

**MECHANICAL AND GAS PERMEABILITY
PROPERTIES OF NANOCOMPOSITE FILMS
MADE FROM LOW DENSITY POLYETHYLENE
AND CARBON NANOTUBES**

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ABSTRACT

MECHANICAL AND GAS PERMEABILITY PROPERTIES OF NANOCOMPOSITE FILMS MADE FROM LOW DENSITY POLYETHYLENE AND CARBON NANOTUBES

It is important to develop new food packaging materials with enhanced properties. In this work, nanocomposite was prepared by melt blending linear low density polyethylene (LLDPE) and multiwalled carbon nanotubes (MWCNT) by using twin-screw extruder, then hot-pressing was applied to produce nanocomposite films. The effect of the addition of three different dimensions of MWCNT on the mechanical and gas permeabilities properties was investigated, along with overall migration.

According to the film characterization results by scanning electron microscopy, the dispersion of MWCNT in general was considerably average. The presence of interaction networks between LLDPE–MWCNT was observed, so did the presence of carbon nanotubes agglomerations. Relatively better dispersion was achieved by the nanocomposite films containing 0.25 wt. % MWCNT at any dimension. It was observed that the dispersion of carbon nanotubes corresponded with the improvement in mechanical and gas barrier properties. The consistent improvement was shown in Young's modulus with the increment up to 26.9 % as the content of MWCNT increased. Moreover, the addition of MWCNT could enhance the gas barrier properties by lowering the gas permeabilities up to 26.5 % and 32 % for oxygen and carbon dioxide, respectively. The results from mechanical properties and gas permeabilities revealed that the content of MWCNT was more crucial to affect the improvement rather than its dimension. In terms of overall migration, the results were found below the limit required by European Union Commission (10 mg/dm²). Considering these outstanding results, the developed material could be applied in food packaging, particularly in active packaging system.

ÖZET

DÜŞÜK YOĞUNLUKLU POLİETİLEN VE KARBON NANOTÜPLERDEN ÜRETİLEN NANOKOMPOZİT FİMLERİN MEKANİK VE GAZ GEÇİRGENLİK ÖZELLİKLERİ

Özellikleri iyileştirilmiş yeni gıda ambalajlama materyallerinin geliştirilmesi önemlidir. Bu çalışmada lineer düşük yoğunluklu polietilen (LLDPE) ve çok katmanlı karbon nanotüpler (MWCNT) erimiş halde çift-vidalı ekstruder kullanılarak karıştırılmış ve ardından sıcak presleme uygulanmasıyla nanokompozit filmler üretilmiştir. Üç farklı boyuttaki MWCNT'lerin filmlere ilave edilmesinin total migrasyonun yanısıra mekanik ve gaz geçirgenlik özelliklerine etkisi incelenmiştir.

Taramalı elektron mikroskobu sonuçlarına göre MWCNT'lerin dağılımı genel olarak orta düzeydedir. LLDPE–MWCNT'ler arasındaki etkileşim ağı belirgin olarak gözlemlenirken karbon nanotüplerin yer yer yığınlar oluşturduğu da görülmüştür. Herhangi bir boyutta %0,25 MWCNT içeren nanokompozit filmlerde daha iyi dağılım sağlanmıştır. Dağılımın iyi olmasıyla ilişkili olarak mekanik ve gaz bariyer özelliklerinde de iyileşme olduğu gözlemlenmiştir. Ayrıca MWCNT miktarı arttıkça Young's modulus değerinde belirli bir artış (%26.9) da görülmüştür. Öte yandan MWCNT'lerin ilavesi gaz bariyer özelliklerini, oksijen ve karbondioksit gazları için sırasıyla %26,5 ve %32 düşürerek iyileştirmiştir. Mekanik özellikler ve gaz geçirgenlik sonuçları bu özelliklerin iyileştirilmesinde MWCNT'lerin miktarının boyutlarına göre daha önemli olduğunu ortaya koymuştur. Total migrasyon sonuçları Avrupa Birliği Komisyonunun belirlediği limitten (10mg/dm^2) daha düşük bulunmuştur. Bu önemli sonuçlar geliştirilen malzemenin gıda ambalajlamada özellikle aktif ambalajlama sisteminde kullanılabileceğini göstermiştir.

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CHAPTER 1

INTRODUCTION

Packaging is one of the most important aspects in food industry. This is due mainly to its significant role in keeping the food product in the same quality as produced, from storage, during transportation-distribution, till end-user. For food package itself, a good package should possess some basic functions such as containment, protection, preservation, information-communication, and convenience (Robertson, 2012).

There are several materials which can be used and materialized for food package, for example paper and paperboard, metal, glass, and plastics. As for plastics, it contributed almost 30% of sales in the world of packaging consumption between 2003 and 2009 (World Packaging Organisation [WPO], 2008). Plastics packaging is expected to increase in the future, especially for rigid plastic packaging. Therefore, it is necessary to develop novel plastic materials with enhanced properties, thus it can be efficient to be used as packaging, especially for protection and preservation of food products.

The presence of nanotechnology has opened up a way for several innovations in the food packaging sector, especially in the field of improvement in mechanical and barrier properties, by the creation of nanocomposite (Smolander & Chaudhry, 2010). Nanocomposite term means polymers reinforced nanoparticles in order to obtain composite material having enhanced properties, such as mechanical and permeability properties. The particle added or filled should be in size of nano (10^{-9} m). There are many types of nanoparticles which are generally used as reinforced material, for example nano-clays/nano-silicates, nanocrystalline cellulose, exfoliated graphite (graphene), carbon nanofibers, nanosilver, and carbon nanotubes (CNTs). The latest becomes increasingly studied due to its unique characteristics.

Since the discovery of carbon nanotubes by Sumio Iijima in 1991, this nanoparticle has been attracted many scientists and stimulated many extensive research activities for its use and application. This is due mainly to the characteristics of CNTs showing promising application in many fields of science such as in the field of physics for its extraordinary electronic properties, chemist for its potential as nanotest-tubes, and

material science for its amazing stiffness, strength and resilience (Harris, 1999). According to Meyyappan (2004), the application of CNTs is wide ranging, e.g., nanoelectronics, quantum wire interconnects, field emission devices, chemical sensors, biosensors, detectors, composites, etc. As for composite, many research activities have been attempted to fabricate and develop hybrid nanocomposite materials for several uses including packaging.

In the work of nanocomposites, for the last decade, example of the polymer matrices which are commonly used together with carbon nanotubes come from polyolefin groups (polyethylene (PE) and Polypropylene (PP)), polystyrene (PS), polycarbonate (PC), polyethylene terephthalate (PET), polyvinyl acetate (PVA), epoxy, Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV), and Polyaniline (PANI) (Spitalsky, Tasis, Papagelis, & Galiotis, 2010; Lai et al., 2004; Cochet et al., 2001). Among any other materials, nanocomposite material made from polyolefin, especially polyethylene, and CNTs is commonly studied and investigated. Moreover, several works focusing on polyethylene-CNTs nanocomposite are increasing. However, there is not much work of nanocomposite using linear low density polyethylene (LLDPE) and CNT. Therefore any work studying the nanocomposite made from LLDPE and CNT is important, since it can add new information and perspective and can be used as a reference for further study and investigation on nanocomposite for several purposes including packaging.

Polyethylene is used as a material for food packaging due mainly to its inexpensiveness. LLDPE tends to improve mechanical properties compared with LDPE at the same density, because the increment of regularity of the structure and narrower molecular weight distribution. As a result of this linearity, LLDPE has higher tensile strength, puncture resistance, tear properties, and elongation than LDPE.

The improvement on mechanical properties of composite made from LLDPE and CNTs has been reported by many researchers. Aalaie (2007) reported that addition of CNTs (5wt. %) has caused a slight increase of Young's modulus. According to Mezghani, Farooqui, Furquan, and Atieh (2011), the addition of CNTs (0.08-1 wt. %) has improved ductility and tensile strength. Terife and Narh (2011) also found that the elastic modulus of the nanocomposites increased by up to 28% compared with the unfilled polymer. Jin-hua, Guo-qin, Huang, and Lin-jian (2012) observed that the impact strength of LLDPE-MWCNT (multiwalled carbon nanotubes) composite film was increased with the MWCNT content up to 1 wt. %. The same increment also found for tensile strength. Additionally, Vasileiou, Docoslis, Kontopoulou, Xiang, and Ye

(2013) studied that nanocomposite made from LLDPE-MWCNT with finely dispersed MWCNT gave significant improvement in mechanical properties. Since the presence of CNTs in nanocomposite has proven to give significant improvement on mechanical properties, it is also suspected that it might be benefitted to other properties such as mass transfer properties (barrier properties).

The barrier properties are important, especially in food package system, as these may contribute to the preservation of food product's quality. In the case of plastic material made from polyethylene, it is known to have low capability for barrier properties. Therefore, it is required to develop some hybrid materials, polyethylene based, which not only have good mechanical properties but also barrier properties. Nonetheless, the study about the effect of addition of CNTs in the polyethylene matrix on barrier properties is limited. To the best of our knowledge, there are only two publications so far, which are the work of Ko and Chang (2009) and Salehifar, Nejad, Alizadeh, and Azizi (2013).

This research was carried out to develop nanocomposite with the intention to investigate the effect of elongated nanoparticle, MWCNT, in the LLDPE matrix on mechanical and gas permeability properties, along with overall migration. It is expected that the results from this research can be used as a reference for the application of the particular nanocomposite as food packaging. Furthermore, the research is not only a study on one particular dimension but also on three different dimensions of MWCNT. The research covers several works as listed below:

1. Fabrication of LLDPE-MWCNT nanocomposite and film's preparation,
2. Nanocomposite film characterization,
3. Mechanical properties test,
4. Gas permeabilities test, and
5. Overall migration test.

CHAPTER 2

LITERATURE REVIEW

2.1. Nanocomposite

The development of food science, technology, and engineering has triggered many research activities in many aspects of food such as food quality, nutrition, functionality, processing, preservation, sanitation, safety, and packaging. The latest becomes increasingly studied due to the attempts to minimize food losses and to optimize food resources (Smolander & Chaudhry, 2010). There are many studies having objective to improve the capability of food packaging system and to create novel material with enhanced properties, such as study on modified atmosphere packaging, edible film packaging which contains antimicrobial agents, composite polymer material made from several polymers, etc. For composite itself, there is a breakthrough in a way to make composite material. Unlike the conventional method which composite material resulted from bilayer or multilayer polymer, the recent method to create composite material is by involving nanotechnology.

Nanotechnology, as a new approach in technology, promises the possibility to create novel materials to be used as food packaging. Further, this novel material is known as a nanocomposite. Morgan and Wilkie (2007) defines nanocomposite as a hybrid material having new properties (intrinsically) due to the nanometer-scale component or structure give rise to it. The new properties are previously not present in the respective macroscopic composites or the pure component. Moreover, nanocomposites consist of a polymeric material, could be thermoplastics, thermosets, or elastomers, and a reinforcing material in nanoscale (nanoparticle). The nanoparticle has at least on dimension in nanometer scale (Koo, 2006).

There are many different types of commercial nanoparticles which are available in the market and can be used as nanofiller in nanocomposite e.g., montmorillonite organoclays (MMT), polyhedral oligomeric silsesquioxane (POSS®), carbon nanofibers (CNFs), carbon nanotubes (multiwalled (MWCNT), singlewalled (SWCNT), doublewalled (DWCNT)), nonaluminum oxide, nanosilica (N-silica), nanotitanium

oxide, etc. (Koo, 2006). For the polymer matrix itself, it is not limited only from plastic polymers but also from biopolymers. Table 2.1 summarizes the nanocomposites which have been studied so far and proven to give improvement in several properties.

Table 2.1 Summary of several types of nanocomposite

Nanocomposite	Finding	References
Linear low density polyethylene (LLDPE) + Multiwalled carbon nanotubes (MWCNT)	<ul style="list-style-type: none"> • Shear stress and viscosity is proven to be increased by the addition of carbon nanotubes. • Slight increase in Young's modulus may be caused by the addition of carbon nanotubes. It also happens in embrittlement. 	Aalaie et al., 2007.
Chitosan + Nanocrystalline cellulose (NCC)	<ul style="list-style-type: none"> • Tensile strength is improved as shown by nanocomposite. • A barrier property, especially to water vapor, is also improved. 	Khan et al., 2012.
Polypropylene (PP) + Montmorillonite (MMT)	<ul style="list-style-type: none"> • The ability of the nanocomposite as oxygen barrier is increased. • MMT, clay nanofillers, can be acted as filter for harmful UV radiation. 	Zehetmeyer et al., 2013.
Poly(ethylene terephthalate) (PET) + Calcium carbonate	<ul style="list-style-type: none"> • Addition of calcium carbonate as nanofillers is proven to induce better thermal stability of PET/calcium carbonate nanocomposite. 	Gao, Ma, Liu, Wang, & Zhu, 2013.
Poly(vinyl chloride) (PVC) + Titanium oxide	<ul style="list-style-type: none"> • Nanocomposites made from PVC and titanium oxide proves to improve mechanical properties of composite. Hence the presence of titanium oxide can improve photostability of composite as well. 	Sokhandani et al., 2013.
Poly(vinylidene fluoride)(PVDF) + Graphene oxide nanosheets (GOn)	<ul style="list-style-type: none"> • Addition of GOn can induce the improvement of maximum degradation temperature of PVDF. • As the GOn ratio increases, the thermal stability of hot pressed composite increases as well. 	Liu, Huo, Huang, Lei, & Jiang, 2014.
Polystyrene (PS) + Graphene	<ul style="list-style-type: none"> • Low loading addition of graphene proved can improve thermal, mechanical, and conductivity properties of nanocomposite. 	Zhang, Shi, Wu, & Zhou, 2013.
Poly carbonate (PC) + Silica	<ul style="list-style-type: none"> • Nanocomposite made from PC and silica is proven to toughen tensile property and improve thermostability. 	Feng et al., 2014.

Based on various findings which summarized in Table 2.1, it is obvious that research on nanocomposite generally aimed to get better properties of composite. The new properties resulted can be advantageous for several purposes such as for medical application, material for aerospace, electrical material, food packaging, etc. As for food packaging, the important properties that subjected to be improved by developing nanocomposite are mechanical, barrier properties to gasses and ultraviolet, microbial properties (active packaging), and the possibility to trace and monitor the condition of food products during transport and storage (biosensor-intelligent packaging) (Silvestre, Duraccio, & Cimmino, 2011). Besides, the safety for the risk of migration is also important, so that the new nanocomposite material will be truly applicable and acceptable in all aspects.

2.2 Polyethylene and Linear Low Density Polyethylene

Polyethylene (PE) becomes one of the most fabricated materials which is commonly used as packaging. According to Piringer and Baner (2000), worldwide production of PE at early 1990s was 40×10^6 metric tons per year with low density polyethylene (LDPE) counted about 16×10^6 tons and placed as number one, then followed by linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) as the second and third, respectively. Bureau and Multon (1996) stated that principal markets for PE, especially in France and some European community, are for milk (15% of milk) and oil (7% of edible oil) packaging. However, there is also application of PE for fruit juices (more than 50% is sold in Tetra Brick® pack) and for nonalcoholic drinks, wine (0.5%), and fruit drinks (1%).

There are several types of PE, as can be seen in Figure 2.1. Among any other type of polyethylene, LDPE is the most widely used material for plastic based packaging. As shown in Figure 2.1, LDPE can be categorized into two main groups, homopolymer and copolymer. For LLDPE itself, it is a copolymer of a 1-alkene and ethylene, typically 1-hexane, 1-butane or 1-octane, while branched alkenes such as 4-methyl-1-pentene are also used (Abdel-Bary & Rapra Technology, 2003). The addition of linear means there is no presence of long chain branches. LLDPE has short branches, so that can affect the improvement of crystallization-dependent mechanical properties.

LDPE is widely manufactured due to its characteristic such as excellent flexibility, good impact strength, fair machinability, good oil resistance, fair chemical resistance, good heat sealing, and low cost (Hernandez, Selke, & Culter, 2004). However, at the same density, LLDPE tends to improved mechanical properties compared with LDPE. It is due to the increment of regularity of the structure and narrower molecular weight distribution. As a result of this linearity, LLDPE has higher tensile strength, puncture resistance, tear properties and elongation than LDPE. Table 2.2 presented the typical properties of polyethylene films.

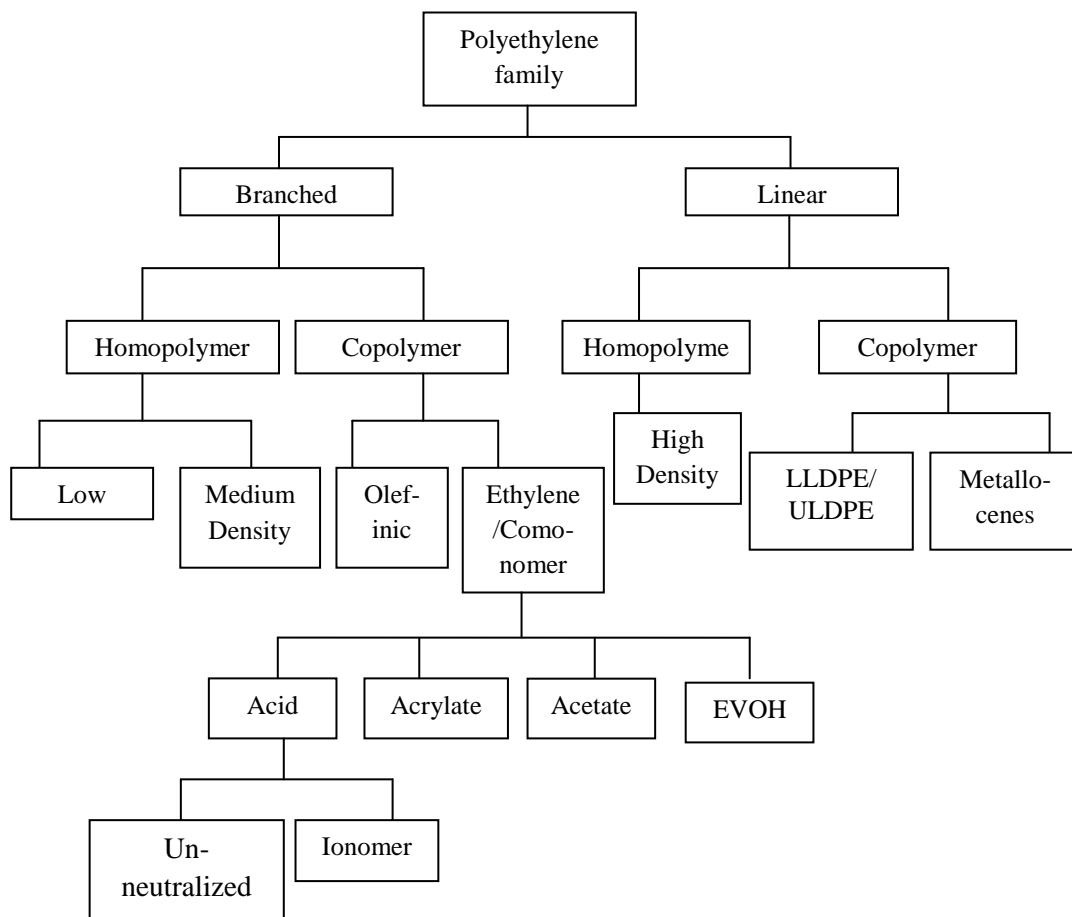


Figure 2.1. The family of polyethylene (PE)
(Source: Hernandez et al., 2004)

In terms of properties, PE is proven to have good properties for cold resistance and good barrier to water vapor. Nevertheless, LDPE is reported to have low barrier properties to gases, fats and aromas (Piringer & Baner, 2000). Therefore, in this research LDPE, especially in the linear form, is used as polymer matrix for nanocomposite. So it is easier to detect any changes in the gas permeability test and if there is, it will become significant improvement for gas barrier properties. Beside, information about the effect of incorporating carbon nanotubes, multiwalled carbon nanotubes, into this matrix polymer on barrier properties is inadequate. Therefore it is necessary to do such investigation.

Table 2.2. Typical properties of polyethylene films
(Source: Abdel-Bary & Rapra Technology, 2003)

Property	LDPE	LLDPE	HDPE
Glass transition temperature (T _g ; °C)	- 120	- 120	- 120
Melting temperature (T _m ; °C)	105 – 115	122 – 124	128 – 138
Heat distortion temperature at 455kPa (°C)	40 – 44		62 – 91
Density (g/cm ³)	0.915 – 0.940	0.915 – 0.935	0.94 – 0.97
Tensile modulus (GPa)	0.2 - 0.5		0.6 – 1.1
Tensile strength (Mpa)	8 – 31	20 – 45	17 – 45
Elongation (%)	100 – 965	350 – 850	10 – 1200
WVTR* at 37.8 °C and 90 % RH (g µm/m ² d)	375 – 500		125
O ₂ permeability, at 25 °C (10 ³ cm ³ µm/m ² d atm)	160 – 210		40 – 73

*WVTR: water vapor transmission rate (d= day, 24 h)

RH: relative humidity

There are several types of nanocomposite being made from LLDPE as polymer matrix such as LLDPE/CNT nanocomposite, LLDPE/TiO₂, LLDPE/SiO₂, LLDPE/nanoscale calcium carbonate, LLDPE/clay nanocomposite, etc. Those nanocomposites are studied for different objectives. LLDPE with nanofillers such as carbon nanotubes, nanoscale calcium carbonate, and SiO₂ are generally studied for their mechanical, thermal, and rheological properties (Zaman, Hun, Khan, & Yoon, 2012; Kontou & Niaounakis, 2006; Xiao, Zhang, & Zarudi, 2007), while LLDPE/clay nanocomposite is subjected to the study of barrier properties (Durmuş, Woo, Kaşgöz, Macosko, & Tsapatsis, 2007).

2.3. Carbon Nanotubes

Carbon nanotubes (CNTs) are one of the examples of many types of nanoparticles. It is considered as nanoparticle with two nanometric dimensions (Wautelet & Institution of Engineering and Technology, 2009). Simple definitions of CNTs are cylindrical shells which can be made by rolling graphene sheets into a seamless cylinder (Zhang & Li, 2009). This nanoparticle shows remarkable properties, for example in mechanical, thermal, and electronic properties. Therefore, carbon nanotubes have high potential of application in many fields of work such as biosensing devices, chemical sensors, field effect transistors, high performance nanocomposites, and other nanoscale devices and circuits (Mittal, 2009a).

There are several methods to produce carbon nanotubes, namely laser evaporation, carbon arc methods, gas-phase catalytic growth from carbon monoxide, and chemical vapor deposition (CVD). The CVD is processed at 1100⁰C and involves decomposing a hydrocarbon gas, for example methane (CH₄). As the gas decomposes, carbon atoms are produced, and then condense on a cooler substrate which may contain various catalysts such as iron. Unlike other methods, the CVD method produces tubes with open ends. This procedure also allows continuous fabrication and can be considered as favorable method for scale up and production (Poole & Owens, 2003). Additionally, it is the most perspective method due to the fact that it is possible to regulate CNT dimension, diameter and length, high yield and selectivity and there is less purification process since the result from this method most likely yielding high purity of MWCNT (higher than 90 wt. %).

In general CNTs can be divided as three categories, namely singlewalled carbon nanotubes (SWCNT), doublewalled carbon nanotubes (DWCNT), and multiwalled carbon nanotubes (MWCNT). Table 2.3 summarized the structures and properties of CNTs. In the case of composite application, singlewalled and multiwalled CNTs are the most common type of CNTs which have been used so far. Table 2.4 presented the use of CNTs (both SWCNT and MWCNT) in polymer nanocomposite material.

Among any other types of CNTs, MWCNT is a type of CNT which is commonly used for nanofillers in nanocomposite. The main reason is that it is considerable cheaper (Lai, 2004) and easier to produce compared to other type, especially SWCNT. Moreover, it has many ranges of dimension, for example MWCNT

which is produced by NanoAmor Europe. They produce two kinds of MWCNT, first in regular length and second in short length. Within this length difference, they also make variation in terms of outside diameter and inside diameter.

Table 2.3. Summary of structures and properties of CNTs
(Source: Nanocyl, 2014; Mittal, 2009a; Grady, 2011)

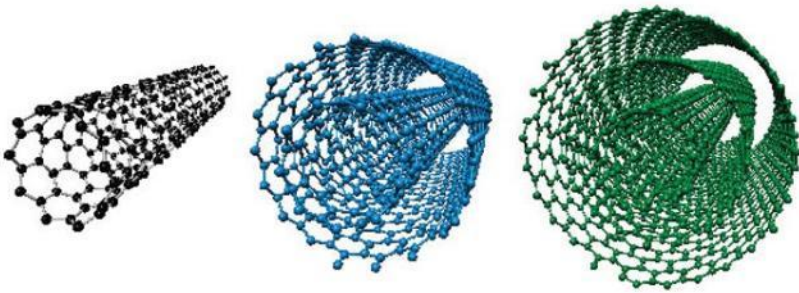
Structure	CNTs
Definition	Tube-shaped material which made of carbon and having diameter on the scale of nanometer.
Categories	<p>SWCNT: It can be formed by rolling a sheet of graphene into a cylinder along a lattice vector in the graphene plane. It consists of one concentric tube.</p> <p>DWCNT: It consists of two concentric tubes.</p> <p>MWCNT: It can be classified as either graphite sheets arranged in concentric seamless cylinders or a single sheet of graphite rolled in around itself. It consists of more than two concentric tubes.</p>
Visualization of structure	 <div style="display: flex; justify-content: space-around; margin-top: 10px;"> SWCNT DWCNT MWCNT </div>
Properties	
Specific Gravity	0.8 g/cm ³ for SWCNTs and 1.8 g/cm ³ for MWCNT
Specific Density	1.3-2
Elastic modulus	~1 TPa for SWCNTs and ~0.3-1 TPa for MWCNT
Strength	50-500 GPa for SWCNTs and 10-60 GPa for MWCNT
Strain at break (%)	10
Thermal Conductivity	3000 W m ⁻¹ K ⁻¹
Magnetic susceptibility	22 x 10 ⁶ EMU/g (perpendicular with plane), 0.5 x 10 ⁶ EMU/g (parallel with plane)
Thermal expansion	Negligible
Thermal stability	>700 ⁰ C (in air); 2800 ⁰ C (in vacuum)
Specific surface area	10-20 m ² /g

Table 2.4. The use of CNTs in polymer nanocomposite material
(Source: Grady, Pompeo, Shambaugh, & Resasco, 2002; Lai et.al, 2004; Cochet et.al, 2001)

Polymer	SWCNT	MWCNT
Polystyrene (PS)	✓	✓
Polycarbonate (PC)		✓
Poly(methyl methacrylate (PMA)	✓	✓
Poly(methyl Acrylate) (PMA)		✓
High density polyethylene (HDPE)	✓	✓
Low density polyethylene (LDPE)		✓
Ultrahigh molecular weight polyethylene (UHMWPE)	✓	✓
Polyethylene terephthalate (PET)	✓	
Polyvinyl acetate (PVA)		✓
Polypropylene (PP)		✓
Polyamide		✓
Polyurethane		✓
Poly(vinyl chloride) (PVC)		✓
Epoxy		✓
Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV)		✓
Polyaniline (PANI)		✓

MWCNT is constituted with various concentrically aligned tubular graphene sheets having typical diameter in range of 8-300 nm. In comparison to SWCNT, MWCNT has significantly lower physical and mechanical properties, yet still higher compared with properties of commonly used reinforcement additives and construction materials (Mazov, Kuznetsov, Romanenko, & Suslyaev, 2012). Nowadays, the use of MWCNT is considerably wide-ranging such as for chemical sensors (Sumanasekera, Pradhan, Adu, Romero, & Eklund, 2004), components of catalytic systems, electromagnetic shielding material, for biomedical purpose, selective drug delivery (Hilder & Hill, 2008), and can be used as components of composite material with polymer, ceramic, or metal matrices (Wang, Kou, Liu, Pan, & Guo, 2007).

Several works on polymer nanocomposites which use CNT as nanofillers generally discuss about the effect of this nanofillers on mechanical, electrical, rheological, thermal, and flame retardancy properties. This means that carbon nanotubes show promising application in many fields. Despite it is proven to improve mechanical properties of nanocomposite, it may lead to many other improvements such as barrier properties, although it may not be the case always (Mittal, 2009b).

2.4. Polyethylene Carbon Nanotubes Nanocomposite

In packaging systems, it is necessary to choose materials based on two important parameters, low cost and efficiently processed (Hannay, 2002). Plastic is considered as material which possess these two parameters and polyethylene, as one of the example of it, is commonly used for food packaging. This is due mainly to its important criteria for food packaging such as food approval, approximate hot fill temperature, moisture barrier, impact strength, clarity, and moulding (Hannay, F., 2002). However, there is one disadvantage of using polyethylene, which is having low barrier properties to gases, especially oxygen.

Nanocomposites come as a solution for the world of packaging since it can improve some properties of material such as mechanical, thermal, and barrier properties. However, the work on developing polyethylene nanocomposite using CNT as nanofillers to overcome gas barrier issue is considered as limited. Up to date, the works on polyethylene, especially LDPE and LLDPE reinforced with CNT are focused only for certain properties as summarized in Table 2.5.

Recently there is a study on gas barrier properties of LDPE/CNT nanocomposite. As reported by Salehifar (2013), films made from LDPE/MWCNT, by solvent casting method, is proven to decrease the permeability of oxygen and water. As a result, these films which applied to cover Iranian Lavash bread could extend the shelf life of the bread. It is due mainly to the ability to lowering the level of water and oxygen permeability down and also the antimicrobial property owned by CNT. They concluded that the films are suitable for package of bakery products.

Table 2.5. Summary of works focussing on LDPE/LLDPE-CNT nanocomposite

Composite material	Fabrication method	Objective	Reference
LDPE+MWCNT	Melt compounding	To investigate the electrical properties of the nanocomposite as a function of CNT volume content, frequency, and temperature	Liang & Tjong, 2005.
LLDPE+MWCNT	Melt blending	To investigate the rheological behavior, mechanical and electrical properties of the nanocomposite	Aalaie et al., 2007.
LDPE+MWCNT	Melt mixing	To investigate the effect of CNTs on the electrical and rheological properties of the nanocomposites made with met mixing method	Valentino et al., 2008.
LDPE+MWCNT	Melt blending	To investigate the effect of coupling treatment on dispersion of MWCNT and its electrical property	Na, Oingjie, Chongguang, Chenglong, & Yuanyuan, 2010.
LDPE+MWCNT	Melt blending	To investigate the effect of aspect ratio and chemical modification of MWCNT on the nanoisothermal crystallization kinetics	Abbasi, Hussein, Parvez, 2011.
LLDPE+MWCNT	Melt extrusion	To investigate the effects of CNT with different ratio to mechanical properties of the nanocomposite	Mezghani et al., 2011.
LLDPE+MWCNT +Polyethylene glycol	Melt mixing	To investigate the dispersity of CNT in the matrix and the electrical properties of the nanocomposite	Müller, Krause, Pötschke, 2012.
LLDPE+MWCNT	Melt extrusion	To investigate the mechanical properties and thermal behavior of the nanocomposite	Jin-hua et al., 2012.
LDPE+MWCNT	Melt blending	To investigate the radiation resistance of LDPE	Jung et al., 2013.
LLDPE+MWCNT	Melt compounding	To investigate the effect of matrix viscosity and compatibilization on the microstructure, as well as on the electrical and mechanical properties of the composite	Vasileiou et al., 2013.

The good performance of nanocomposite can only be achieved if there is good interaction between polymer matrix and nanofillers (A. Koval'chuk in Mittal, 2009b). In the case of CNT, the good dispersion plays an important role since it may improve the properties such as strength, stiffness, thermal and electrical conductivities (Ramsden, 2011). In order to achieve such condition, high shear mechanical stirring or ultrasonic treatments are generally performed (Seyhan & Tanoğlu, 2008). Therefore, the method on how to fabricate the particular nanocomposite is important, since it may affect the interaction between nanofillers-polymer matrix and the dispersion of the nanofillers.

2.5. Fabrication Methods of Nanocomposite

There are several methods to fabricate or prepare nanocomposite made from polyethylene and CNT. The methods include melt blending, solution blending, in situ polymerization, ball milling, interfacial polymerization, electro-spinning, and non-conventional approaches such as mechano-chemical and adsorption techniques. However, the most common methods for fabricating CNT/PE nanocomposite are melt blending, solution blending, and in-situ polymerization.

2.5.1. Melt Blending

In another term, melt blending can also be called as melt mixing. The principle work of this method is that the method must be in the melt state where thermoplastic polymers are blended or mixed with various inorganic fillers, such as CNT, by applying shear forces. It aims to break nanotubes aggregates by using fluid shear forces. The shear forces can be resulted by utilizing mixer or compounder (A. Koval'chuk in Mittal, 2009b). This method is commonly used by many researchers to prepare polyolefin/CNT and it includes PE. Several techniques that correspondent to this method are extrusion, compression molding, and injection molding. The benefit of this method is that it suits industry and practitioner who wants to do a large-scale fabrication of nanocomposite and it may not need any further treatments such as pre-treatment of polymer and nanofillers, post treatment, etc.

There are key factors that need to be noted when choosing this method to prepare nanocomposite in order to get good dispersion of CNT, first is real mixing times and shear (as dependent on CNT concentration) (Huang, Ahir, & Terentjev, 2006), and second is screw rotation (Zou, Feng, Wang, & Liu, 2004). Relevant mixing time is needed since it may help better dispersion of CNT in a polymer melt to reach consistent and reproducible state of such dispersion. For shear, the shear stress energy applied during mixing should be exceeding the van der Waals force so that CNT may have a chance to well disperse in the matrix polymer. The role of screw rotation is that relatively higher screw rotation may lead to better dispersion of CNT. According to Villmow, Pötschke, Pegel, Häussler, & Kretzschmar (2008), the agglomerate size of CNT is decreased as the rotation speed of screw increased.

Melt blending method, especially by using extrusion technique, is relatively favorable to achieve well disperse nanofillers since, as mentioned before, it applies mechanical shear. Mechanical shear can provide a kinetic driving force for further dispersion of nanofillers and it helps accelerate substantially the kinetics of nanofillers dispersion (Morgan & Wilkie, 2007). Furthermore this method is favorable for industry since there is no demand for applying additional steps such as chemical treatment for CNT Functionalization, etc. It also helps the disentanglement of CNT when iteratively done and can decrease the surface resistance of composite, so that CNT can disperse effectively (Oh, Ahn, & Hong, 2010). Additionally, Esawi, Morsi, Sayed, Gawad, and Borah (2009) reported that extrusion can cause some alignment of the nanotubes at the outmost surface which it helps the dispersion of CNT in the polymer matrix.

Extruder, a typical machine for extrusion process, can be categorized in several types, for example based on the number of shafts. This categorization divides extruder into three types, single screw, twin-screw, and multiple screw extruders, as shown in Figure 2.2. Co-rotating twin-screw extruder can be adapted easily to process various requirements and product characteristics. One example of producer of this kind of extruder is Thermo Scientific, Waltham, MA USA.

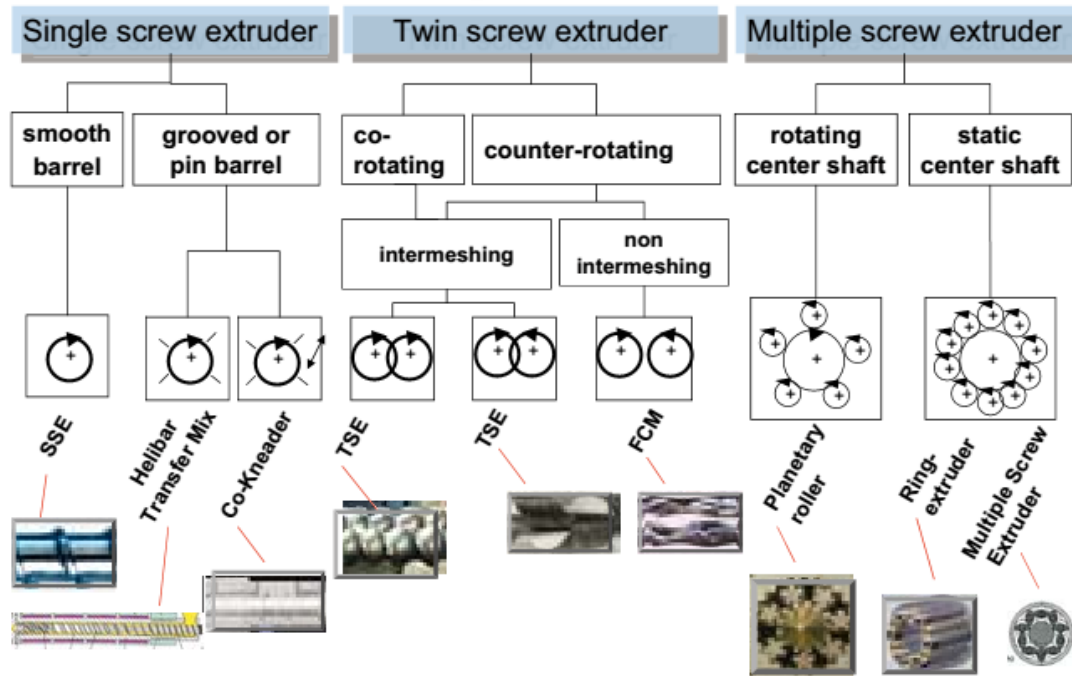


Figure 2.2. Classification of extruders by the number of shafts
(Source: Kohlgrüber & Bierdel, 2008)

Basically, the principal mechanism of twin-screw extruder is thermal processing which high heat, high pressure, and shear forces are being involved in the process. The benefits of using this extruder are that it is low cost, applying speed, having high productivity, and its versatility (Zong et al., 2014). In general, there are seven zones that applied in twin-screw extrusion process, orderly: solid feeding, melting, filler feeding, dispersing, homogenizing, degassing, and discharging. The zonation of twin-screw extruder is depicted in Figure 2.3. Each zone represents each process and it has its own function, starting from input material, conveying, mixing, distributing, dispersing, etc. It links from one to another, thus it can not be considered as individual process. Since it employs screws, the arrangement of the screws is also important. It may influence the performance of extrusion such as product transformation, residence time distribution, and mechanical energy input (Colas, Doumeng, Pontalier, & Rigal, 2013).

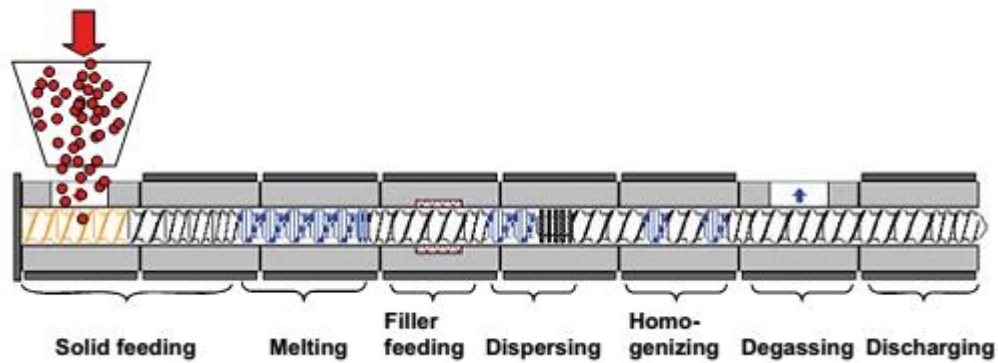


Figure 2.3. Zonation of twin-screw extruder
(Source: Rudolf, 2008)

2.5.1.1. Masterbatch Approach

In the case where extrusion technique to melt blending nanofillers and matrix polymer is applied, generally the users feel hesitate to directly incorporated nanofillers (in the form of ultrafine powders, which normally happens for CNT) into polymer matrix. Therefore, masterbatch two-steps approach is usually preferred. The principle for this approach is that first a polymer is formulated at relatively high nanofillers loadings (of about 20-25 wt. %), which can be processed and palletized in the similar form to normal polymer resin. Then, this concentrate subsequently is diluted to pure polymer resin to achieve several filler loading concentration as desired. In masterbatch two-steps approach, there do exist such favorable thermodynamic for mixing, which not only can help to get effectively disperse condition, but also it can stabilize the dispersed nanocomposite structure (Morgan & Wilkie, 2007).

Villmow et al. (2008) stated that by doing two-steps masterbatch approach, several benefits can be gained such as accurate amount of CNT can be achieved, easy handling of the process, and it can result high melt viscosity which can lead to high shear stress during melt mixing. This approach is described in some literature as the appropriate approach to disperse and distribute CNT in the polymer matrix melt.

2.5.2. Solution Blending

In the case of lab-scale practice, solution blending method is commonly used for preparation of polymer/CNT nanocomposite. The principle work of this method includes three basic steps, namely dispersion of CNT in solvent, mixing process of CNT suspension with polymer, and the extraction of composite by using solvent removal or polymer precipitation (A. Koval'chuk in Mittal, 2009b). Solution blending method is considered as unpractical method for preparing nanocomposite since it requires quite large volumes of solvent, great effort to purify nanocomposite, and most of polyolefin polymer, such as PE and PP, is hardly soluble in common organic solvents, though elevated temperature is applied. Hence, this method may not be transferable directly towards large-scale process (Villmow et al., 2008).

2.5.3. In-situ Polymerization

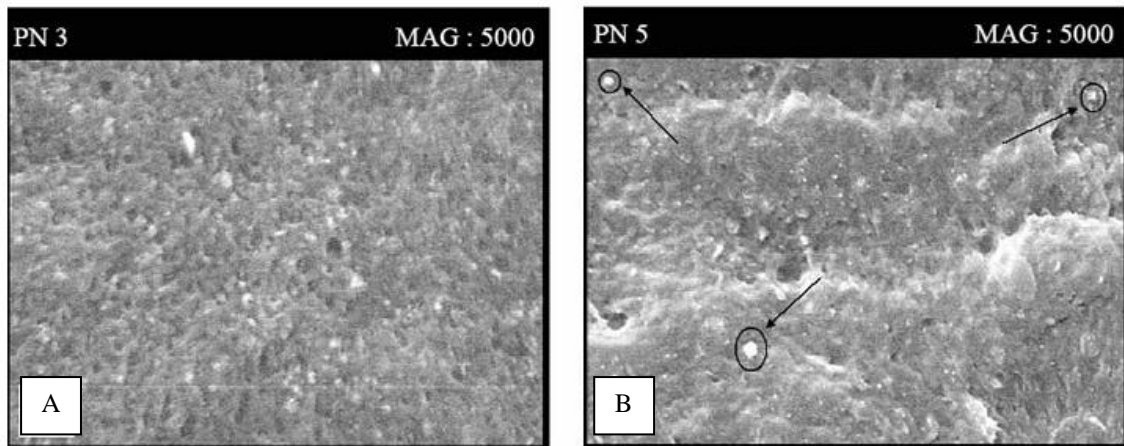
In this method the formation process of composite combines dispersion of nanotubes in a suitable monomer or solvent, and subsequent monomer polymerization. Therefore, the polymer matrix is formed when there is a presence of the separated CNT, and the synthesis of composite is carried out in the single step (A. Koval'chuk in Mittal, 2009b). Moreover, the in-situ polymerization technique involves the attachment of catalyst to the surface of nanofillers before the polymerization process started (Kumar in Vikas, 2009b). This technique is important especially for the polymers which having insoluble and thermally unstable characteristic, which cannot be processed by melt or solution processing (Choudhary & Gupta, 2011). Although this method promises uniform filler distribution and good enhancement of interfacial adhesion, it is barely used for CNT/nanocomposite fabrication process. It is due mainly to the requirements for several steps of treatment prior to the fabrication of nanocomposite.

2.6. Characterization of Carbon Nanotubes Nanocomposite

There are two main processes involved in characterization, first structure analysis and second property measurements. Structure analysis is generally carried out by using sort of microscopic and spectroscopic techniques, whereas property characterization more diverse and it depends on the possibility of application. The common techniques which are used for characterization such as wide-angle x-ray diffraction (WAXD), transmission electron microscopy (TEM) and spectroscopy, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) (Koo, 2006).

SEM and TEM have been frequently used for characterization of nanocomposite. Those techniques offer some advantages such as very high resolution image topographically and compositional maps of the elements which presence in the matrix (Saheb et al., 2014). In SEM technique, magnification happens from an electron beam, which is produced by a source into a probe, then scans across the surface of a sample and this happens in raster fashion. Various types of emissions then produced as a result of the interaction between the sample and the electron probe, and subsequently captured by different detector placed in appropriate positions (Suga et al., 2014).

There are several works which are reported about the use of SEM technique for nanocomposite characterization, especially for LLDPE/CNT nanocomposite such as the work done by Aalaie et al. (2007). They reported that CNTs in polymer matrix are seen as individual white points and it scattered in the matrix, while most of them are clumped together in the form of aggregates. The SEM picture for this result is given in Figure 2.4. Another result of SEM characterization for LLDPE/CNT nanocomposite is presented in the work of Vasileiou et al. (2013), as can be seen in Figure 2.5. The presence of CNTs is observed in the aggregates form and it is indicated by white circle.



Remarks: Picture A indicates the individual CNT scattered in polymer matrix, as indicated with white points. Picture B shows the aggregates of CNT.

Figure 2.4. SEM images result
(Source: Aalaie et al., 2007)

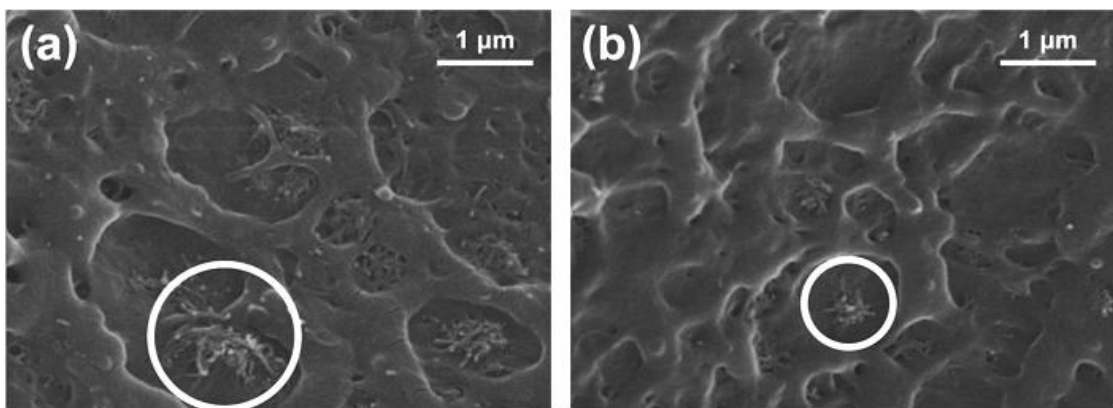


Figure 2.5. SEM images result of cryo-fractured surface of LLDPE/CNT nanocomposite
(Source: Vasileiou et al., 2013)

2.7. Properties of Polyethylene Carbon Nanotubes Nanocomposite

The improvement of properties in nanocomposite is firmly resulted from good dispersion of nanofillers in polymer matrixes and solid interaction between the nanofillers and polymer matrices. As mentioned earlier, in the case of PE/CNT nanocomposites, several properties which proven to be improved are mechanical, rheological, electric conductivity, and thermal stability and flammability.

2.7.1 Mechanical Properties

Mechanical strength is one of the important factors that need to be considered when choosing packaging film, especially made from plastic polymer. Mechanical strength is one of many parameters that included in mechanical properties. The definition for mechanical properties is all properties that describe on how a material reacts in response to application of forces, in particular its behavior under some mechanical loads (Lee, Yam, & Piergiovanni, 2008). Mechanical properties for packaging usually consist of tensile, impact, tear strength and puncture resistance.

Tensile properties consist of some parameters such as modulus of elasticity, the elastic limit, resilience, the ultimate strength or tensile strength, toughness, brittleness, creep, and stress relaxation (Hernandez, et al., 2004). Generally the value of those parameters is obtained by analyzing the graph resulted from tensile test. In order to do so, there is a general method to test mechanical properties which is by using universal testing machine such as ZWICK, Instron, etc. In the tensile test, sample can be formed in dog-bone shape or rectangular strip and it will undergo some changes due to the application of forces. The basic mechanism of tensile test and its specimen is illustrated in Figure 2.6 and the graph resulted from tensile test is shown in Figure 2.7.

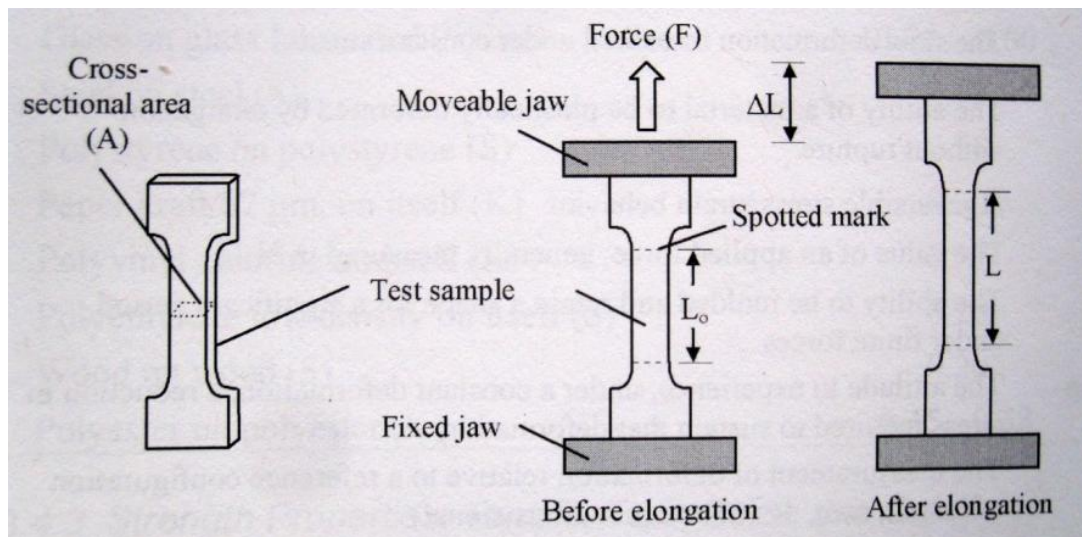


Figure 2.6. Sample specimen and the basic mechanism of tensile test
(Source: Lee et al., 2008)

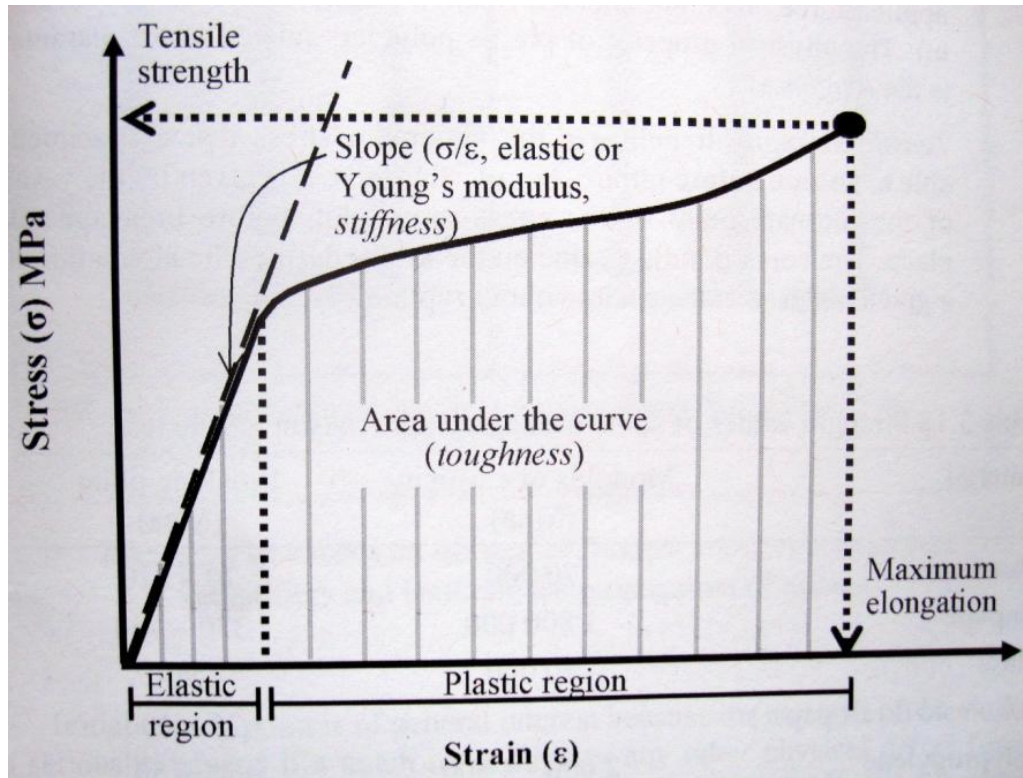


Figure 2.7. The graph resulted from tensile test (in the form of stress-strain)
(Source: Lee et al., 2008)

The stress-strain graph is drawn based on the deformation that happened in specimen test during tensile test. It covers from the start of the deformation up to the specimen breakage. The calculation of the stress and strain is presented below:

1. Stress: this value uses as ordinate of the graph and it is measured by dividing the force (F) to cross-sectional area (A) of the specimen. It expresses usually in MPa (Nmm^{-2}).

$$\text{Stress} = \sigma = \frac{F}{A} \quad (2.1)$$

2. Strain: this value uses as abscissa and it is dimensionless. Strain value is expressed by the ratio of the length.

$$\text{Strain} = \varepsilon = \frac{L - L_0}{L_0} = \frac{\Delta L}{L_0} \quad (2.2)$$

Following the completion of the graph, the tensile properties which can be measured are tensile strength, elastic or Young's modulus, elastic limit, and ductility. The explanations for each property are presented below (Lee et al., 2008; Hernandez et al., 2004):

1. Tensile strength (some call it the ultimate strength) represents the maximum tensile stress a material can sustain before failure. Generally tensile strength occurs either at the break point or the yield point of material.
2. Elastic or Young's modulus is the ratio between the stress applied and the strain produced indicating the material's resistance to elastic deformation. It also gives a measure of the material's stiffness. It is expressed in MPa. It can be said that the higher the elastic value of a given material, the higher its stiffness.
3. The elastic limit marks the maximum stress the material can experience without undergoing permanent deformation.
4. Ductility is the strain at failure. It is usually expressed as percent (White, 2012).

For the last decades, many works report about the mechanical properties of PE/CNT nanocomposite, starts from ultrahigh molecular weight of PE (UHMWPE), high density of PE (HDPE), low density of PE (LDPE), and linear LDPE (LLDPE). Ruan, Gao, Yang, and Yu (2003) reported about the improvement in tensile properties such as toughness, tensile strength, and elastic modulus. Based on their investigation, the increment of toughness could be achieved up to 150%, whereas tensile strength and modulus increased up to 49.7 and 38 %, respectively. The increment is achieved from the nanocomposite made from UHMWPE with the addition of 1% MWCNT. The main reason for improvement in tensile strength is most likely due to the analog effects of CNT and the formation of 'taut-tie' molecules which may cause load bearing effect.

Tang, Santare, and Advani (2003) reported that the addition of MWCNT could improve tensile strength and Young's modulus as the content of MWCNT increased from 1 wt. % to 5 wt. %. The final improvement valued around 5 % and 8 % for tensile strength and Young's modulus, respectively. The improvement is closely related to the dispersion of MWCNT in the HDPE polymer matrix. SEM and TEM examinations revealed that MWCNT are well dispersed in polymer matrix although in the form of small aggregates.

Improvement in Young's modulus and tensile strength of PE/CNT nanocomposite is also reported by Xiao et al. (2007). They developed LDPE/MWCNT nanocomposites with the loading content of MWCNT ranged between 1-10 wt. %. They found that Young's modulus and tensile strength of the nanocomposites are increased up to 89 and 56 %, respectively, when the loading of nanotubes reach 10 wt. %. However, it is said that this superior property of MWCNT has not been fully utilized due to the MWCNT in polymer matrix performed in curving and coiling nature. They also concluded that the improvement in tensile properties caused by the effective reinforcement of MWCNT. It means that there are continuous MWCNT networks performed in polymer matrix and it changed the structural of the composite. Hence, the curving and coiling nature of MWCNT caused the strong mechanical interlocking among nanotubes and it promotes the reinforcement.

As for LLDPE/MWCNT nanocomposite, the same trends for improvement in mechanical properties are also occurred. It is explained in the work of Jin-hua et al. (2012). They reported that at low concentration, MWCNT could disperse uniformly in polymer matrix and provide the nanocomposite with much improved mechanical properties. It is recorded that the improvement happened in Young's modulus and tensile strength (but it is limited until 1 wt. %) and the increments are 54% and 22%, respectively. Theoretically, it can be said that improvement of mechanical properties in nanocomposite is caused by several factors (A. Koval'chuk in Mittal, 2009b) such as:

- Nanotube orientation, where superior strength and modulus will be superior if the alignment of CNTs in the form of uniaxial alignment rather than isotropic (unidirectional), though the improvement is also improved.
- Interfacial interaction between nanotubes and polymer chains, if the solid interaction happened, the improvement will be expected.
- Dispersion of CNTs in the polymer matrix, where well dispersed will contribute to improvement of mechanical properties.

2.7.2. Barrier Properties

In general barrier properties of material resemble the ability of specified material to be a barrier from some gases, for example from O₂ and CO₂ gas, water vapor, aroma, volatiles, light, etc. In the world of food packaging, the ability of the food package to be a barrier of those substances and moisture is essential. It is due mainly to the presence of such substances and moisture can very much influence the keeping quality of the packed food and its shelf life (Lee et al., 2008; Hernandez, 2004). Thus, avoiding the contact between food and some substances can help to minimize the risk of adverse reaction which may reduce the organoleptic and/or quality and safety of the product (Pereira de Aubreu, Paseiro Losada, Angulo, & Cruz, 2007). For example in meats and nuts product, the packages should have the ability to keep the oxygen away from those products, so that the fats will not be turning into rancid (due to lipid oxidation). Hence, apart from the oxidation of food lipid, the presence of oxygen in some food stuff can also contribute to off-flavors, loss of color and nutrient value.

However, this is not always the case. For some packaging systems, especially in modified atmosphere packaging for fresh produce, the presence of several gases such as oxygen and carbon dioxide (through the exchange process), is required to accommodate the respiration and transpiration process and to maintain the gas composition in the package. Still, for most packages made of plastic, the barrier properties are one of the most challenging issues and need to be rectified. Therefore, there are many interests in studying polymer nanocomposite to overcome this problem, since some research show that gas barrier properties can be improved by creating organic-inorganic nanocomposites (Sorrentino, Gorassi, & Vittoria, 2007; Pereira de Aubreu et al., 2007).

Unfortunately, in the work of carbon nanotube-polyethylene nanocomposite, there is very limited information about the study of these properties. Hence, to the best of our knowledge, there are only two works which discuss about the barrier properties of polyethylene/carbon nanotube nanocomposite. First work is done by Ko and Chang (2009). They studied about thermomechanical properties, morphologies, electrical conductivities, and gas permeabilities of ultrahigh molecular weight polyethylene (UHMWPE) nanocomposite films containing two types of functionalized MWCNT, prepared by solution casting. They concluded that gas permeabilities of the hybrid films, nanocomposite films, are lower than the pure UHMWPE film. Second work is done by

Iranian colleagues in 2013. They studied about the oxygen and water vapor permeability in LDPE/MWCNT nanocomposite films fabricated by solvent casting technique (Salehifar et al., 2013). They found that adding MWCNT into LDPE films inhibited the oxygen permeabilities significantly. Considering the lack of the information in this subject, it is important to study such properties in PE/CNTs nanocomposite, since in the future this composite might be applicable for food packaging.

Theoretically, gas and vapor are transported through the package by two main mechanisms, namely permeation and leak. If permeation involves the transfer of gas and/or vapor through the plastic film and food package's wall, leak involves the transfer process through pinholes or channel leaks (Lee et al., 2008). There are three part of processes of permeation that happen through a film of package's wall: first, solution/absorption of gas and vapor (permeant) into the surface of polymer, then migration/diffusion of permeant through polymer(s), and lastly emergence/desorption of permeant from the opposite surface of polymer (Coles, McDowell, & Kirwana, 2003). The schematic process of three-part permeation is depicted in Figure 2.8, where P_H is indicated the pressure at the high level, P_L is indicated low pressure, and circles is indicated the permeant molecules.

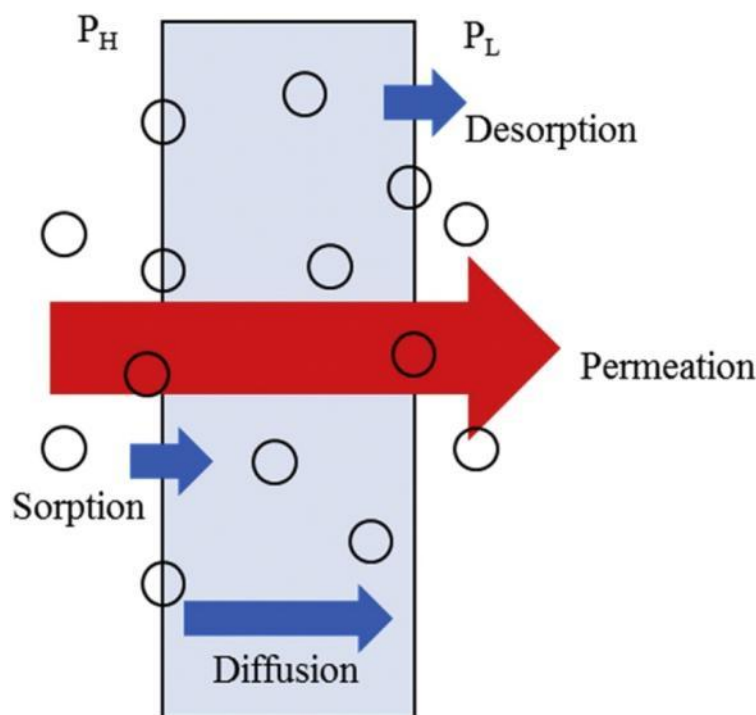


Figure 2.8. Schematic diagram of permeation
(Source: Yeo, Jung, Song, 2014).

Several methods have been introduced to measure the permeation process such as the continuous flow method (isotactic method), gravimetric method, volume variation method and pressure rise method. For the purpose of permeation measurement, in this research manometric gas permeability test by using LYSSY L100-5000 was chosen. The principle work of this manometric testing method is based on pressure difference (as a driving force). So the specified gas permeates through the sample due to the forcing force of the atmospheric pressure in the upper chamber which flow through the film material and reach the below chamber, where vacuum process is happened. The measurement records the time required for the lower chamber pressure to increase from pre-defined lower limit to pre-defined upper limit. Then this time interval needed is calculated into gas permeability rate and expressed in $\text{ml/m}^2/24\text{hr}$. The process repeats until the sample has reached the equilibrium and stabilized, or continues until the testing is stopped (PBI Dansensor, 2005). The picture of the machine is shown in Figure 2.9.



Figure 2.9. LYSSY L100-5000
(Source: PBI Desensor, 2005)

2.7.3. Migration

Apart from transfer of gasses through package, transfer of substance from the surface of packaging to the enclosed product by physical or chemical action is also crucial. The latter is called migration and the compound and/or substance that transferred is called migrant (Hernandez et al., 2004). The migration testing is important since it can ensure the food safety and protect the consumer (Piringer and Baner, 2000). Hence, the presence of migrant in food can change the nature of the food product so that the organoleptic aspect will be changing as well. This obviously can change the quality of the food product.

According to the number of migrants, there are two types of migration, first is overall migration (OM) and second is specific migration (SM). The OM measures all mobile substances which being transferred from the internal surface to the food per unit area of package under the influence of any specific predetermined conditions or by contact. Meanwhile the SM measures only to the specific substance (Robertson, 2006 in Arvanitoyannis & Kotsanopoulos, 2014). The measurement of global migration can only be used as a reference index and it does not provide any information on the harmful or toxicity of products originating in the packaging.

Considering that migration of permeant is resembles food safety, there is regulation about this overall migration. Based on the Commission Regulation EU no. 10/2011, the limit for overall migration value is not to exceed 10 mg/dm^2 . This limit is applied to material made from plastic and it means that this plastic material shall not transfer its constituents to food simulants exceeding 10 mg in quantities of the total constituents released per dm^2 of food contact surface. According to de Kruijf and Rijk (1997), the introduction of OM limit is aimed to control the total amount of substances which migrating from a package into food, irrespective of the significance of toxicological of these substances, and to minimize the number of specific migration so that determinations can be proceeded to ensure that the packaging material is fit for package and in contact with food stuff.

Generally the OM test is performed by means of simulation test. In order to do so, there are several different food simulants which can be used as a representative of certain food product. Food simulants (FS) is used since there is a complexity of the food, with their chemical composition and physical structure. So by using food

simulant, it will make migration test easier and more reliable. The definition of food simulants (FS) itself is solid or liquid substances, having known and simple composition, able to emulate the extraction solubility and capacity of food stuff (Lee et al., 2008). Examples of food simulants are presented in Table 2.6.

Table 2.6. Food simulants which is commonly used in migration testing
(Source: Lee et al., 2008)

Category of FS	Simulant
Aqueous	Distilled water
Acidic	3% (m/v) acetic acid in water
Alcoholic	Ethanol in water (8-50% v/v)
Fatty	Olive oil, sunflower oil, corn oil, synthetic mixture of triglycerides
Solid	Adsorbent polymer (polyphenylene oxide, Tenax®, charcoal, milk chocolate)
Solvent	Heptane, iso-octane, ethanol, ethanol-water

Gravimetric method is the most classical method to measure the OM. The principle of this method is by measuring the difference weight of sample material after the evaporation (for volatile simulant) or the removal of simulant (for oil), after contact with food simulants in certain time periods. The weight difference tells the amount of solid substances which have migrated. Stéphane Peyron (2013) developed a methodology to measure OM. Detailed explanation of this method is presented in Chapter 3, OM test section (3.2.6). Basically this method measure the value of OM based on contact of sample material in food simulants for certain period of times. The contact of sample material is set to have the ratio of approximately 6 dm² surface area in 1 L volume of FS. The formula to measure the OM is presented in equation 2.3.

$$OM \left(\frac{\text{mg}}{\text{dm}^2} \right) = \frac{\text{mass loss of the sample film (mg)}}{\text{surface area in contact with FS (dm}^2\text{)}} \quad (2.3)$$

In this research, ethanol 95% was used as food simulant. It was chosen due to the fact that it can give the prominent changes, in terms of mass, if put in contact with polyethylene material. Hence, in European Regulation, 95% ethanol may represent the alternative FS for fatty food simulant and specifically has been used for non-polar polymer such as polyolefins (de Kruijf & Rijk, 1997).

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Linear Low Density Polyethylene (LLDPE) was obtained from Polimeri Europa (Mardyck, France) in the form of granule with commercial name Flexirene® FG 30. According to the supplier, it is a butane copolymer linear low density polyethylene (C4-LLDPE), with antioxidants, and suitable for blown film extrusion. Flexirene® FG 30 complies with the rules and regulations of the European Union, as well as other countries, regarding the use of plastic materials in food contact application. Main properties of Flexirene® FG 30, as confirmed by supplier, are presented in Table 3.1.

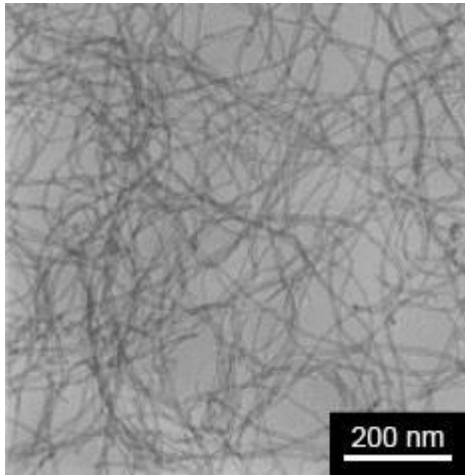
Table 3.1. Main properties of Flexirene® FG 30
(Source: Polimeri Europa, 2008)

Resin Properties	Value	Unit
Melt flow rate (190 °C/ 2.16 kg)	1.0	g/10min
Density	0.925	g/cm ³
Melting point	124	°C
Brittleness point	< -70	°C
Vicat softening point (1 kg)	105	°C
<hr/>		
Film Properties*	Value	Unit
Tensile stress at yield	12-13	MPa
Tensile strength at break	33-45	MPa
Elongation at break	600-800	%
1% secant modulus	250-290	MPa
Elmendorf tear resistance	20-180	N/mm

(*) Typical value for extruded between 190 °C – 230 °C, thickness 25 µm.

Three different types of multiwalled carbon nanotubes (MWCNT) were used in this work. They were purchased from Nanostructured & Amorphous Materials Inc. (Houston, USA). The specification for each MWCNT is presented in Table 3.2. All types of MWCNT were produced by catalytic chemical vapor deposition (CVD). They were in the form of black powder and used as received.

Table 3.2. Specification of each MWCNT

Type 1 MWCNT (small diameter/SD)	Remarks
Commercial name	MWCNT 1203 YJ
Purity	> 95%
Diameter	Inside: 2-5 nm, outside: < 8 nm
Length	10-30 μm
Specific surface area	350-420 m^2/g
Particle morphology	Long tubes
Melting point	3652-3697 $^{\circ}\text{C}$
Density, bulk	0.05 g/cm^3
Density, true	$\sim 2.1 \text{ g}/\text{cm}^3$
Optical morphology	
(Source: NanoAmor, n.d.)	
Type 2 MWCNT (medium diameter/MD)	Remarks
Commercial name	MWCNT 1229 YJ
Purity	> 95%
Diameter	Inside: 5-10 nm, outside: 20-30 nm
Length	10-30 μm
Specific surface area	110-130 m^2/g
Particle morphology	Long tubes
Melting point	3652-3697 $^{\circ}\text{C}$

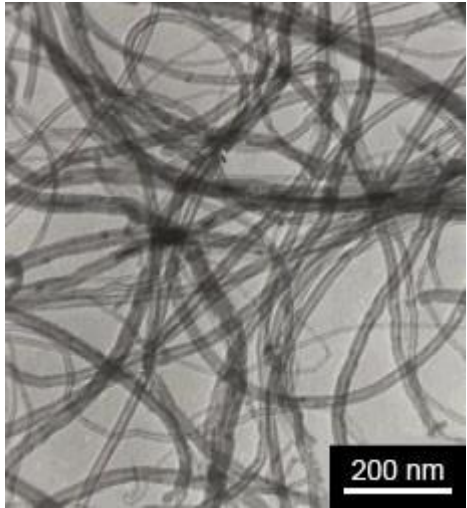
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Table 3.2 (Cont.).

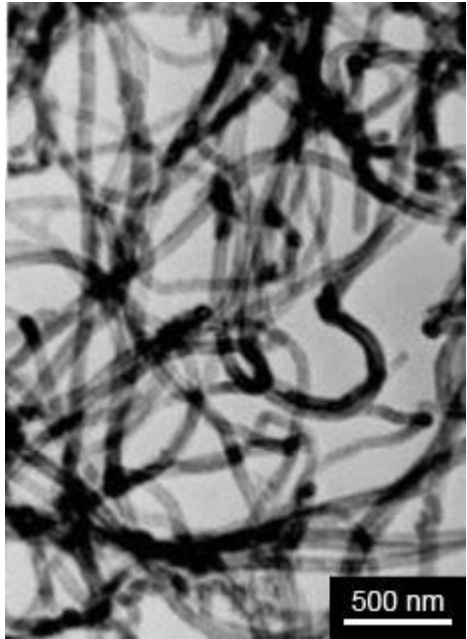
Density, true

~2.1 g/cm³

Optical morphology



(Source: NanoAmor, n.d.)

Type 3 MWCNT (big diameter/BD)	Remarks
Commercial name	MWCNT 1233 YJ
Purity	> 95%
Diameter	Inside: 5-15 nm, outside: 50-80 nm
Length	10-20 μm
Specific surface area	60-80 m ² /g
Particle morphology	Long tubes
Melting point	3652-3697 °C
Density, true	~1.7-1.9 g/cm ³
Optical morphology	

(Source: NanoAmor, n.d.)

3.2. Methods

3.2.1. Fabrication of LLDPE-MWCNT Nanocomposite

MWCNT-LLDPE nanocomposite was fabricated by melt blending method by extrusion with the use of Prism EuroLab 16 Twin-screw Extruder (manufactured by Thermo Fisher Scientific, USA). The fabrication process was done in two steps, which were the making of masterbatch (MB) as a first step and the dilution of MB to get several content ratios of carbon nanotubes (CNTs) as the second step. The fabrication process of this nanocomposite is presented in Figure 3.1.

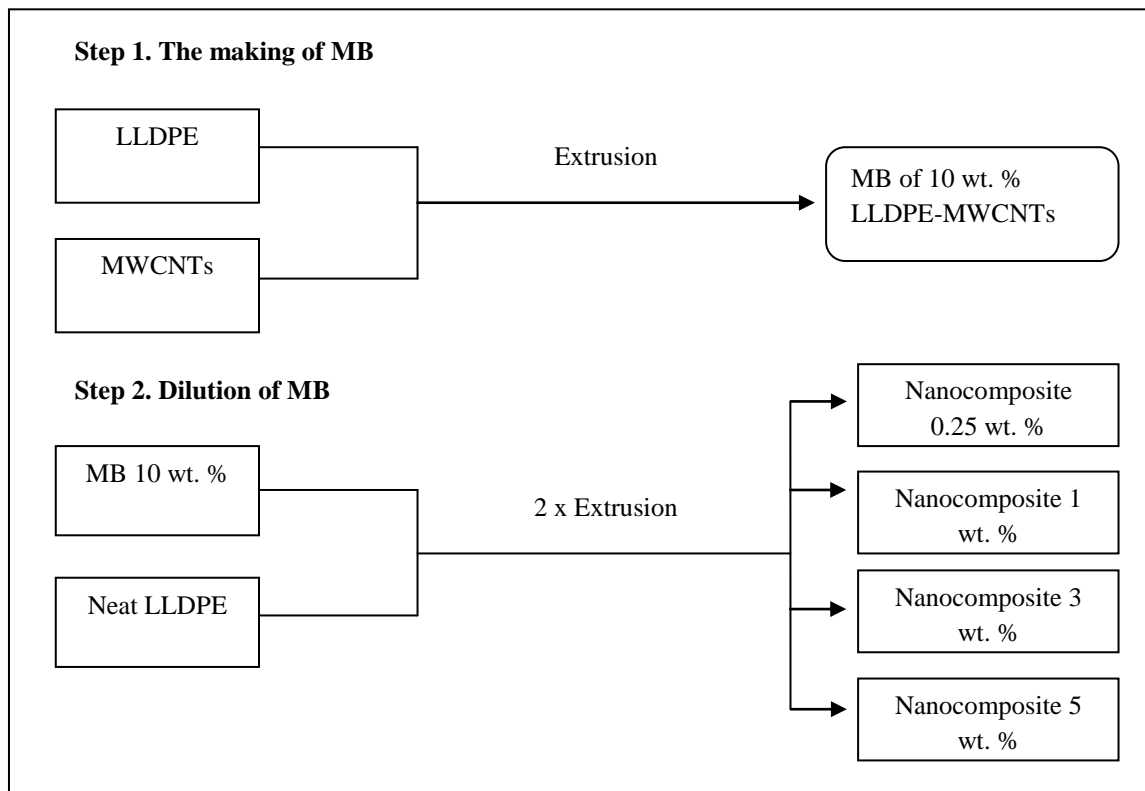


Figure 3.1. Steps of fabrication process of nanocomposite

The making of MB was done by melt blended LLDPE granule and MWCNT by extrusion to obtain nanocomposite having 10 wt. % of CNTs. LLDPE granule was dried in oven (60 °C) overnight prior to extrusion. Temperature profile of extruder was 160 °C, 165 °C, 165 °C, 170 °C, 170 °C, 175 °C, 175 °C, 175 °C, 170 °C, and 165 °C, respectively, from input (feeding spot) to the output (die spot). The screw speed of the

extruder was 50 rpm. LLDPE granule entered the main feeder spot of extruder by volumetric feeder and once the LLDPE granule melted in the extruder, MWCNT was filled into the extruder, manually, from second feeder spot and the amount of each input was persistently controlled. The nanocomposites resulted from the extrusion process were in the form of long tubular and they passed through the cooling bath before entering pelletizing machine. The pelletizing step is aimed to get uniformly nanocomposite pellet. The scheme of twin-screw extruder is depicted in the Figure 3.2 and the overall process system is shown in Figure 3.3.

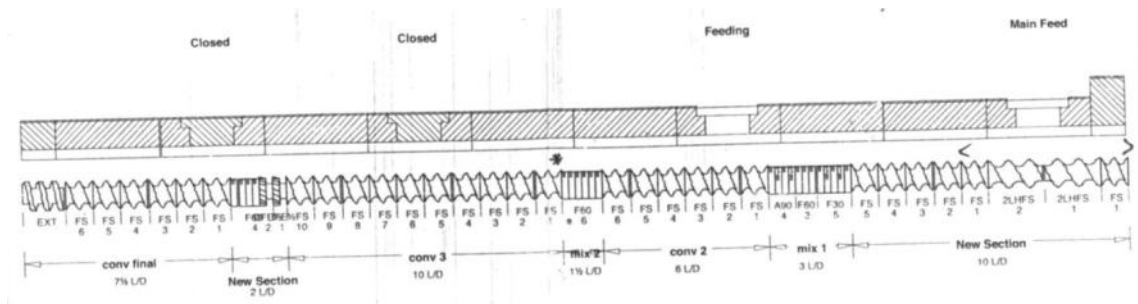


Figure 3.2. Scheme of twin-screw extruder

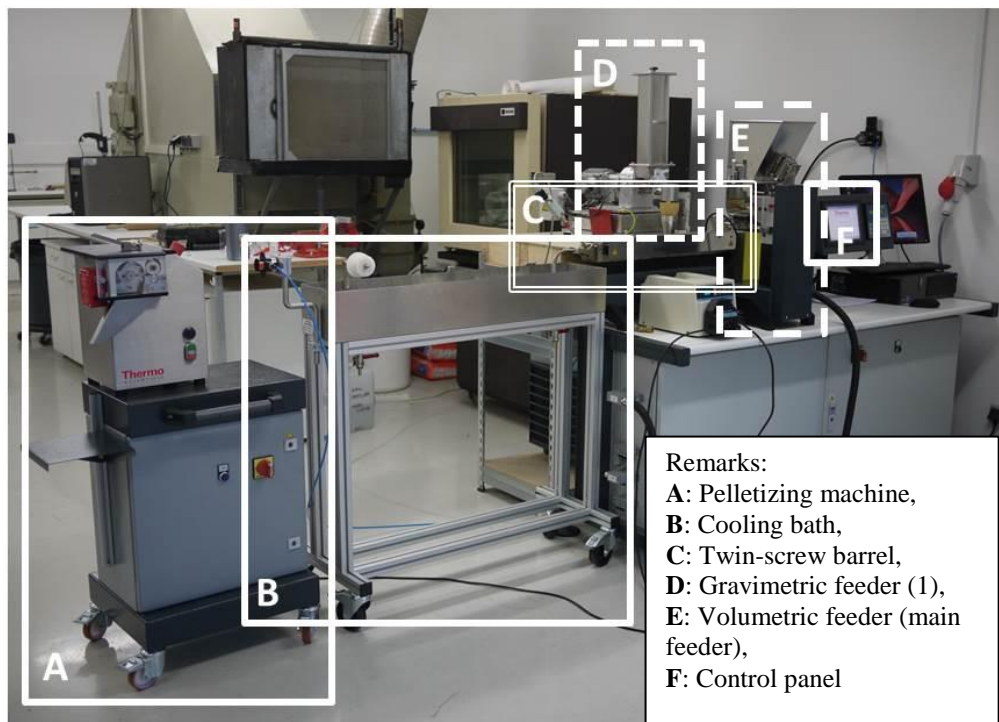


Figure 3.3. Overall process system of nanocomposite fabrication

The dilution step of MB was done subsequently after finishing the making of MB and overall process is similar to the procedure of making MB. Neat LLDPE was diluted with MB 10 wt. % to get several ratios of nanocomposites which are 0.25 wt. %, 1 wt. %, 3 wt. %, and 5 wt. %. In order to achieve well dispersed CNTs inside the polymer matrix (LLDPE), special treatment was given to this step which is the extrusion was done twice. The first extrusion was done in 50 rpm screw speed and the second was done in 100 rpm. The similar procedure was also applied for making composite with different types of MWCNT and control (with no MWCNT).

3.2.2. Preparation of Nanocomposite Film

Nanocomposite films were prepared by hot-pressed the nanocomposite pellets within 5 minutes at 160 °C of temperature and 150 bars of pressure by using hot-pressing machine (France). The preparation of film specimens to be used in mechanical properties test, SEM characterization, and overall migration test was done by hot-pressed approximately 7 gr of nanocomposite pellets which previously placed in Teflon paper (14 cm x 14 cm). The resulted films from this process were having thickness range from 300 µm to 400 µm. Special for gas permeability test, the film specimens were tailored with the thickness range from 160 µm to 190 µm. Control films were prepared with the similar procedure. At the end, there were three types of nanocomposite films, namely nanocomposite 1 (SD), 2 (MD), and 3 (BD), containing type 1, 2, and 3 MWCNT, respectively, and control film. The hot-pressing machine is shown in Figure 3.4.

3.2.3. Scanning Electron Microscopy Characterization

Nanocomposite films were characterized by scanning electron microscopy (SEM) using Hitachi S-4800 and FEI QUANTA 250 FEG on fractured surface of the sample films. The film was covered either with palladium or gold prior to characterization.



Figure 3.4. Hot-pressing machine

3.2.4. Mechanical Properties Test

Mechanical properties test for each nanocomposite and control films were conducted by using ZWICK Z2.5 (France) at a crosshead speed of 50 mm/min. The test was done at constant room temperature and relative humidity with 9 replications for each film. Prior to the test, the film specimen was shaped as dog-bone shape by using specimen cutter, as shown in Figure 3.5. The recorded data from each film then calculated for its mechanical properties e.g., modulus of elasticity (Young's modulus), elastic limit, tensile strength, and ductility.



Figure 3.5. Specimen cutter

3.2.5. Gas Permeability Test

The test for gas permeability was measured to record the oxygen and carbon dioxide permeability. The test was performed according to ASTM D3985 and it was done by using Lyssy L100-5000 (Illinois, USA), at constant room temperature and 0% relative humidity. The gas flow was set at 5-10 cm³/minute. The test was done on control film and film with the lowest content (0.25 wt. %) and highest content (5 wt. %) of carbon nanotubes. There were 3 replications for each type of the film.

3.2.6. Overall Migration Test

The test was done by following the method developed by Stéphane Peyron (2013). First, 4 sample films were shaped in circle with 4 mm of inner diameter and 3.1 cm of total diameter. These sample films were put in the desiccator until the weight is constant. Then, the initial weight was taken. Next, these films were placed in the modified beaker glass. 100 mL of 95% ethanol, as liquid food simulant (FSL), was poured into the beaker glass. Then, this complete system was closely sealed to prevent any possibility of evaporation of FSL during the test and it was put in the oven at 40 °C of temperature for 10 days. The final weight of the film was recorded and the overall migration value was calculated based on the reference formula (2.3). The illustration of the system is shown in Figure 3.6. The test was done with 3 replications from each type of film samples. Overall migration test (OMT) was done on control film and film with the lowest content (0.25 wt. %) and highest content (5 wt. %) of carbon nanotubes.

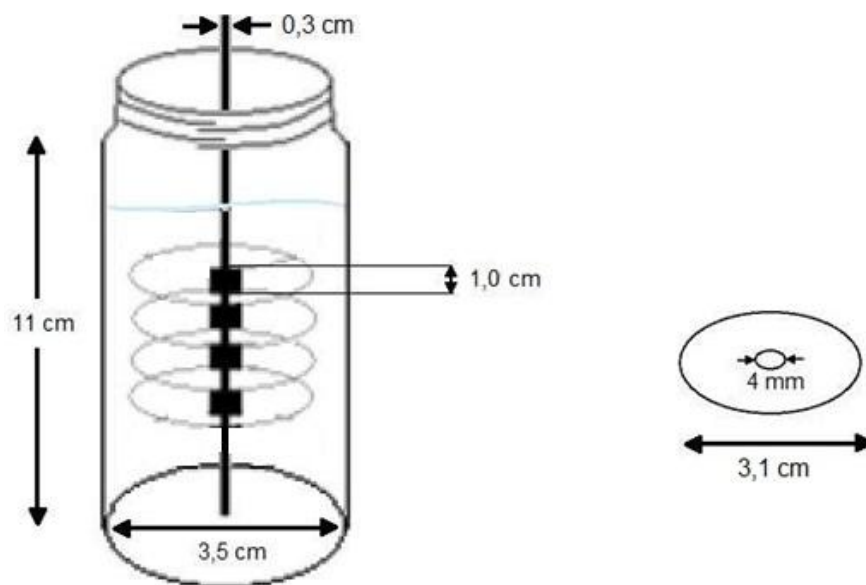


Figure 3.6. Illustration of the OMT system

3.2.7. Statistical Analysis

All the data were subjected to statistical analysis and they were analyzed by analysis of variance (ANOVA) using Minitab[®] 15.1.20.0. The data were expressed as mean values \pm standard deviation. The statistical difference were considered at a significance level of 95% ($p < 0.05$).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Fabrication of Nanocomposite and Film

Several attempts had been done in order to fabricate nanocomposite made from LLDPE and MWCNT. First attempt was done by applying solution casting method. However, considering the amount of solvent needed, post-treatment after the films was obtained, the number of films which can be obtained in respect of time, and due to some practical reasons, it had been decided that it is necessary to fabricate the nanocomposite with another method. Since our lab is equipped with twin-screw extruder machine, the melt blending method by using this machine is preferable.

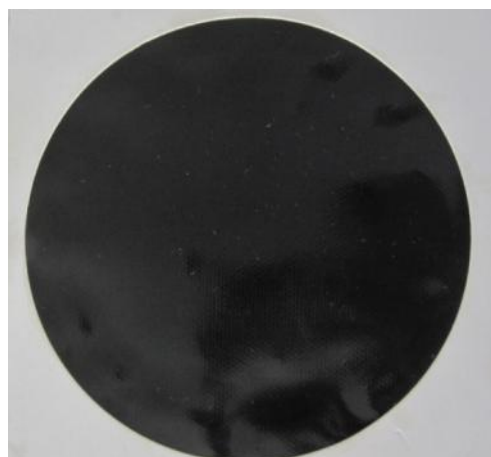
The main consideration for taking melt blending method was due mainly to some practical reasons, such as it might be applicable for large scale application and the large amount of the total of nanocomposite which can be obtained in respect of time. Moreover, the melt blending method is capable of providing well dispersed nanofillers in the polymer matrix as long as some factors for achieving well dispersed nanofillers (as stated in Chapter 2) are considered and taken into account. Unfortunately, there is a lack of information about using the twin-screw extruder, with specification as ours, to perform melt blending method. Therefore, many efforts had been done to achieve a suitable procedure for fabricating nanocomposite with the machine e.g., the modification of screw profile, zoning temperature, screw speed, and number of repetition of extrusion process. Finally, the set up procedure for melt blending method by using twin-screw extruder was achieved, as stated in Chapter 3.

The physical appearance of nanocomposite films with several contents and types of MWCNT can be seen in Figure 4.1. The pictures of the film were taken with having the text underneath the film. It was done in order to show transparency of the films. Based on the observations, it can be said that films with lower content of MWCNT, 0.25 wt. %, exhibited transparency compared to other films. It could be seen from their appearance, especially when they get exposed to the light. The most transparent result was shown by the films containing MWCNT type 1 at 0.25 wt. %. As for the rest of the

films (1 wt. %-5 wt. %), they had similar appearance which look blackish in color and naturally did not show any transparency when they get exposed to the light.



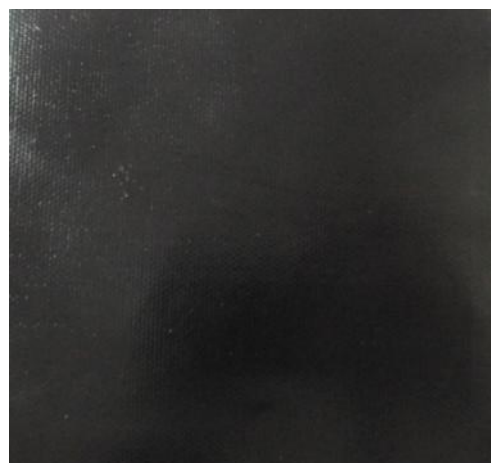
a. Control (neat LLDPE)



b. 0.25 wt. % of MWCNT



c. Type 1 MWCNT at 0.25 wt. % of MWCNT



d. 1 wt. % of MWCNT



e. 3 wt. % of MWCNT



f. 5 wt. % of MWCNT

Figure 4.1. Nanocomposite Films

4.2. Film Characterization

Scanning electron microscopy (SEM) was used to characterize the nanocomposite films. It was done on cryo-fractured sample of the films. The results for each type of nanocomposite film are presented below.

4.2.1. Nanocomposite film 1

Nanocomposite film 1 is designated for composite containing type 1 MWCNT (small diameter). The SEM examination results for these films are shown in Figure 4.2 - Figure 4.5. As can be seen from the pictures, the dispersion of MWCNT in LLDPE matrix could be considered as average. It is because there were some agglomerations which were found in some sample films. Agglomerations were started to be seen at 1 wt. % of MWCNT content (Figure 4.2 and Figure 4.5). Nevertheless, the MWCNT–LLDPE networks were observed and they were existed throughout the nanocomposite sample (Figure 4.1 and Figure 4.4). In the figures below, the presence of MWCNT and the MWCNT-LLDPE network was indicated by the white circle.

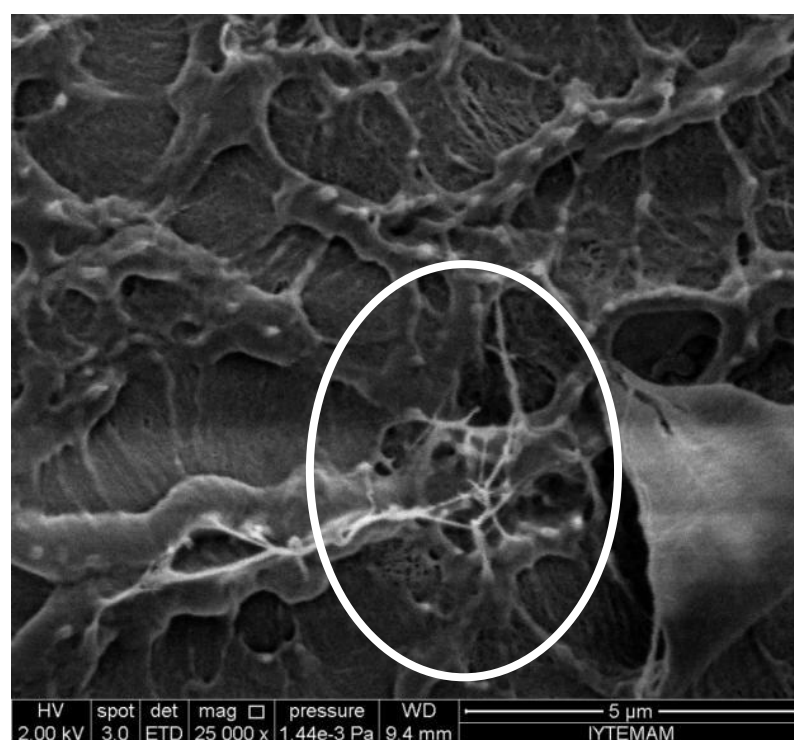


Figure 4.2. Nanocomposite film 1 with 0.25 wt. % of MWCNT

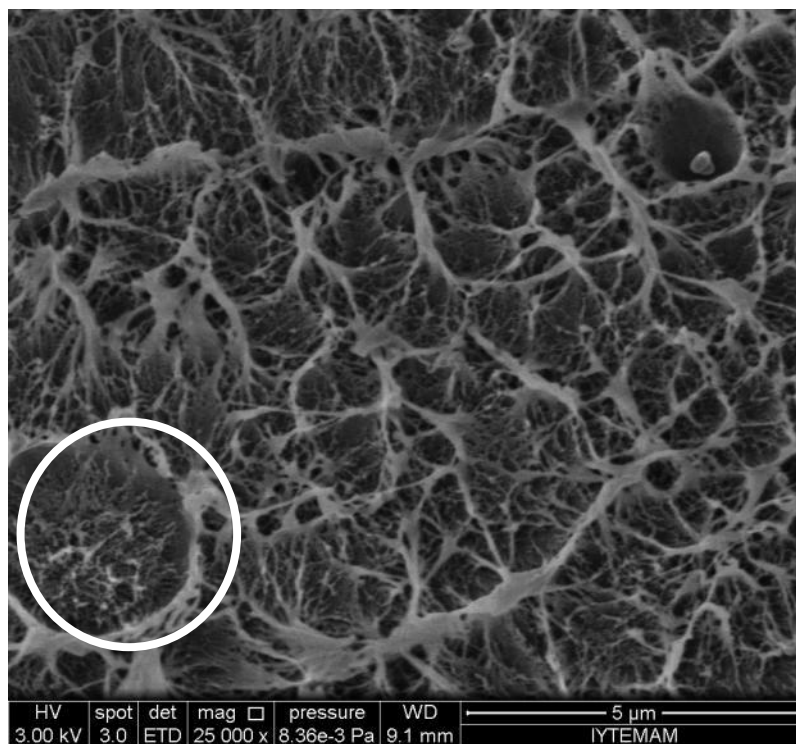


Figure 4.3. Nanocomposite film 1 with 1 wt. % of MWCNT

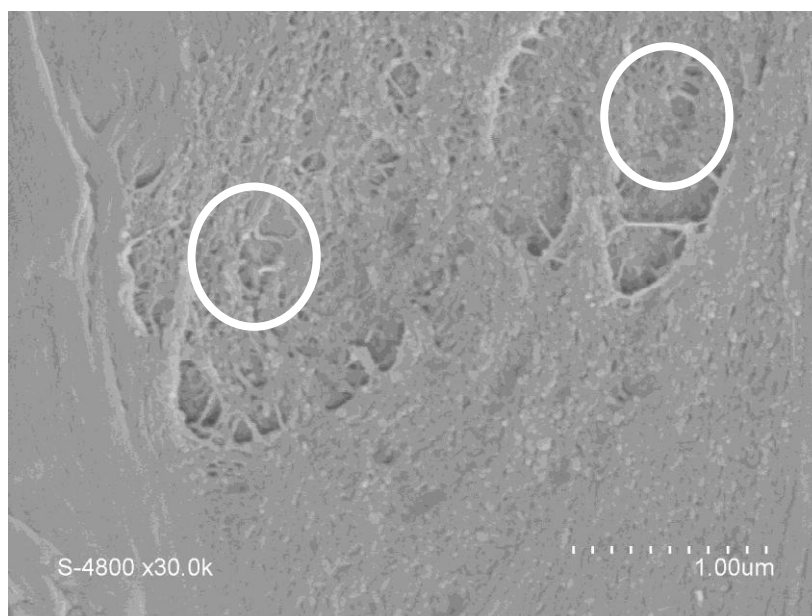


Figure 4.4. Nanocomposite film 1 with 3 wt. % of MWCNT

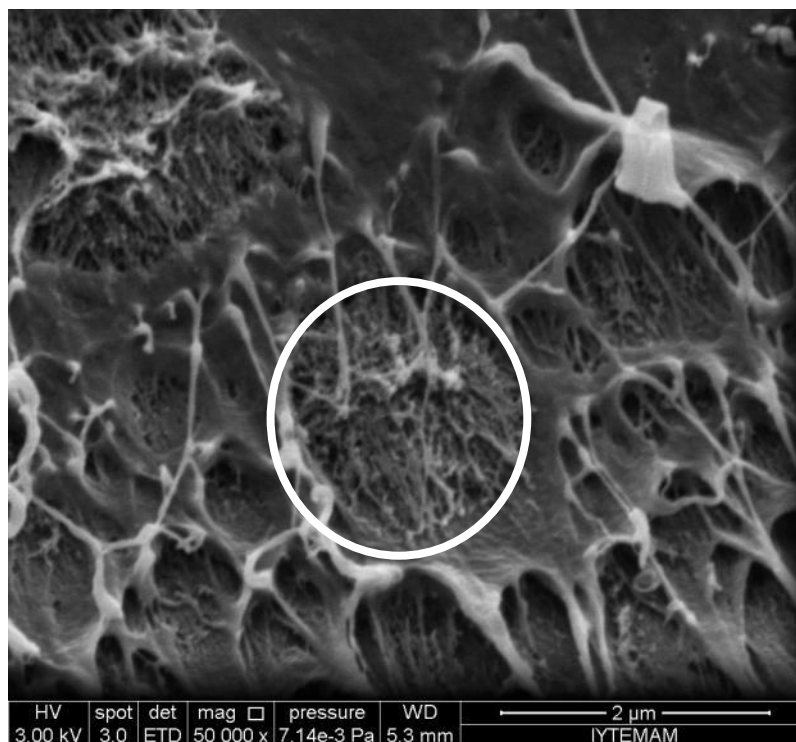


Figure 4.5. Nanocomposite film 1 with 5 wt. % of MWCNT

4.2.2. Nanocomposite film 2

Nanocomposite film 2 is designated for composite containing type 2 MWCNT (medium diameter). Figure 4.6 – Figure 4.9 shows SEM examination result from films containing different content of MWCNT. Similar with the previous result, the dispersion of MWCNT was considered as average with relatively better dispersion was found at higher content of carbon nanotubes. The agglomerations of CNT were started to appear at lowest content (0.25 wt. %) of MWCNT. However, as the content of CNT increased, the presence of MWCNT–LLDPE network was obvious. In the figures, the presence of MWCNT (Figure 4.6) and the MWCNT–LLDPE network (Figure 4.7 and Figure 4.8) was indicated by the white circle. There were some coiled MWCNT existed in sample film containing 5 wt. % of MWCNT (Figure 4.9).

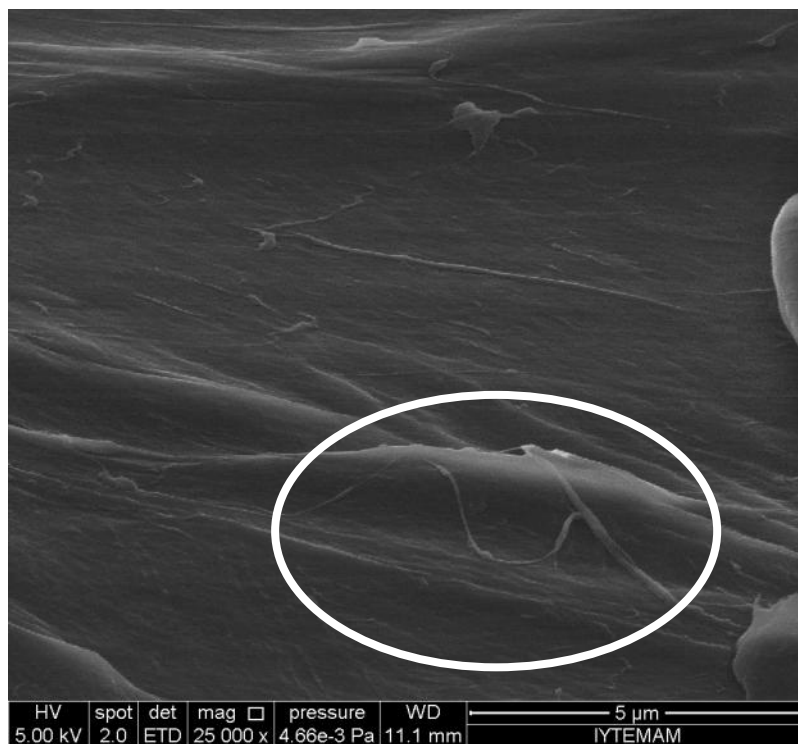


Figure 4.6. Nanocomposite film 2 with 0.25 wt. % of MWCNT

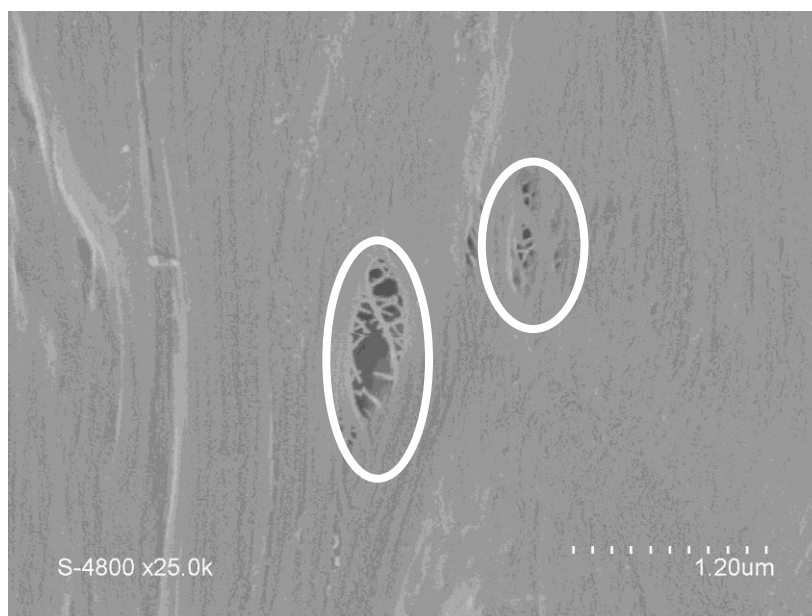


Figure 4.7. Nanocomposite film 2 with 1 wt. % of MWCNT

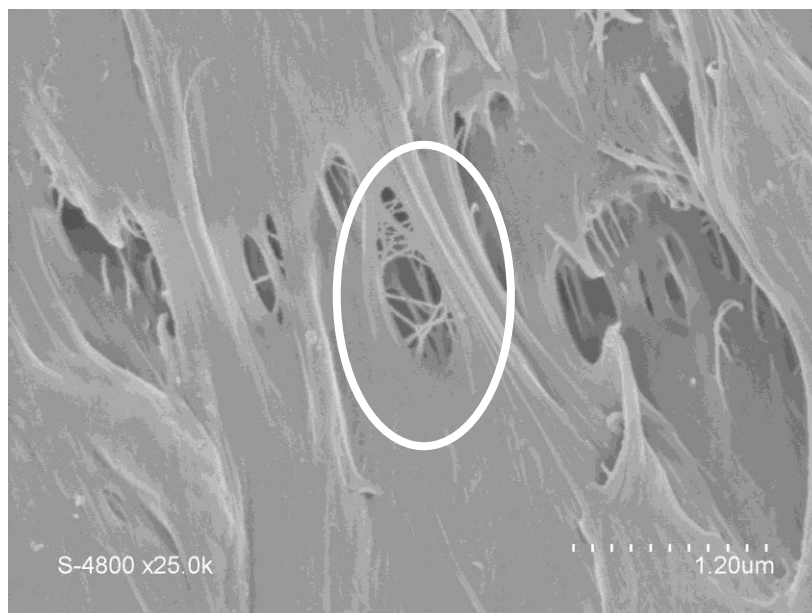


Figure 4.8. Nanocomposite film 2 with 3 wt. % of MWCNT

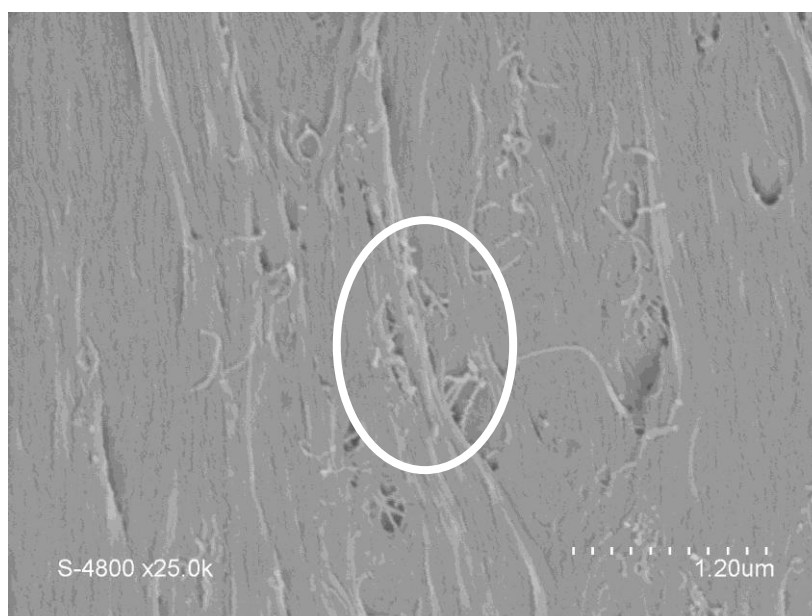


Figure 4.9. Nanocomposite film 2 with 5 wt. % of MWCNT

4.2.3. Nanocomposite film 3

Nanocomposite film 3 is designated for composite containing type 3 MWCNT (big diameter). The results for SEM examination from these nanocomposite films at different content are shown in Figure 4.10 – Figure 4.13. As can be seen from the pictures, the dispersion of MWCNT in LLDPE matrix could be considered as relatively better compared with the last two results. The interfacial networks which were formed between MWCNT–LLDPE were prominent, especially at the highest content of MWCNT (5 wt. %). White circles which were found in the pictures below indicate the presence of carbon nanotubes (Figure 4.11) and its interfacial network (Figure 4.10 and Figure 4.12) with polymer matrix and MWCNT's agglomeration (Figure 4.13), respectively.

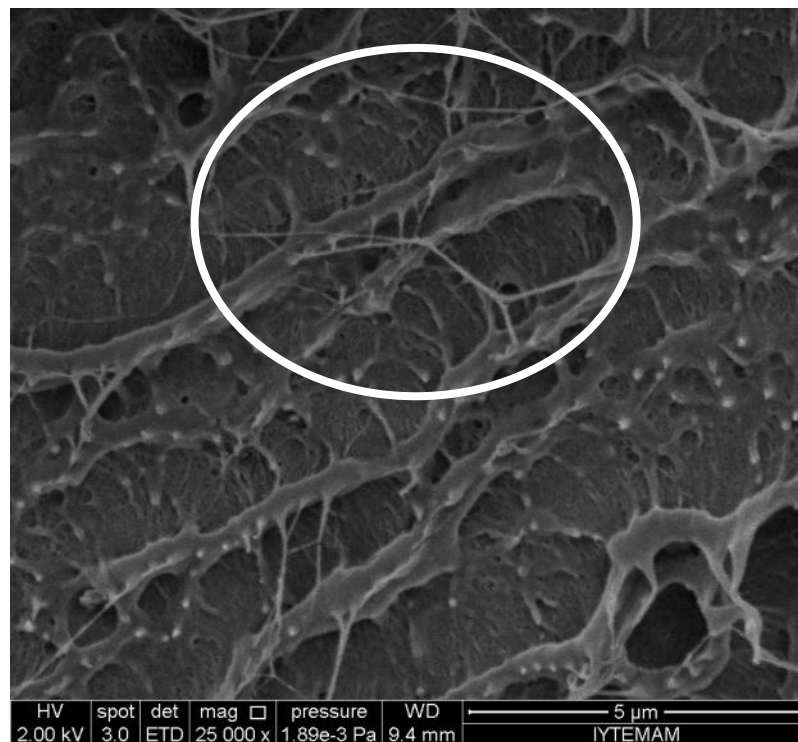


Figure 4.10. Nanocomposite film 3 with 0.25 wt. % of MWCNT

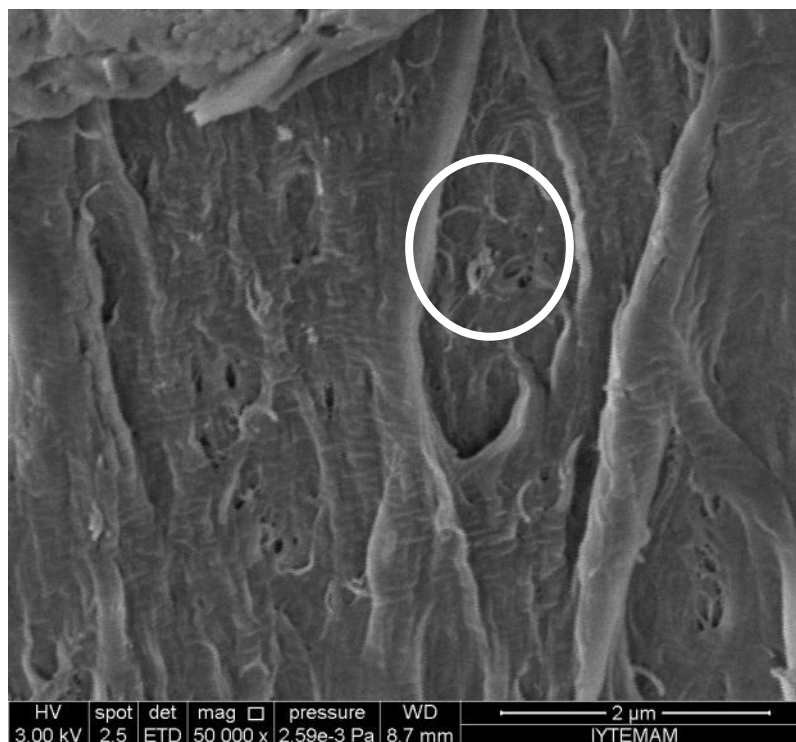


Figure 4.11. Nanocomposite film 3 with 1 wt. % of MWCNT

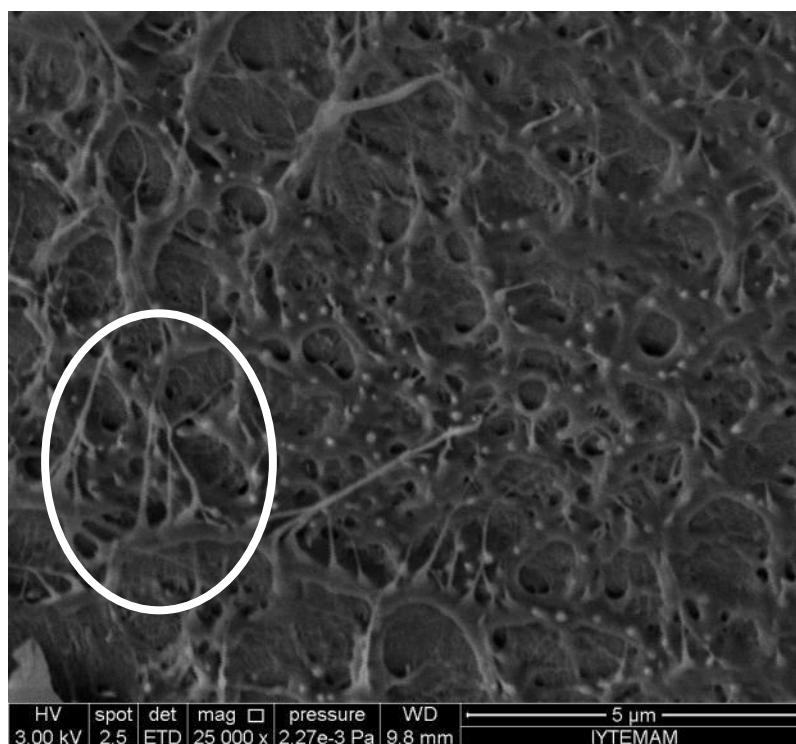


Figure 4.12. Nanocomposite film 3 with 3 wt. % of MWCNT

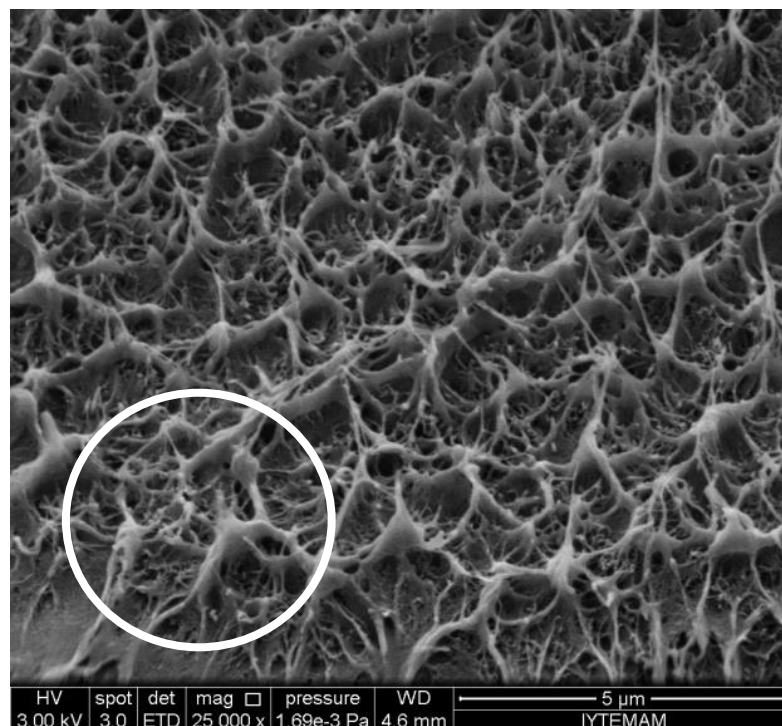


Figure 4.13. Nanocomposite film 3 with 5 wt. % of MWCNT

4.3. Mechanical Properties

4.3.1. Elastic Limit

The results for elastic limit (MPa) are presented in Table 4.1 along with the percent of increment-decrement, as indicated by the values inside the bracket. Based on the results, it could be stated in general that the addition of MWCNT decreased the elastic limit (see the trend in Figure 4.14). However, the slight increment was recorded at the addition of 0.25 wt. % of MWCNT type 1 and 3 and the given values were 4.4 % and 2.9 %, respectively. Although the increment was slight, it was considered as statistically different compared with the neat LLDPE (control). The results were also indicated that as the content of MWCNT increased, the elastic limit decreased as well. Interesting finding is that there was no significant effect of different type of MWCNT on elastic limit at any concentration but 5 wt. %. It could also be seen that mostly the statistically different results were shown at different contents of MWCNT rather than the different types.

Table 4.1. Elastic limit result (MPa)

Composite Film	MWCNT Content (wt. %)				
	0 (control)	0.25	1	3	5
1 (SD)	28.82 ± 2.48 ^b	30.08 ± 1.73^a (4.4%)	26.82 ± 1.92 ^{bc} (-6.9%)	27.92 ± 1.24 ^b (-3.1%)	25.63 ± 2.38 ^{c, B} (-11.1%)
2 (MD)	28.82 ± 2.48 ^a	27.31 ± 1.84 ^b (-5.2%)	26.28 ± 1.85 ^b (-8.8%)	26.11 ± 1.09 ^b (-9.4%)	24.39 ± 0.92 ^{c, B} (-15.4%)
3 (BD)	28.82 ± 2.48	29.66 ± 3.32 (2.9%)	27.32 ± 1.58 (-5.2%)	28.70 ± 3.82 (-0.4%)	27.68 ± 1.78 ^A (-3.9%)
Control		n.s			28.82 ± 2.48 ^A

Values correspond to the mean ± standard deviation

^{a-c}Different letters in the same row indicate significant differences (p<0.05)

^{A-B}Different capital letters in the same column indicate significant differences (p<0.05)

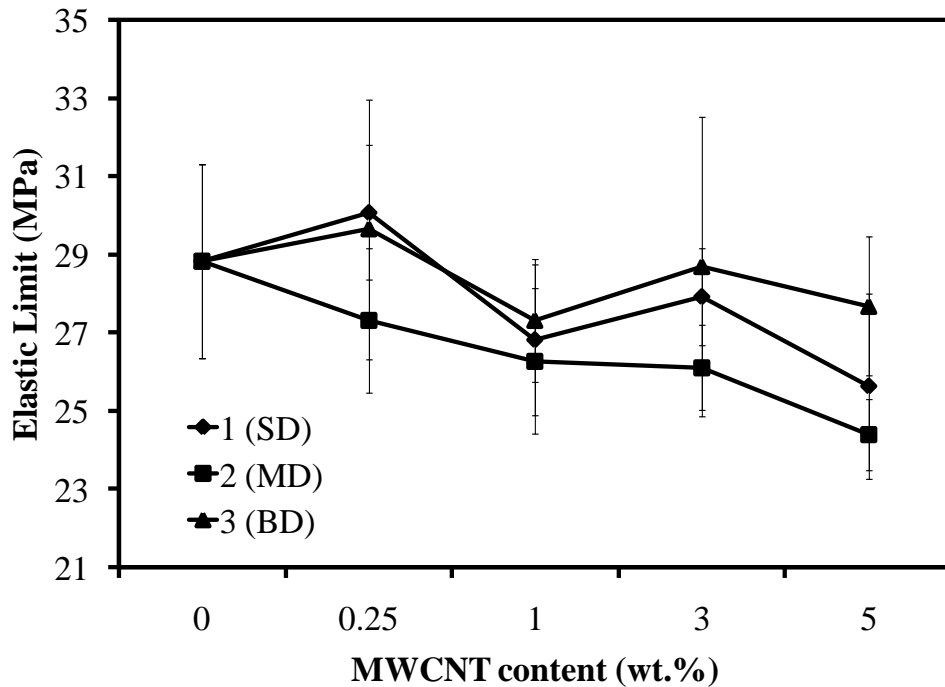


Figure 4.14. The effect of addition of MWCNT on Elastic Limit

As can be seen in Figure 4.14, the elastic limit value, somehow, was increased for the lowest content of MWCNT (0.25 wt. %) then decreased as the content increased. The recorded increment might be resulted as the consequence of better dispersion of MWCNT in the polymer matrix (as shown in Figure 4.2). The decrement phenomenon

which was occurred in elastic limit for nanocomposite film 1 and 2 at relatively higher content of CNT was considered as statistically different. Therefore, considering overall result it could be said that nanocomposite film containing type 3 MWCNT in general gave relatively better result compared to others. This finding is relevant to the result which was obtained by Morcom, Atkinson, and Simon (2010) which indicating that a bigger dimension of MWCNT is the most effective in increasing the yield stress value.

4.3.2. Tensile Strength

Tensile strength is one of the parameters that always be recorded in mechanical properties. The results for tensile strength (MPa) are presented in Table 4.2 along with the percent of increment-decrement, as indicated by the values inside the bracket. Almost having a similar trend with elastic limit, the tensile strength results in general show that the addition of MWCNT, for any types, decreased the tensile strength of the nanocomposite film (see the trend in Figure 4.15). The prominent increment was only recorded at the lowest content of MWCNT (0.25 wt. %) and the values were 12.6 % and 11.2 %, which were resulted from nanocomposite film 1 and 3, respectively. The slight increments were also recorded at 3 wt. %. As can be seen from the statistical result, the significantly different results were noted mostly for different contents of MWCNT than different types.

Table 4.2. Tensile strength result (MPa)

Composite Film	MWCNT Content (wt. %)				
	0 (control)	0.25	1	3	5
1 (SD)	17.37 ± 3.85 ^a	19.56 ± 2.16^a (12.6%)	15.15 ± 2.86 ^b (-12.8%)	17.62 ± 2.50 ^a (1.4%)	15.96 ± 3.17 ^{ab, B} (-8.1%)
2 (MD)	17.37 ± 3.85 ^a	17.46 ± 2.47 ^a (0.5%)	14.71 ± 3.85 ^{ab} (-15.3%)	16.34 ± 2.14 ^a (-5.9%)	13.50 ± 2.33 ^{b, B} (-22.3%)
3 (BD)	17.37 ± 3.85	19.31 ± 3.21 (11.2%)	17.12 ± 2.49 (-1.4%)	17.83 ± 3.18 (2.6%)	17.70 ± 1.75 ^A (1.9%)
Control			n.s		17.37 ± 3.85 ^A

Values correspond to the mean ± standard deviation

^{a-b}Different letters in the same row indicate significant differences (p<0.05)

^{A-B}Different capital letters in the same column indicate significant differences (p<0.05)

According to Mezghani et al. (2011), the increment can be resulted from the good interfacial bonding between carbon nanotubes and polymer matrix. It is because the bonding can act as the transfer path for the load which was being transferred from polymer matrix to the carbon nanotubes, so it can increase the tensile strength.

The decrements in tensile strength as the content of carbon nanotubes increased are also reported by several researchers such as McNally et al. (2005), Yang, Pramoda, Xu, and Goh (2007), Aalaie et al. (2007), and Campo and Visco (2010). The decrement of tensile strength in relatively higher content of MWCNT could be happened due to the uneven distribution of MWCNT (see Figure 4.4 and Figure 4.13). As the content of CNTs increased, it tended to form agglomeration which can affect the performance of nanocomposite film, especially in tensile strength. The carbon nanotubes agglomerates are also can act as stress concentrators and ultimate failure points during a tensile test which can affect the tensile strength (Vasileiou et al., 2013).

Looking at the trend as depicted in Figure 4.15, in comparison to type 1 and 2, type 3 MWCNT gave relatively better result for tensile strength. This finding is supported by the distribution of MWCNT in the polymer matrix as can be seen SEM result for nanocomposite film 3.

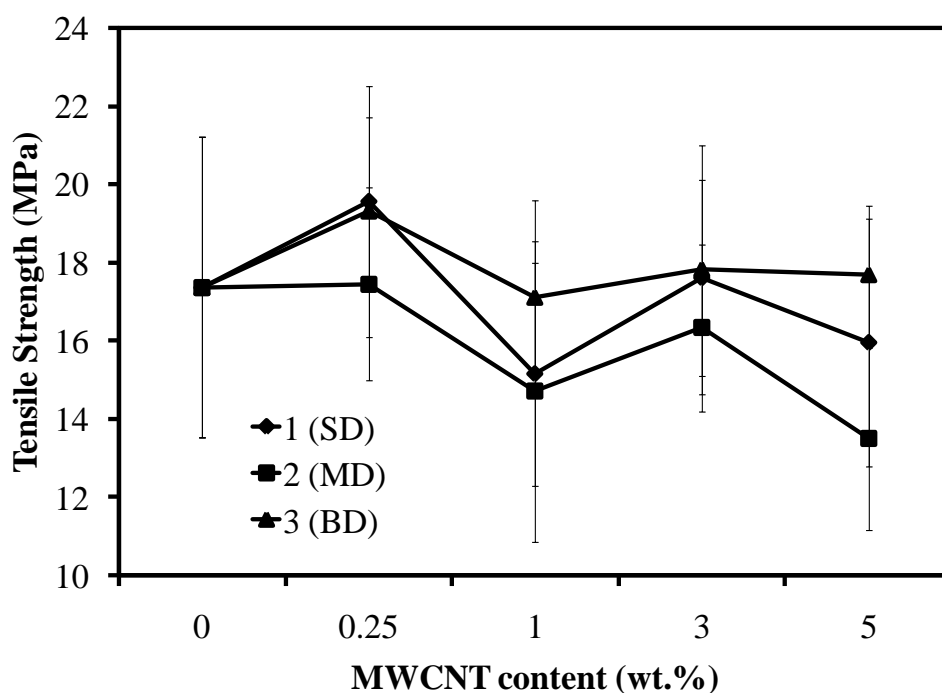


Figure 4.15. The effect of addition of MWCNT on Tensile Strength

4.3.3. Young's Modulus

Overall improvement results in Young's Modulus (MPa) are presented in Table 4.3 along with the percent of increment-decrement, as indicated by the values inside the bracket, and then the state of improvement is depicted in Figure 4.16.

According to the results, generally it could be concluded that the addition of MWCNT improved the Young's modulus and the increment of Young's modulus was in line with the increment of MWCNT content. As can be seen here, the prominent increment was achieved by the highest content of carbon nanotubes (5 wt. %) for all type of MWCNT. The highest value was 26.9 % and resulted from nanocomposite film 3 at 5 wt. % and then followed by film 1 and 2 at the same level and the given values were 26.4 % and 24 %, respectively. Either different contents or different types of MWCNT were recorded to be significantly different compared to control.

Table 4.3. Young's modulus result (MPa)

Composite Film	MWCNT Content (wt. %)				
	0 (control)	0.25	1	3	5
1 (SD)	368.3 ± 29.8 ^e	398.2 ± 15.6 ^{d, A} (8.1%)	409.4 ± 15.6 ^{c, A} (11.2%)	435.8 ± 8.9 ^{b, A} (18.3%)	465.4 ± 18.9 ^{a, A} (26.4%)
2 (MD)	368.3 ± 29.8 ^e	386.3 ± 10.5 ^{d, AB} (4.9%)	397.2 ± 11.2 ^{c, A} (7.8%)	424.2 ± 8.2 ^{b, A} (15.2%)	456.7 ± 12.5 ^{a, A} (24%)
3 (BD)	368.3 ± 29.8 ^c	409.4 ± 43 ^{b, A} (11.2%)	408.3 ± 34.4 ^{b, A} (10.9%)	429.4 ± 57.6 ^{a, A} (16.6%)	467.7 ± 20.2^{a, A} (26.9%)
Control	n.s	368.3 ± 29.8 ^B	368.3 ± 29.8 ^B	368.3 ± 29.8 ^B	368.3 ± 29.8 ^B

Values correspond to the mean ± standard deviation

^{a-e}Different letters in the same row indicate significant differences (p<0.05)

^{A-B}Different capital letters in the same column indicate significant differences (p<0.05)

The reinforcement effect of MWCNT on Young's modulus is also reported from several works. According to Mahfuz, Adnan, Rangari, and Jeelani (2005), the improvement is a result of infusion of carbon nanotubes as a much stiffer material into relatively softer material, polyethylene (LLDPE). Xiao et al. (2007) reported that the improvement in Young's modulus as the addition and increment of MWCNT content is due mainly to the change in the structural composition with the increasing tube content. As the CNT content increases, the continuous MWCNT network is formed throughout

the matrix. Hence, the coiling and curving nature of MWCNT makes strong mechanical interlocking within nanotubes be appeared and it can promote the reinforcement. Aalaeie et al. (2007) and Tarife and Narh (2011) stated that the degree of crystallinity, associated with the presence of MWCNT in the polymer matrix, may improve the Young's modulus. Ko and Chang (2009) explained that the improvement in this parameter can be happened due to the resistance which was exerted by the MWCNT and also due to the aspect ratio of nanotubes. Temporary bonding between polymer chains and the filler surface is another reason why the Young's modulus is increased, i.e., it plays an important role in physical cross-linking network thus enhance the modulus matrix (Jin-hua et al., 2012).

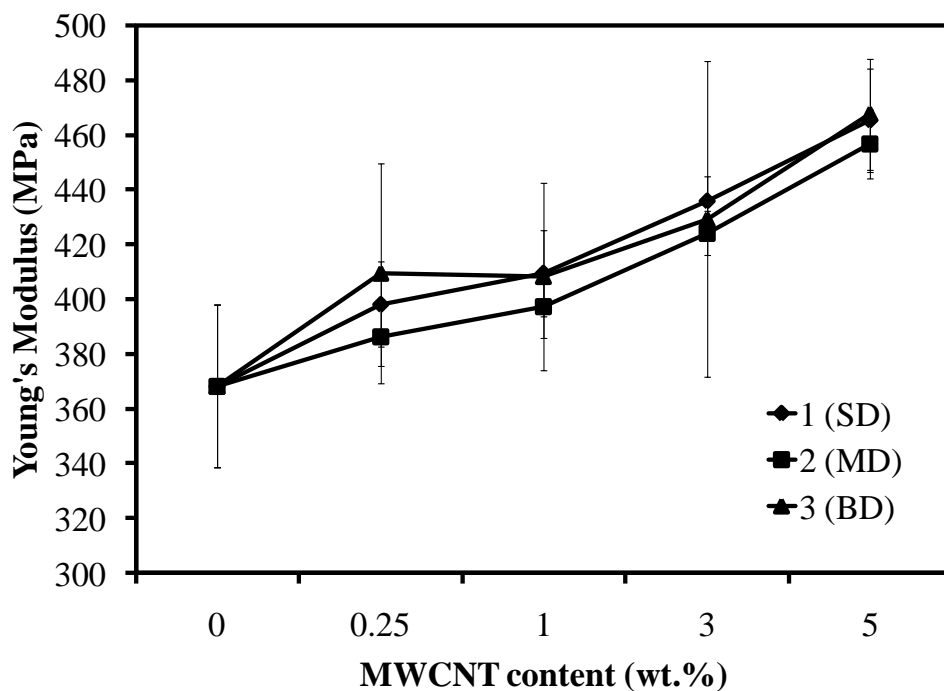


Figure 4.16. The effect of addition of MWCNT on Young's Modulus

Based on the figure above, it appears that type 1 MWCNT gave relatively better result in terms of Young's modulus compared with others. This finding supports that theoretically small diameter of carbon nanotubes leads to much higher composite elastic modulus (Coleman, Khan, Blau, & Gun'ko, 2006; Morcom et al., 2010).

4.3.4 Ductility

The results for ductility (%) are presented in Table 4.4 along with the percent of increment-decrement, as indicated by the values inside the bracket. Figure 4.17 depicted the effect of addition of MWCNT on ductility.

As can be seen from the data, in general the addition of MWCNT decreased the ductility of nanocomposite polymer. The decrements for this parameter were recorded to have a range between 2.2-18.9 %. The highest decrement was resulted from nanocomposite film 2 at 5 wt. %. Nevertheless, it was also found that nanocomposite film 1 and 3 at lowest content (0.25 wt. %) increased the ductility by 2.6 % and 2.1 %, respectively. According to statistical result, it was found that nanocomposite film 1 and 2 gives significant different result in ductility for different content of MWCNT. Moreover, the significant different results were also found in same contents of MWCNT with different types of MWCNT, which were at 1 wt. %, 3 wt. %, and 5 wt. %.

Table 4.4. Ductility result (%)

Composite Film	MWCNT Content (wt. %)				
	0 (control)	0.25	1	3	5
1 (SD)	718.4 ± 48.1 ^a	737.3 ± 43.4^a (2.6%)	654.5 ± 42.5 ^{bc, A} (-8.9%)	680.8 ± 28.9 ^{b, A} (-5.2%)	621.9 ± 52.0 ^{c, A} (-13.4%)
2 (MD)	718.4 ± 48.1 ^a	674.3 ± 38.8 ^b (-6.1%)	643.7 ± 45.7 ^{b, AB} (-10.4%)	636.1 ± 24.8 ^{b, A} (-11.5%)	582.5 ± 18.5 ^{c, B} (-18.9%)
3 (BD)	718.4 ± 48.1	733.6 ± 69.2 (2.1%)	690.6 ± 35.2 ^B (-3.9)	702.3 ± 58.3 ^B (-2.2%)	680.1 ± 30.6 ^A (-5.3%)
Control	n.s	n.s	718.4 ± 48.1 ^A	718.4 ± 48.1 ^A	718.4 ± 48.1 ^A

Values correspond to the mean ± standard deviation

^{a-c}Different letters in the same row indicate significant differences (p<0.05)

^{A-B}Different capital letters in the same column indicate significant differences (p<0.05)

Wang, Cheng, Liang, and Wang (2005) reported the similar finding regarding to the increment at 0.25 wt. % and continues with the decrement as the content of carbon nanotubes increased. They suspected that the decrement might be resulted by the agglomeration of carbon nanotubes which can only be happened at the higher content of MWCNT. It might be valid, since the SEM result for the content of 1 wt. % and 3 wt. % was shown the existence of MWCNT's agglomeration (see Figure 4.3).

The existence of MWCNT aggregates in the nanocomposite polymer with LLDPE matrix is also observed by Vasileiou et al. (2013). They stated that this aggregation can result the reduction of the elongation at break. Aalaeie et al. (2007) and Pöllänen, Pirinen, Suyanto, and Pakkanen (2011) explained that carbon nanotubes aggregation may acts as initiation site for failure which can cause the premature failure during the tensile test or accelerate the final breakage, thus it can decrease the elongation at break. Another theory for the decrement in ductility is also stated by Jin-hua et al. (2012). It has been said that higher content of carbon nanotubes, which naturally rigid, increases rigidity of the final composite material and it may inhibit the elongation of nanocomposite and make it less ductile. The decrement effects of the addition of MWCNT into polymer matrix on elongation at break are also reported by McNally et al. (2005), Morcom et al. (2010), and Campo and Visco (2010).

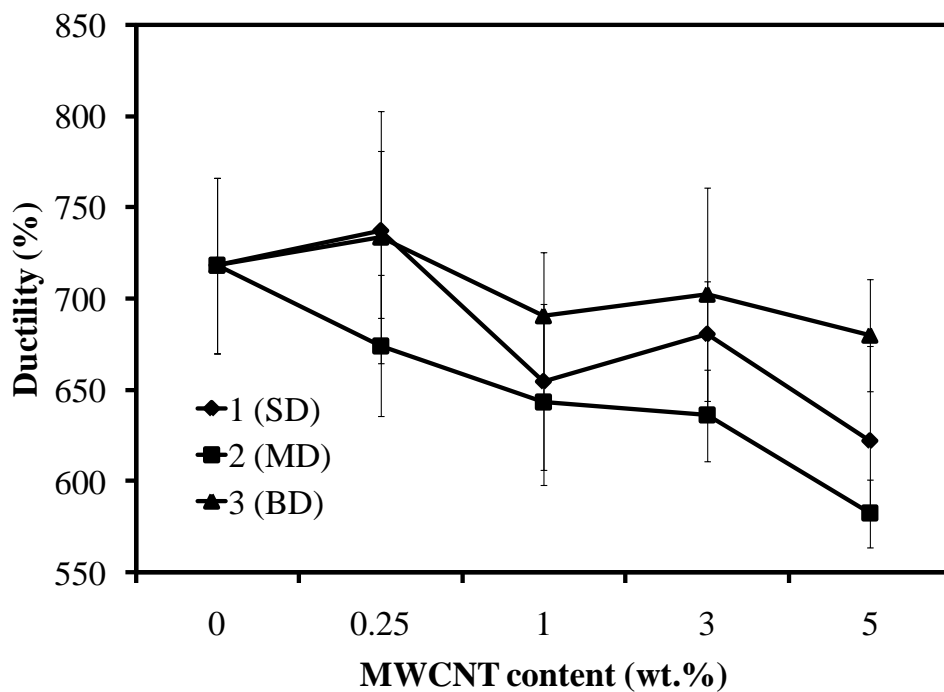


Figure 4.17. The effect of addition of MWCNT on Ductility

Comparing the result for three different types of MWCNT in the graphic as depicted in Figure 4.17, it appears that nanocomposite containing type 3 MWCNT gave relatively better result. In fact for this type, the different content of MWCNT did not result any significant different compared with control.

In summary, the prominent reinforcement effect of MWCNT was achieved in Young's modulus and the trend was in line with the increasing content of MWCNT. Other consistent improvements were also shown by the lowest content of MWCNT (0.25 wt. %) in elastic limit, tensile strength, and ductility. However, as the content of the MWCNT increased, the trend was decreasing. In agreement with these findings, Nourredine Aït Hocine in Mittal, V. (2010) stated that the Young's modulus is increased when the uniform dispersion in nanoscale size is achieved. It typically increases with the nanoparticles volume fraction, since the degree of exfoliation and sufficient dispersion of the nanoparticles are ensured. Nonetheless, nonlinear mechanical properties, such as elongation at break, tensile strength, or impact strength, generally decreased beyond a critical proportion of reinforcing particles. The fact that the Young's modulus is evaluated at low strains, whereas other properties are determined above catastrophic break where the loading transfer between fillers and matrix is important, might be explained this phenomena.

Basically, the good mechanical properties of nanocomposite polymer will be achieved if there is a good interaction between nanofillers and polymer matrix, a good dispersion state of the nanofillers and its alignment, and the natural characteristic of the nanofillers, for the case of carbon nanotube is its rigidity. The interaction can be in the form of adhesion (van der Waals) and/or mechanical interlocking (Pöllänen et al., 2011). In this research, it was observed that a good dispersion could bring improvement in mechanical properties, as supported by SEM result. Most of the times the good dispersion of nanofillers was achieved at lower contents of MWCNT. Therefore, the increments in mechanical properties which were seen in this work were achieved at that level. Amoli, Ramazani and Izadi (2012) also stated that the best dispersion and distribution can only be attained at lower MWCNT contents.

The interesting finding was on relatively sharp decrement at 1 wt. % after an increment resulted from 0.25 wt. % content of MWCNT in some mechanical properties such as elastic limit, tensile strength, and ductility. It might be related to the agglomeration of MWCNT which likely could happen at this level, as can be seen in SEM results (Figure 4.3). Agglomeration of MWCNT, in another case might be called as the aggregation of MWCNT, is responsible for the slight or no improvement in mechanical properties of nanocomposite polymer. This can be explained by the fact that the aggregation of MWCNT will likely act as stress concentrators and slip under applied stress, reducing the overall strength of the nanocomposites (Tarife & Narh, 2011). It

may also act as defects and decrease the strength, as can be seen from the results in this work. Hence the agglomeration can cause profoundly deleterious effect for they induce premature fracture and frequently become sources of secondary cracks (Pöllänen et al., 2011). This agglomeration can exist due to van der Waals forces owing by carbon nanotubes and it was supported by the high surface area of carbon nanotubes (Ashori, Shesmani, & Farhani, 2013). According to Sulong and Park (2010), agglomeration tends to be performed by higher aspect ratio of MWCNT at higher concentration.

In the case of MWCNT dimension, the bigger dimension, owned by type 3 MWCNT, was proven to yield relatively better mechanical properties compared to other types. The improvement might be resulted from relatively better dispersion of type 3 MWCNT in the polymer matrix, as can be seen from SEM results. The corresponding finding is also highlighted by Morcom et al. (2010) using the relatively similar dimension of MWCNT. They proposed three main possibility reasons how this dimension may give the reinforcement effect on nanocomposite polymer, as follows:

1. As for their case, although the dispersion of thin nanotubes studied is predicted to be thermodynamically favorable, increasing nanotube diameter decreases the attraction between nanotubes, resulting in the driving force towards dispersion being higher for larger diameter nanotubes.
2. For nanotubes become thinner, it is thought the dispersion is become increasingly more difficult, so does to wet, due to the distance between nanotubes approaching the size of polymer molecules.
3. As for their case, the bigger diameter of nanotubes is reported to have aligned and separated form, which significantly lower bulk density. The implication of this is that they have large spacing between nanotubes and it allowed an easy path for the thermoplastic melt to penetrate the bundles and wet the nanotubes during melt mixing. Plus, the alignment would likely encourage exfoliation since it can reduce the entanglement of nanotubes.

4.4. Gas Permeabilities

4.4.1. Oxygen Permeability

The ability of material to be a barrier, non-permeable, for several gasses is one of the important factors that need to be considered when choosing material for food packaging. The main reason is that the composition of certain gasses inside the food package system may alter the quality and shelf life of the food stuff. Oxygen and carbon dioxide are two of the most common gasses which can contribute to such phenomenon. Therefore, studying its permeability in certain material is necessary.

The complete data results for oxygen permeability ($\text{ml/m}^2/\text{day}$) test are presented in Table 4.5 along with the percentage of decrement, as indicated by the values inside the bracket. In this test, film samples were taken only from control, lowest content (0.25 wt. %), and highest content (5 wt. %) of MWCNT. It is because these film samples represent the biggest difference in terms of CNT content. The oxygen permeability test was done in sample films having average thickness between 0.17-0.19 mm and there was no significant difference in terms of thickness. The effect of addition of MWCNT in the film samples on oxygen permeability can be seen in the graphic as depicted in Figure 4.18.

Table 4.5. Oxygen permeability result ($\text{ml/m}^2/\text{day}$)

Composite Film	MWCNT Content (wt. %)		
	0 (control)	0.25	5
1 (SD)	325.32 ± 0.00^a	$250.25 \pm 5.98^{b, B}$ (-23.1%)	$272.86 \pm 13.60^{b, B}$ (-16.1%)
2 (MD)	325.32 ± 0.00^a	$246.80 \pm 0.00^{c, B}$ (-24.1%)	$281.83 \pm 21.37^{b, B}$ (-13.4%)
3 (BD)	325.32 ± 0.00^a	$238.99 \pm 25.82^{b, B}$ (-26.5%)	$260.92 \pm 6.51^{b, B}$ (-19.8%)
Control	n.s	325.32 ± 0.00^A	325.32 ± 0.00^A

Values correspond to the mean \pm standard deviation

^{a-c}Different letters in the same row indicate significant differences ($p < 0.05$)

^{A-B}Different capital letters in the same column indicate significant differences ($p < 0.05$)

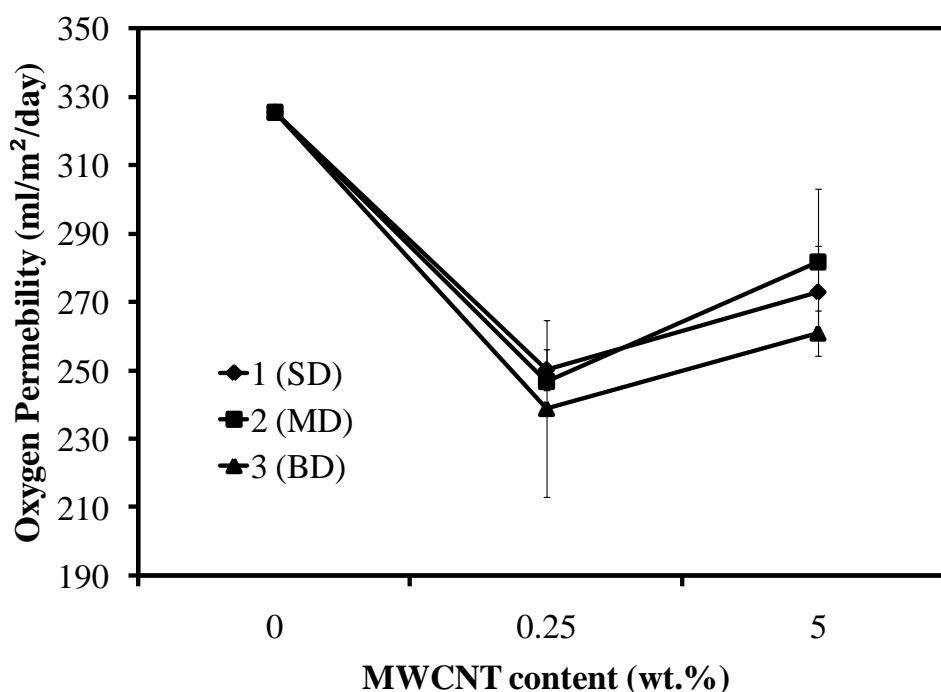


Figure 4.18. The effect of addition of MWCNT on Oxygen Permeability

As can be seen from the figure above, generally the addition of MWCNT into LLDPE polymer enhanced the oxygen barrier property of nanocomposite films by lowering the gas permeability. It was observed that lowest content of MWCNT (0.25 wt. %) decreased the oxygen permeability by almost more than 20 % compared with control. The highest result in oxygen barrier property was shown by the nanocomposite films containing type 3 MWCNT and then followed by type 2 and 1, with the given value were 26.5 %, 24.1 %, and 23.1 %, respectively. The results were also shown that by increasing the content of MWCNT it could decrease the oxygen barrier property of nanocomposite film. However, all the improvement which was resulted from the film samples, both by differentiation in MWCNT types and contents, was considered as significantly different compared to neat LLDPE film (control film). Based on the result, it could be said that the content of carbon nanotubes in the films was more crucial in resulting improvement of oxygen barrier properties compared with the type of MWCNT.

Referring to the previous statement, stated in Chapter 2, the work on gas permeability (oxygen and carbon dioxide) in nanocomposite film made from MWCNT and polyethylene, especially LLDPE, is limited. However, the results which were obtained from this research experiment can be still related to any other works which using MWCNT in different types of polymer matrix and investigating the gas permeabilities.

Ko and Chang (2009) reported about the oxygen permeabilities of ultrahigh molecular weight polyethylene (UHMWPE)/functionalized MWCNT nanocomposite films. Similar to our results, they found that gas permeabilities of nanocomposite films were lower than the pure UHMWPE films. They concluded that this kind of behavior can be attributed to the presence of rigid bundle of MWCNT having a high aspect ratio in the polymer matrix. Hence, by increasing the content of MWCNT from 0.25 to 2 wt. %, the barrier properties of the hybrid films are increased as well.

Recent findings on oxygen permeabilities test of nanocomposite films made from LDPE/MWCNT are reported by Salehifar et al. (2013). They prepared the films by solvent casting method and then used the films to package Lavash bread. They found that the films, containing 0.1–0.5 wt. % of carbon nanotubes, capable to inhibit oxygen permeability significantly so that increase the shelf life of Lavash bread. Therefore, they suggested that LDPE/MWCNT films can be considered as appropriate package for bakery products. Clearly, their results show similar trend with the results which were obtained from this research.

Other reinforcement effects of addition of MWCNT into polymer matrix on oxygen permeabilities were also reported from several works. Sanchez-Garcia, Lagaron, & Hoa (2010a) stated that low addition of nanofillers, carbon nanotubes and carbon nanofibers, into polymer matrix result in the best morphology and consequently in the best improvement in oxygen permeability. Additionally, they investigated this property in the nano-bio-composites of polycaprolactone (PCL) and polyhydroxybutyrate-co-valerate (PHBV), prepared by solvent casting method (Sanchez-Garcia, Lopez-Rubio, & Lagaron2010b). They found that increasing carbon nanotubes content, from 1, 3, 5, to 10 wt. %, results in reduction of the oxygen barrier due to agglomeration of carbon nanotubes. This trend is in line with our results (as supported by the result of SEM which can be seen in Figure 4.19). Therefore, it can be suggested that the best reduction in the oxygen permeability can be achieved only at low content of carbon nanotubes.

According to Pradhan and Swain (2012a), the improvement in oxygen barrier properties can be caused by several factors, such as longer diffusive path of the penetration of the oxygen in the presence of MWCNT in the polymer matrix. The aspect ratio of MWCNT also plays an important role in order to efficiently maximize the path length. Furthermore, the presence of these nanofillers, such as MWCNT, introduces a torturous path for which the oxygen travels longer diffusive path. Not to forget, the well dispersion of MWCNT in the polymer matrix can also be a reason for this improvement. It is because the well dispersion of nanofillers may provide the huddles for oxygen permeation through its composites (Pradhan & Swain, 2012b). Nevalainen et al. (2013) also mentioned that typically, composite films made of polyolefins and nanosized fillers with low filler contents (6 wt. %) may reduce the oxygen permeability rate by more than 10 % and up to 20 % over that of unfilled matrix. This statement supports our results in which the improvement ranged between 13-26 %. However, the ability of nanofillers to improve the oxygen barrier is clearly affected by several factors such as filler content, filler aspect ratio, processing method and condition, void formation, polymer chain orientation, and polymer matrix crystallinity. As for the last factor, it is because the changes in crystallinity complicate gas permeation and the addition of carbon nanotubes is proven to change the degree of crystallinity (Mirzadeh & Kokabi, 2007).

4.4.2. Carbon Dioxide Permeability

Similar with the test for oxygen permeability, the test for carbon dioxide (CO₂) permeability was done with film samples taken only from control, lowest content (0.25 wt. %), and highest content (5 wt. %) of MWCNT. The complete result data for carbon dioxide permeability (ml/m²/day) are presented in Table 4.6 along with the percent of decrement, as indicated by the values inside the bracket. The average of film samples thickness was not statistically different and it was ranged between 0.17-0.19 mm. The effect of addition of MWCNT on carbon dioxide permeability can be seen in the graphic as depicted in Figure 4.19.

Table 4.6. Carbon dioxide permeability result (ml/m²/day)

Composite Film	MWCNT Content (wt. %)		
	0 (control)	0.25	5
1 (SD)	2024.9 ± 250.70	1638.9 ± 167.20 ^A (-19.1%)	1735.4 ± 0.00 (-14.3%)
2 (MD)	2024.9 ± 250.70	1735.4 ± 0.00 ^A (-14.3%)	1879.9 ± 250.50 (-7.2%)
3 (BD)	2024.9 ± 250.70 ^a	1376.9 ± 119.40^{b, B} (-32.0%)	1735.4 ± 0.00 ^a (-14.3%)
Control	n.s	2024.9 ± 250.70 ^A	n.s

Values correspond to the mean ± standard deviation

^{a-b}Different letters in the same row indicate significant differences (p<0.05)

^{A-B}Different capital letters in the same column indicate significant differences (p<0.05)

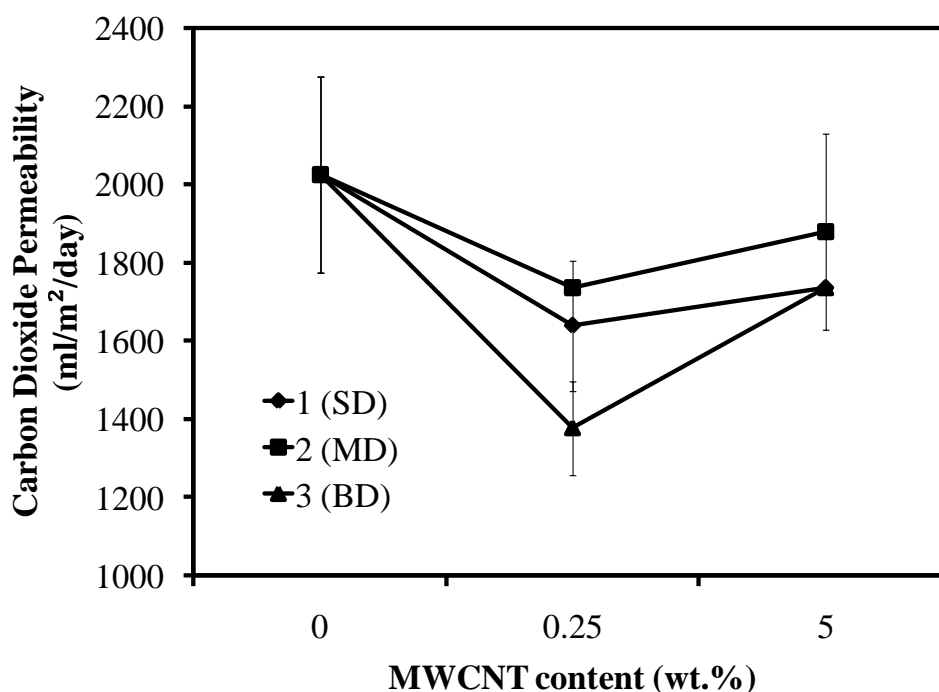


Figure 4.19. The effect of addition of MWCNT on Carbon Dioxide Permeability

Showing the similar trend with oxygen permeability results, the carbon dioxide permeability results were observed as giving the prominent result when the content of MWCNT is 0.25 wt. % in the nanocomposite film, which is by lowering the permeability. Nonetheless, it could be concluded that the addition of MWCNT enhanced

the barrier property of carbon dioxide gas. Interesting finding was that only films containing type 3 MWCNT were proved to be significantly different, where 0.25 wt. % gave highest result compared with others. For the rest, although it did not show any significant difference compared with control film, the decrements of CO₂ were still recorded and it was in range between 7.2 and 19.1 %.

The improvement in CO₂ barrier property of nanocomposite sample films might be related to the well dispersion of MWCNT in the polymer matrix, especially in the lower content. As noted before, the well dispersion of nanofillers can help minimizing the gap which exists in the nanocomposite so that the gas will be difficult to pass through.

In conclusion, considering the reinforced effect of addition of MWCNT on gas barrier properties, both for O₂ and CO₂, of nanocomposite films, it could be said that these nanocomposites films could be prospectively developed as one of the alternatives material for food package. This is supported by the fact that the presence of undesirable concentration of oxygen and carbon dioxide inside the package of certain food products may alter its quality and shorten the shelf life.

4.5. Overall Migration

The complete data results for overall migration test are presented in Table 4.7. In this test, film samples were taken only from control, lowest content (0.25 wt. %), and highest content (5 wt. %) of MWCNT. The average sample films thickness used for this test was ranged between 0.29-0.35 mm.

As can be seen from the results, the overall migration values were below the limit required by European Union Commission (10 mg/dm²). The result indicated that there was no transfer of large quantities of substances which could change the composition of foods. According to statistical result, the values of overall migration from nanocomposite film 1 at any level gave significantly different compared with the control film, with the lowest value was shown at 0.25 wt. %. It was also found that at 0.25 wt. % the types of MWCNT showed significant different, with type 1 appeared to be the significant one.

Almost consistent with the trends which were resulted from previous test, the sample films containing lowest content of MWCNT (0.25 wt. %) showed relatively

better result compared with 5 wt. % content of MWCNT. It was suspected that the better result gained from lowest content of MWCNT connected to relatively better dispersion and good interaction between nanofillers and matrix polymer (Yu, Qin, Sun, Yang, & Yao, 2014).

Table 4.7. Overall migration result (mg/dm²)

Composite Film	MWCNT Content (wt. %)		
	0 (control)	0.25	5
1 (SD)	5.70 ± 0.29 ^a	1.63 ± 0.42^{c,C}	3.26 ± 0.68 ^b
2 (MD)	5.70 ± 0.29 ^a	4.16 ± 0.64 ^{b,B}	5.45 ± 0.54 ^a
3 (BD)	5.70 ± 0.29	4.89 ± 0.34 ^B	6.07 ± 2.62
Control	n.s	5.70 ± 0.29 ^A	n.s

Values correspond to the mean ± standard deviation

^{a-c}Different letters in the same row indicate significant differences (p<0.05)

^{A-C}Different capital letters in the same column indicate significant differences (p<0.05)

CHAPTER 5

CONCLUSION

Nanocomposite made from LLDPE (linear low density polyethylene) and MWCNT (multiwalled carbon nanotubes), the dimension was varied, was successfully fabricated by using melt blending method utilizing twin-screw extruder. The films were then prepared by hot-pressing. The extrusion procedure was carried out by applying two times extrusion process, using normal screw profile, and having temperature profile as follows: 160 °C, 165 °C, 165 °C, 170 °C, 170 °C, 175 °C, 175 °C, 175 °C, 170 °C, and 165 °C, from feeding to the die spot. The effect of elongated nanoparticle on gas permeabilities and mechanical properties of nanocomposite films was studied. First, the characterization of the films was done by scanning electron microscopy (SEM).

Referring to SEM examination result, the dispersion of MWCNT in general was considerably average. The networks formed between LLDPE–MWCNT were observed on several sample films. On the other hand, the presence of carbon nanotubes agglomeration was unavoidable, especially in the higher content of MWCNT, and sometimes it was appeared at the lower content of MWCNT (1 wt. %). It was suspected that the presence of these networks and agglomeration complexes affect the mechanical and gas permeability properties of the sample films.

In terms of mechanical properties, the addition of MWCNT (at any dimension) increased the Young's modulus and the trend was increased in line with the increasing content of carbon nanotubes. For the rest of the properties, such as elastic limit, tensile strength, and ductility, the improvements were recorded only at the lowest content (0.25 wt. %), where the dispersion of carbon nanotubes was good. Although the decrement trend was found in mechanical properties, except Young's modulus, generally it can be considered as not statistically different compared with neat LLDPE film (control film). Nanocomposite films containing type 3 MWCNT (inside diameter 5-15nm; outside diameter 50-80 nm, and length 10-20 nm) gave relatively better result compared with other types of nanocomposite films. However, statistically speaking, the mechanical properties were affected significantly by the content of MWCNT rather than its dimension.

In accordance with mechanical result, the reinforcement effect of the addition of MWCNT on gas permeabilities was exhibited by the nanocomposite films. It can be stated that the addition of MWCNT in general increased the oxygen and carbon dioxide barrier properties. The prominent result of this improvement was achieved at the lowest content (0.25 wt. %). Therefore, it can be said that the content of MWCNT in the polymer matrix more important to affect the properties rather than its dimension. Nevertheless, nanocomposite films containing type 3 MWCNT showed relatively better result compared with others. The improvement in barrier properties might be occurred due to the presence of MWCNT in the polymer matrix, which can cause the longer diffusive path for gas to penetrate and the forming networks by LLDPE-MWCNT establish a tortuosity path which can hinder the gas to diffuse along the film.

According to the result of overall migration test, the amount of substances which possibly transferred into food stuff were considerably low and below the limit required by European Union Commission (10 mg/dm²). The lowest value for overall migration was achieved by the nanocomposite films containing type 1 MWCNT.

Considering our outstanding results, it can be concluded that the future application of the particular nanocomposite as food packaging is possible and promising. Moreover, the gas barrier improvement in polyethylene after being filled with carbon nanotubes assure the broaden application of polyethylene polymer, such as the application as packaging for several food products which affected by oxygen/carbon dioxide and water vapor. Hence, carbon nanotubes are suspected to have antimicrobial activity, so the nanocomposite containing this particle could be used in accordance with this aspect.

Further, the particular nanocomposite is not only can satisfy the mechanical, barrier, and migration requirement but also with further exploration it can be developed for active packaging. As we might be aware, the presence of nanoparticle in nanocomposite polymer which used as packaging allows the dynamic role played by this nanoparticle to preserve the food as a result of in contact with food and environment. Therefore, it is expected that the findings of this research could trigger further studies especially by exploring the use of this composite in food packaging and to be applied in active packaging systems.

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