

The XRD pattern of all PVOH-MMT-CNT when subjects to various irradiation dosages (0 kGy, 10 kGy, 20 kGy and 30 kGy) as shown in *Figures 4.1 to 4.2*. The 2θ , d-spacing and inter-chain separation of deflection peak (002) are summarized in *Tables 4.1 to 4.3*.

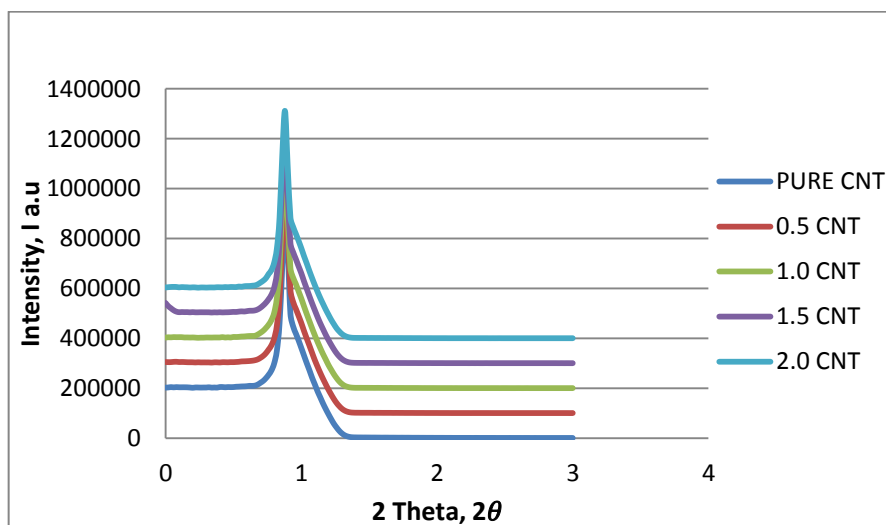
By referring to *Figure 4.5*, a significant, sharp deflection peak A can be observed to occur on XRD curves of all PVOH-MMT-CNT nanocomposites at 2θ range of 0.89° to 1.25° . The increasing of loading level of CNT was observed to pose an insignificant effect on the shifting of 2θ value for deflection peak A of all non-irradiated nanocomposites as shown in *Figure 4.5*. This indicates that the increasing of CNT amounts did not provide significant effect in promoting the dispersion state of CNT particles in polymer matrix of PVOH-MMT-CNT nanocomposites (Bee et

al., 2014). This can be further confirmed with the calculated d-spacing and inter-chain separation of all non-irradiated PVOH-MMT-CNT nanocomposites as tabulated in *Table 1*. The d-spacing and inter-chain separation values of non-irradiated nanocomposites were found to pose an insignificant change with increasing of CNT amounts. From *Tables 1* to *3*, the addition of MMT particles or CNT particles into PVOH matrix was observed to significantly increase the calculated d-spacing and inter-chain separation values of non-irradiated PVOH-MMT-CNT nanocomposites. This also indicates that the good dispersion of CNT and MMT particles in PVOH matrix has caused the intercalation of CNT and MMT particles in PVOH matrix and thus induced the interlayer spacing of MMT and CNT particles (Bee et al., 2017).

On the other hand, the deflection peak A of all irradiated 2 phr and 4 phr MMT added PVOH-CNT nanocomposites in *Figure 4.6 (c)* and *(d)* were slightly shifted to higher 2θ compare to non-irradiated samples. At higher irradiation dosages, the formation of crosslinking networks also found to pose insignificant effect in improving the effective numbers of intercalated CNT and MMT particles. Furthermore, increasing of MMT loading level was significantly induced the d-spacing and inter-chain separation of deflection peak A of all irradiated PVOH-MMT-CNT nanocomposites. The increment of d-spacing exhibited that the higher irradiation dosages could chain scission the PVOH macromolecular chains and weaken the tightening effect of crosslinking. Subsequently, the inter-planar spacing and inter-chains separation was slightly increased.

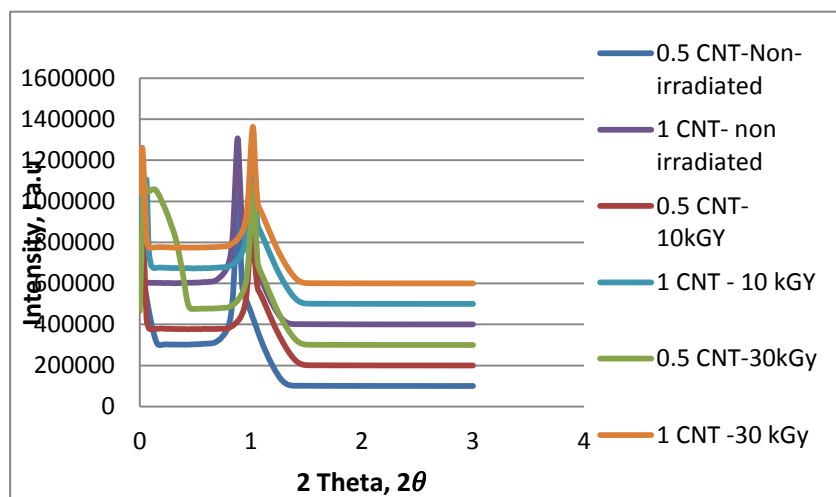


(a)

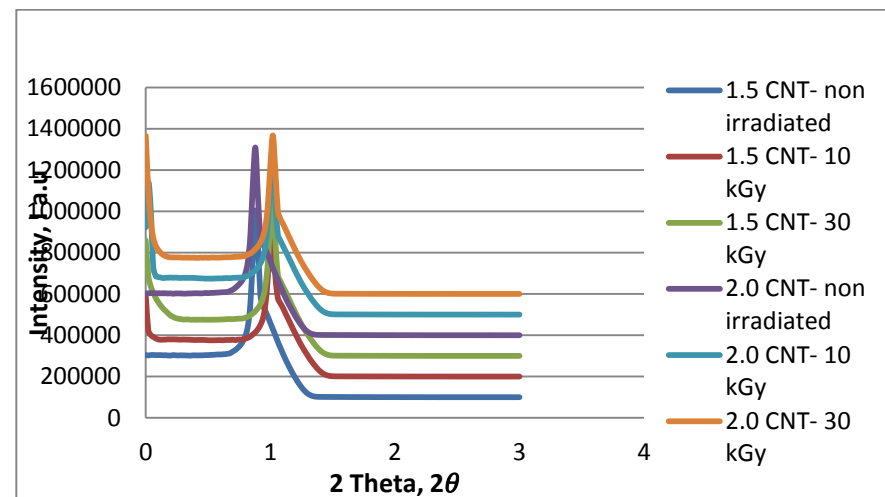


(b)

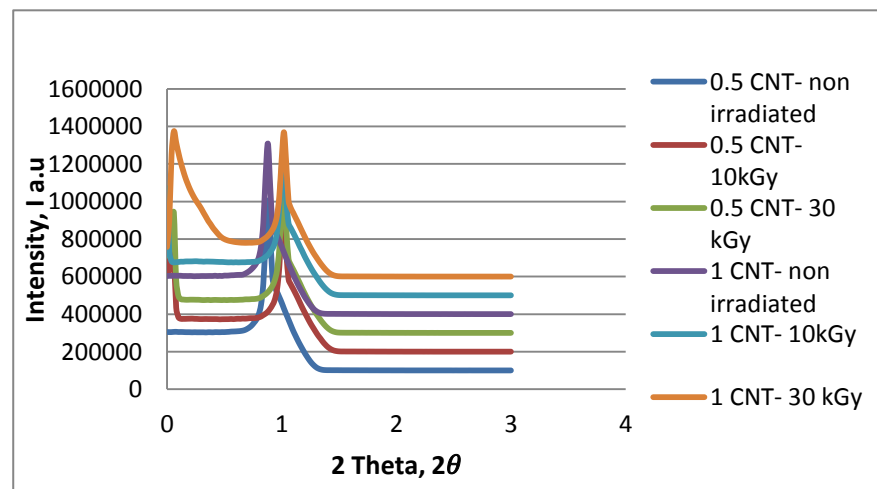
Figure 4.5: XRD analysis of non-irradiated samples of various loading level of MMT and different loading of CNT (pure, 0.5, 1, 1.5 and 2 phr): (a) 2 phr MMT (b) 4 phr MMT



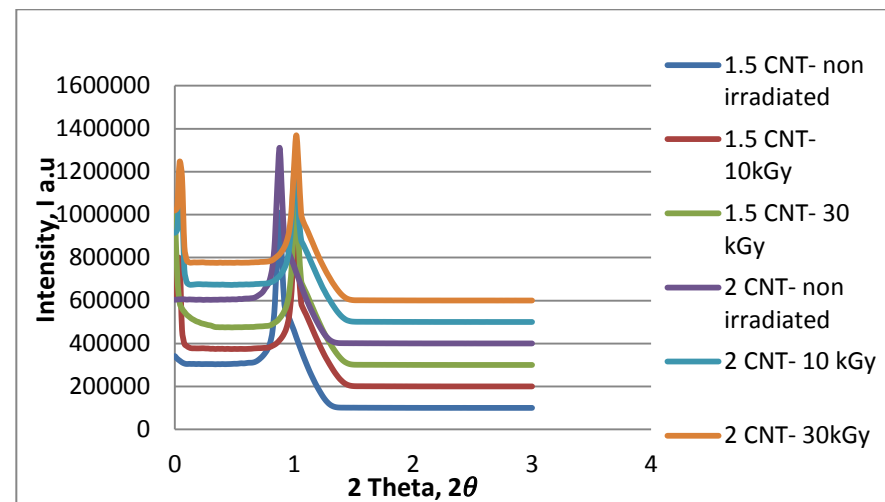
(a)



(b)



(c)



(d)

Figure 4.6: XRD analysis of non-irradiated samples and irradiated samples: (a) 2 phr MMT vary 0.5 and 1 phr CNT, (b) 2 phr MMT vary 1.5 and 2 phr CNT, (c) 4 phr MMT vary 0.5 and 1 phr CNT, (d) 4 phr MMT vary 1.5 and 2 phr CNT

Table 4.1: Inter-chain separation and d-spacing of 0 phr MMT and different loading level CNT added into PVOH composites at different irradiation dosages

Loading level of MMT, phr	Loading level of CNT, phr	Irradiation dosage, kGy	$2\theta, ^\circ$	d-spacing, Å	Inter-chain separation, Å
MMT	-	-	1.2458	70.900	88.53
-	CNT	-	0.9112	96.873	121.04
0	0.5	0	0.8990	98.188	122.69
		10	1.0281	85.858	107.28
		20	1.0369	85.130	106.37
		30	1.0245	86.160	107.66
	1.0	0	0.8918	98.980	123.68
		10	1.0263	86.009	107.47
		20	1.039	84.958	106.16
		30	1.0469	84.317	105.35
	1.5	0	0.8984	98.253	122.77
		10	1.0255	86.076	107.55
		20	1.0344	85.336	106.63
		30	1.0369	85.130	106.37
	2.0	0	0.9018	97.883	122.31
		10	1.0300	85.675	107.08
		20	1.0438	84.567	105.67
		30	1.0288	85.800	107.21

Table 4.2: Inter-chain separation and d-spacing of 2 phr MMT and different loading level CNT added into PVOH composites at different irradiation dosages

Loading level of MMT, phr	Loading level of CNT, phr	Irradiation dosage, kGy	$2\theta, ^\circ$	d-spacing, Å	Inter-chain separation, Å
MMT	-	-	1.2458	70.900	88.53
-	CNT	-	0.9112	96.873	121.04
2	0.5	0	0.9014	97.926	122.36
		10	1.0364	85.171	106.42
		20	1.0381	85.031	106.25
		30	1.0440	84.551	1.0440
	1.0	0	0.8997	98.111	122.59
		10	1.0394	84.925	106.11
		20	1.0372	85.105	106.34
		30	1.0369	85.130	106.37
	1.5	0	0.8979	98.308	122.84
		10	1.0303	85.675	107.05
		20	1.0407	84.819	105.98
		30	1.0334	85.418	106.73
	2.0	0	0.9163	96.334	120.37
		10	1.0292	85.767	107.17
		20	1.0384	85.007	106.22
		30	1.0455	84.430	105.50

Table 4.3: Inter-chain separation and d-spacing of 4 phr MMT and different loading level CNT added into PVOH composites at different irradiation dosages

Loading level of MMT, phr	Loading level of CNT, phr	Irradiation dosage, kGy	$2\theta, ^\circ$	d-spacing, Å	Inter-chain separation, Å
MMT	-	-	1.2458	70.900	88.53
-	CNT	-	0.9112	96.873	121.04
4	0.5	0	0.9008	97.992	122.44
		10	1.0315	85.575	106.93
		20	1.0256	86.068	107.54
	1.0	0	0.9049	97.548	121.89
		10	1.0395	84.917	106.10
		20	1.0392	84.941	106.14
	1.5	0	1.028	85.867	107.29
		10	1.028	85.867	107.29
		20	1.0387	84.982	106.19
	2.0	0	0.8963	98.484	123.06
		10	1.0342	85.352	106.65
		20	1.0369	85.130	106.37
30		1.0414	84.762	105.91	

4.4 Fourier Transform Infrared (FTIR) Spectroscopy

Figure 4.7 shows the infrared spectrum of the non-irradiated PVOH-MMT nanocomposites added with different CNT loading levels. By observing to *Figure 4.7*, a broad and significant peak was found to occur on FTIR spectrum of all the samples at the wavenumber range of 3200-3300 cm^{-1} . This wavenumber band is known as the O-H stretching of functional hydroxyl group. By referring to *Figure 4.7*, the increasing of CNT loading level up to 2 phr has slightly shift to higher wavenumber. This observation can be further proved with the summarized of wavenumber O-H bond as shown in *Table 4.4*. From *Table 4.4*, the wavenumber of O-H stretching has slightly increased from 3264.71 to 3266.45 cm^{-1} when the CNT loading level increased to 1 phr. The increment in the wavenumber of O-H stretching is mainly due to the addition of CNT particles with hydrophobic behavior could disturb the presence of hydrogen bonding in PVOH with hydrophilic behavior. Thus, higher CNT loading level could reduce the hydrophilic nature of PVOH by weakening the hydrogen bonding the PVOH matrix. However, when the CNT loading level was further increased from 1 phr to 2 phr, the O-H wavenumber was marginally reduced to 3265.10 cm^{-1} as shown in *Table 4.4*. The CNT particle tended to agglomerate together at higher loading level due to poor dispersion and interaction effect of CNT particles with PVOH. The agglomeration of CNT particles has slightly weakened the dispersion and interaction of CNT particles with PVOH matrix, and thus the presence of hydrogen bonding in PVOH matrix was also slightly induced (Lee et al., 2016).

Besides that, the C-H stretching can be observed to occur at the region of 2900 cm^{-1} as shown in *Figure 4.7*. The increasing of CNT loading level up to 2 phr has slightly decreased the wavenumber of C-H stretching from 2922.67 to 2920.67 cm^{-1} . This result can be observed from the as summarized in *Table 4.4*. The reduction of wavenumber of C-H stretching indicates that addition of CNT particles can enhance the strength of C-H bonding inside the PVOH matrix by strengthening the structure of PVOH. Thus, the addition of CNT has significantly improved the mechanical properties as discussed in tensile strength and Young's modulus.

Figure 4.8 illustrates the effect of electron beam irradiation on the FTIR spectrums of all PVOH-MMT added with different CNT loading level. By referring to *Figure 4.8*, the wavenumber of O-H stretching of all irradiated samples was slightly increased with increasing of CNT loading level. The wavenumber of O-H stretching has significantly increased from 3258.19 to 3261.06 cm^{-1} when CNT

amount increased from 0.5 phr to 1.5 phr as shown in *Table 4.5*. This also indicates that the addition of CNT particles could also weaken the hydrogen bonding of irradiated PVOH matrix as observed in the wavenumber O-H of non-irradiated PVOH samples. On the other hand, the application of electron beam irradiation has also slightly shifted the O-H stretching peak of all PVOH-MMT-CNT nanocomposites to lower wavenumber value as tabulated in *Table 4.5*. The increasing of irradiation dosage has gradually decreased the wavenumber of O-H stretching for 2 phr MMT with 1 phr CNT nanocomposites from 3266.79 to 3247.62 cm^{-1} . The application of electron beam irradiation has weakened the hydrogen bonding between the polymer chains in the PVOH matrix. This is due to the O-H group of PVOH chains have been attacked by the electrons released by electron beam accelerator to form polymeric free radicals. The generated polymeric free radicals tended to form the crosslinking networks in PVOH matrix by reacting together. Moreover, the reduction of O-H functional groups in PVOH matrix has significantly weakened the hydrogen bonding in PVOH matrix, resulting increased of O-H stretching (Bee et al., 2014).

By referring to *Figure 4.9(a-b)*, the wavenumber of C-H stretching was observed to significantly increase when electron beam irradiated up to 20 kGy. This can be proved by referring to *Table 4.6* where the wavenumber of C-H for 4 phr MMT with 2 phr CNT nanocomposites increased from 2921.77 to 2937.55 cm^{-1} . The increment of C-H stretching is due to the improvement in the strength of polymer structure of PVOH-MMT-CNT nanocomposites. The improvement of strength is mainly related to the formation of crosslinking networks within the polymer matrix. However, further increasing in electron beam irradiation dosages from 20 kGy to 30kGy has gradually reduced the wavenumber of C-H stretching for 4 phr MMT and 2 phr CNT nanocomposites to 2931.76 cm^{-1} . This explained that application of higher electron beam irradiation dosages has weakened the strength of polymer structure of PVOH matrix. This might be due to the chain scissioning reaction of PVOH chains is more likely to occur at higher irradiation dosage. This is because the availability of O-H groups in PVOH matrix was significantly reduced and caused the released electrons tended to attack the C-H bonds to generate polymeric free radicals. Subsequently, the C-H stretching in PVOH matrix has gradually reduced when irradiated to 30kGy

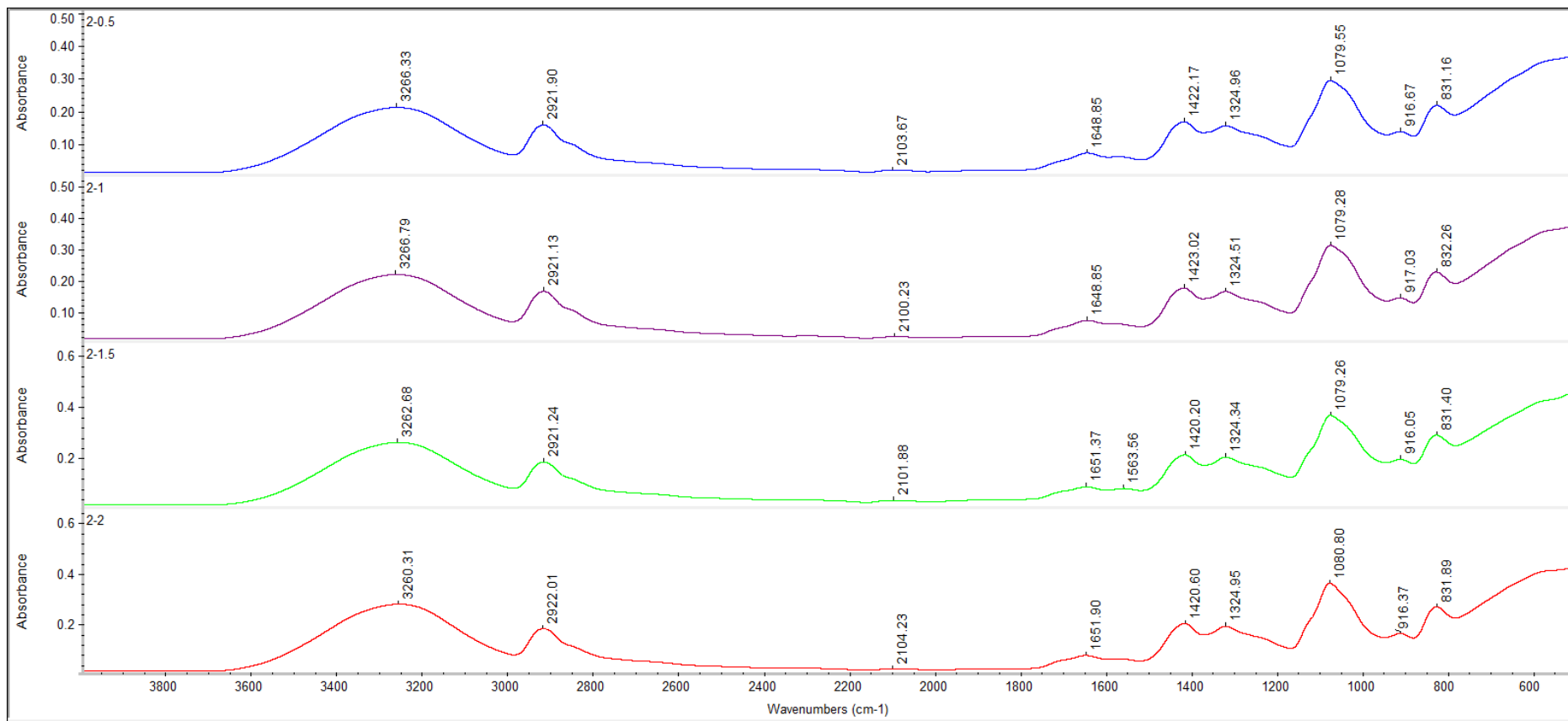


Figure 4.7: FTIR spectral of non-irradiated PVOH nanocomposites with 2 phr MMT and different loading level of CNT

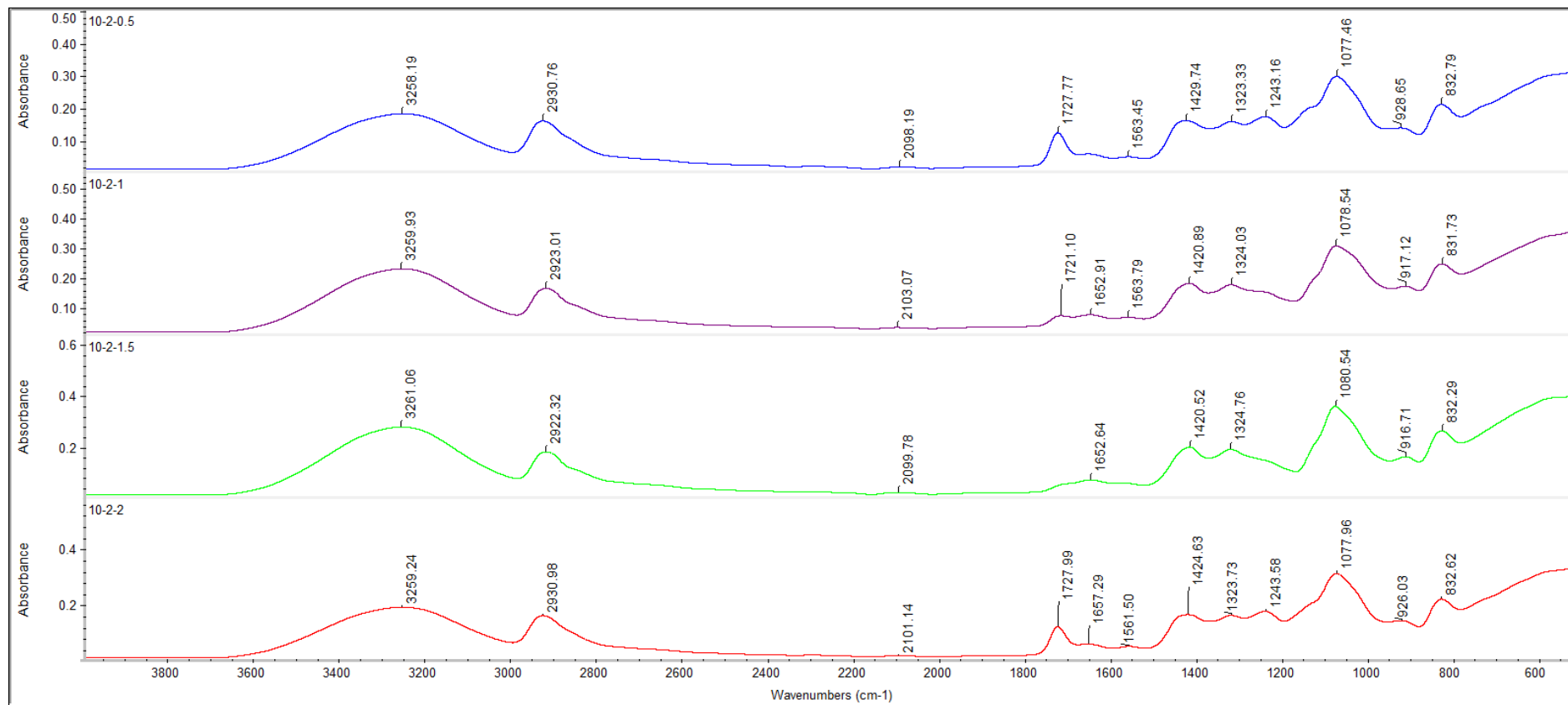
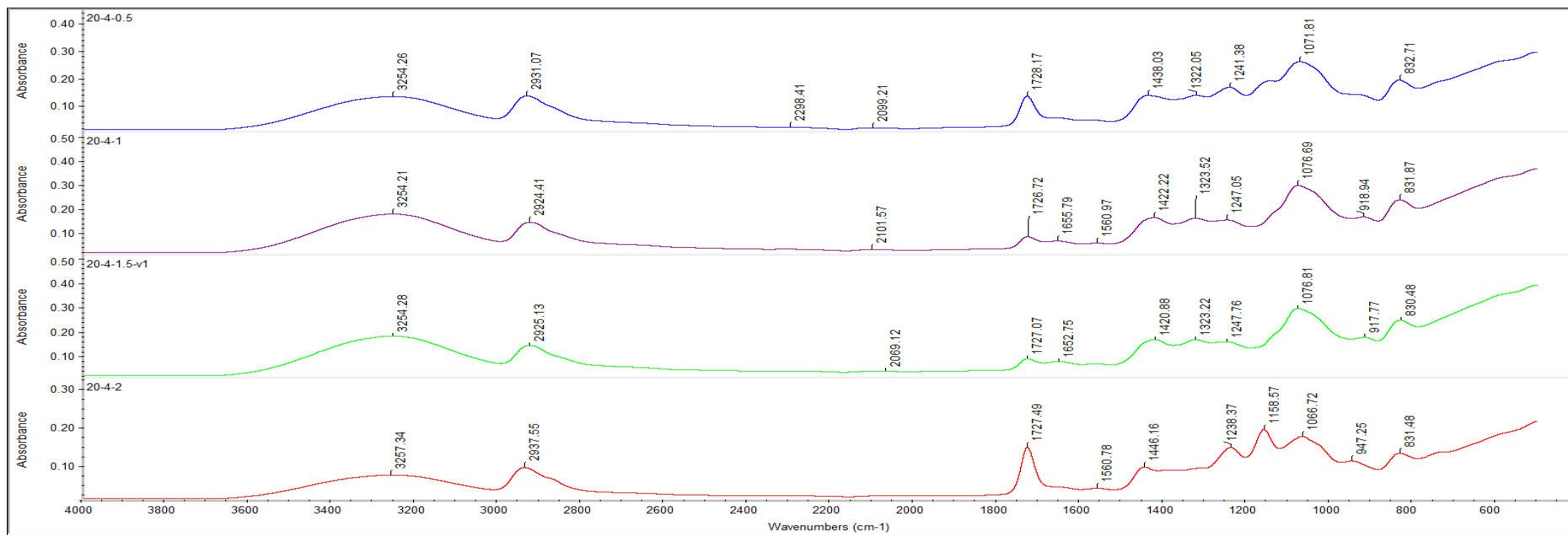
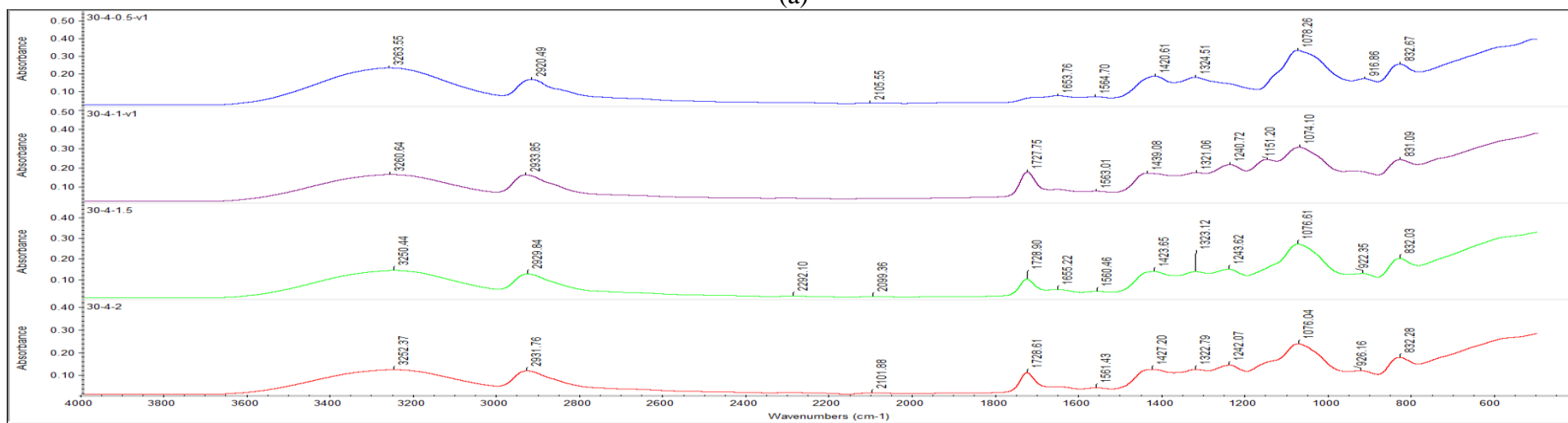


Figure 4.8: FTIR spectral of irradiated PVOH nanocomposites with 2 phr MMT and different loading level of CNT



(a)



(b)

Figure 4.9: FTIR spectral of PVOH nanocomposites for 4 phr MMT with different loading level of CNT under various irradiation dosages: (a) 20kGy and (b) 30kGy

Table 4.4: Wavenumbers of O-H and C-H stretching of non-MMT-PVOH nanocomposites added with various loading levels of CNT when subjected to increasing irradiation dosages

Loading level of MMT, phr	Loading level of CNT, phr	Irradiation dosage, kGy	Wavenumber	
			O-H stretching	C-H stretching
0	0.5	0	3264.71	2921.21
		10	3259.29	2921.66
		20	3258.24	2925.10
		30	3257.64	2922.67
	1.0	0	3266.45	2922.39
		10	3257.91	2923.93
		20	3266.20	2932.95
		30	3255.69	2933.48
	1.5	0	3266.12	2920.82
		10	3258.11	2924.94
		20	3257.67	2924.74
		30	3255.68	2924.80
2.0	0	3265.10	2920.67	
	10	3259.82	2921.73	
	20	3251.12	2922.49	
	30	3249.92	2922.17	

Table 4.5: Wavenumbers of O-H and C-H stretching of 2 phr MMT-PVOH nanocomposites added with various loading levels of CNT when subjected to increasing irradiation dosages

Loading level of MMT, phr	Loading level of CNT, phr	Irradiation dosage, kGy	Wavenumber	
			O-H stretching	C-H stretching
2	0.5	0	3266.33	2921.90
		10	3258.19	2930.73
		20	3255.51	2927.18
		30	3271.91	2946.03
	1.0	0	3266.79	2921.13
		10	3259.93	2923.01
		20	3257.75	2930.60
		30	3247.62	2930.24
	1.5	0	3262.68	2921.24
		10	3261.06	2922.32
		20	3249.57	2945.55
		30	3257.27	2943.41
	2.0	0	3260.31	2922.01
		10	3259.31	2930.98
		20	3259.24	2926.62
		30	3259.62	2949.84

Table 4.6: Wavenumbers of O-H and C-H stretching of 4 phr MMT-PVOH nanocomposites added with various loading levels of CNT when subjected to increasing irradiation dosages

Loading level of MMT, phr	Loading level of CNT, phr	Irradiation dosage, kGy	Wavenumber	
			O-H stretching	C-H stretching
4	0.5	0	3259.72	2922.82
		10	3276.18	2950.12
		20	3254.26	2931.07
		30	3263.55	2950.88
	1.0	0	3261.66	2922.53
		10	3260.88	2950.62
		20	3254.21	2924.41
		30	3250.44	2929.84
	1.5	0	3261.07	2922.10
		10	3257.97	2927.77
		20	3252.46	2945.22
		30	3279.32	2949.71
	2.0	0	3260.52	2921.77
		10	3259.52	2928.79
		20	3257.34	2937.55
		30	3252.37	2931.76

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study was conducted to investigate the effect of carbon nanotube under application of electron beam irradiation on polyvinyl alcohol-montmorillonite nanocomposite. In tensile test analysis, the tensile strength has significantly increased when low loading level of CNT was added into PVOH matrix without subjected to irradiation. This is because the good dispersion between CNT particles and polymer matrix has significantly induced the stress applied to PVOH matrix to be effectively and evenly transferred to whole polymer matrix when subjected to drawing. Thus, the resistance ability of PVOH matrix has been induced when subjected to straining stress. Meanwhile, the tensile strength has significantly reduced when high loading level of CNT was added into PVOH matrix. This can be explained because the agglomerates CNT particles tended to reduce the interfacial adhesion effect between CNT particles and PVOH matrix. The agglomerates CNT particles would act as a stress concentration point in PVOH matrix when subjected to extension. On the other hand, the tensile strength of PVOH-MMT-CNT nanocomposite has rapidly increased due to the formation of crosslinking network when subjected to irradiation. The crosslinking networks in PVOH matrix could resist the chain movement during extension, resulting improvement of mechanical properties. However, higher irradiation dosages would reduce the tensile strength due to the occurrence of chain scissioning reaction in PVOH matrix.

The morphology of PVOH-MMT nanocomposite with high loading level of CNT was seen to have more fibrils than low loading level of CNT. The structure via SEM analysis was also observed to have a smoother surface and thicker width of fibrils. This was mainly due to hydrophilic characteristic of MMT could enhance the dispersion of CNT particles by promoting double reinforcement effect on the properties of PVOH-MMT-CNT nanocomposites. However, the agglomeration of CNT and MMT particles were significantly observed when added with high loading level of MMT and CNT particles due to the poor dispersion and intercalation effect between the CNT particles and PVOH matrix. Besides, the fibrils were seen to be in orientated form and parallel to each other by the formation of crosslinking network in

PVOH matrix when subjected to low irradiation. However, the fracture surface morphology of PVOH matrix was seen to degrade when subjected to high irradiation dosage. This is mainly due to the occurrence of chain scissioning effect by the application of electron beam irradiation.

In XRD analysis, increasing of loading level of CNT particles did not provide significant effect in shifting the 2θ value for deflection peak (002) of all non-irradiated nanocomposite. This indicates the dispersion state of CNT particles in polymer matrix were severely reduced with increasing of CNT amounts. Besides, the addition of CNT and MMT particles into PVOH matrix has increased the d-spacing and inter-chain separation values of non-irradiated samples. This is because the good dispersion of CNT and MMT particles in PVOH matrix has caused the intercalation of CNT and MMT particles in PVOH matrix and thus induced the interlayer spacing of MMT and CNT particles. On the other hand, the deflection peak (002) of all irradiated nanocomposites has been shifted to higher 2θ when compared to non-irradiated samples. This was mainly due to the effective numbers of intercalated CNT and MMT particles has induced by formation of crosslinking networks in PVOH matrix. However, the d-spacing and inter-chain separation has increased when high irradiation dosage applied on PVOH matrix.

The addition of CNT particles and the application of irradiation in PVOH matrix have significantly increased the O-H wavenumber by inducing the hydrogen bonding within the particles and polymer matrix. On the other hand, the C-H wavenumber has significantly decreased with low loading level of CNT particles in PVOH matrix which results improvement of mechanical properties. However, higher irradiation dosage would reduce the tensile strength of nanocomposites by the occurrence of chain scissioning reaction in the polymer matrix.

5.2 Recommendations for future work

The overall properties is mainly depends on the dispersion rate and intercalation within the filler particles and PVOH matrix. Thus, the synthesis process of polymer nanocomposites is very important in order to have good dispersion between filler particles and PVOH matrix. One of the suggestions is replacing solution casting method with in situ polymerization method. This is because in situ polymerization promotes the reinforcement surface are likely to be free of contamination, resulting stronger matrix dispersion bond to be achieved.

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