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**EFFECT OF NANOSEPIOLITE AND  
NANOSILICA CONTENT, POLYETHYLENE-  
GRAFTED-MALEIC ANHYDRIDE AND  
IRGANOX 1010 ON TENSILE AND  
MORPHOLOGICAL OF LOW DENSITY  
POLYETHYLENE NANOCOMPOSITES**

By

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## LIST OF ABBREVIATIONS

CNTs	Carbon Nanotubes
EDX	Energy Dispersive X-Ray Spectrometer
HALS	Hindered Amine Light Stabilizers
HDPE	High Density Polyethylene
ICI	Imperial Chemical Industries
kV	kiloVolt
LDPE	Low Density Polyethylene
MAPE/PE-g-MA	Maleic Anhydride-grafted-Polyethylene
Mg	Magnesium
nm	millimetre
MMT	Montmorillonite
nm	nanometre
O	Oxygen
PE	Polyethylene
PC	Polycarbonate
PMMA	Poly-methyl-methacrylate
PVC	Poly-vinyl Chloride
RPM	Revolution per minute
SEM	Scanning Electron Microscopy
Si	Silicon
Ti	Titanium
TEM	Transmission Electron Microscopy
UV	Ultraviolet

**KESAN KANDUNGAN NANOSEPIOLIT DAN NANOSILIKA, POLIETILENA-  
DICANGKUKKAN-MALIK ANHIDRIDA DAN IRGANOX 1010 KE ATAS  
SIFAT-SIFAT TERIKAN DAN MORFOLOGI BAGI NANOKOMPOSIT  
POLIETILENA BERKETUMPATAN RENDAH**

**ABSTRAK**

Nanokomposit termoplastik bagi adunan polietilena yang diadun dengan nanosepiolit dan nanosilika telah dikaji. Kesemua sampel ujian telah disediakan menggunakan pencampur dalaman Plastograph Brabender EC Plus (Duisberg, Jerman) pada 160°C, pada kelajuan 50 rpm, dan dibentuk menggunakan pemampatan pada suhu 160°C. Keputusan menunjukkan bahawa komposit yang terisi nanosepiolit memberikan sifat tegangan yang lebih baik berbanding komposit terisi nanosilika pada pemuatan pengisi yang sama. Lekatan antara pengisi dan matriks telah dipertingkatkan dengan menggunakan MAPE sebagai agen pengserasi pada muatan 3 phr. Semua sifat telah diperbaiki untuk kedua-dua nanokomposit. Penambahan antioksidan ke dalam nanokomposit menunjukkan bahawa kandungan antioksidan yang paling rendah pada 1 phr memberikan sifat terikan dan modulus Young tinggi berbanding 3 phr dan 5 phr. Kesan penuaan haba juga dikaji dengan mendedahkan nanokomposit di dalam ketuhar pengudaraan kepada suhu 70°C selama 72 jam. Nanokomposit tersebut didapati menunjukkan sifat-sifat yang lebih baik daripada nanokomposit kawalan apabila antioksidan digunakan pada sistem nanokomposit dan ianya disokong oleh analisis morfologi SEM dan analisis FTIR.

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NANOCOMPOSITES**

**ABSTRACT**

Nanocomposites of thermoplastic blend of low density polyethylene (LDPE) filled with nanosepiolite and nanosilica was investigated. All of the test samples were prepared using Brabender Internal Mixer Plastograph EC Plus (Duisberg, Germany) at 160°C, speed of 50 rpm, and moulded using compression at temperature of 160°C. Results showed that the nanosepiolite filled composites gave better tensile properties than nanosilica filled composites at same filler loading. The adhesion between filler and matrix was improved by using MAPE as a compatibilizer at 3 phr content. All the properties were improved for both nanocomposites. The addition of antioxidant into the nanocomposites showed that the lowest content of antioxidant at 1 phr gave higher tensile strength and Young's modulus compared to 3 phr and 5 phr. The effect of thermal ageing was also investigated by exposing the nanocomposites in air circulated oven at 70°C for 72 hours. The nanocomposites were found to show better properties than the control nanocomposites when antioxidant were added to the nanocomposite system and supported by SEM morphology and FTIR analysis.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

Recently, academia and industries gave more attention to polymer/clay nanocomposites. They are now hustling to popularize nanoclays, thermoplastics composites specifically concentrating on automotive parts, packaging and agriculture. By optimizing certain key factors such as additives and processing parameters or nanometre-size of clays in a polymer matrix, properties such as mechanical, thermal, gas barrier and flame resistance has been improved. The first commercial nanocomposites product was an engine cover-belt developed by Japan's Ube Industries after being licensed the patented *in situ* polymerized PS6/Clay nanocomposites (NCH) technology by Toyota Research Centre, following the pioneering work done about one decade ago [Bilotti *et al*, 2009]. In Table 1.1 a series of commercial ventures in polymer-clay nanocomposites are presented.

Table 1.1: Commercial ventures in polymer-clay nanocomposites [Bilotti *et al.* 2009].

<b>UBE</b>	Nylon6 Toyota timing belt cover, engine manifold cover Nylon6 Film for packaging Nylon6/66, 12 Fuel system components
<b>BAYER PLASTICS</b>	Nylon6 Film for meat packaging Nylon6 coating for paper board juice container PC/ABS Flame retardant computer and monitor housings
<b>FORSTER CORP.</b>	Nylon 12 nanocomposites used in catheter tubing
<b>GM</b>	Polyolefin TPO for step on Astro vans to replace talc filled materials
<b>UNITIKA</b>	Nylon6 automotive parts (Mitsubishi engine cover) EVOH, Polylactic acid nanocomposites (various automotive uses)
<b>WILSON SPORTING</b>	Tennis balls (butyl rubber/nanoclay coating from InMat)
<b>HONEYWELL</b>	Nylon6 for food packaging
<b>U.S. ARMY</b>	MRE food tray (EVOH)
<b>KABLEWERK EUPEN</b>	EVA flame retardant cable coating
<b>TNO</b>	Polyacrylate binding system for ceramic moulds
<b>MITSUBISHI</b>	Polypropylene nanocomposites for automotive parts
<b>TRITON SYSTEM</b>	Polyurethane bladder for athletic shoes Polyolefin packaging film for food and pharmaceutical packaging
<b>NANOCOR</b>	MXD-6 Nylon for barrier food packaging

Greenhouses are known to offer most appropriate situations for production. The crops are being observed under controlled condition by keeping up basic supplies such as water, fertilizers, seeds, and plant protection chemicals. It is realized that greenhouses are glazed with clear material that transmits visible light (400-700nm), which is the important basis in photosynthesis [Briassoullis *et al.*, 1997]. In the most recent decades, the expanded research towards greenhouses has increased the inclusion of plastics for use as a cover material [Dintcheva, 2001].

Low density polyethylene (LDPE), being of lightweight, transparent, cheap, and of high mechanical quality, has conquered the utilization of plastic films as greenhouse glazing materials. However, the greenhouse materials are exposed to various ecological factors that centered to chemical and/or physical degradation. It is very much described

in literature that degradation of LDPE is improved by ultraviolet (UV) radiation which transmit its energy to polymer molecules making them to be energized and subject to oxidation [Al Othman, Faiz & Abduh Tuasikal, 2014].

Reinforcing fillers are usually utilized as a part of polymer preparations to enhance the modulus and other mechanical properties of the material. It is the cooperation of the filler particle surface with the plastic matrix and the following development of an interfacial layer that yields the expected enhancement of properties. Therefore, reduction in average particle size of fillers and the subsequent increment in particular surface area are wanted in planning better composites, as it expands the polymer/nano filler interfacial volume. Utilizing nanoscale fillers can enhance the weatherability of nanocomposites by giving more efficient light protecting by the filler particles throughout outdoor exposure too [Redhwi *et al.*, 2013; Redhwi *et al.*, 2013].

Polymer nanocomposites are in limelight because they offer the advantages of polymer composites joint with new promising properties. The filler nanoparticles embedded in matrix have a great surface-to-volume ratio which produce large interfacial areas, compared to macrometer or micrometer scale counterparts [Gonzalez-Benito and Olmos, 2010]. Depending on the size, particle shape, specific surface area and chemical nature, some of the properties of polymer matrix can be modified such as :

- (i) electrical and thermal conductivity
- (ii) polymer phase behaviour and thermal stability
- (iii) mechanical properties such as stiffness, Young' modulus, wear, fatigue and others
- (iv) flame retardancy
- (v) density

(vi) physical properties such as magnetic, optic, or dielectric properties

LDPE characteristics can be improved by embedding various organic and inorganic nanofillers into the LDPE matrix. LDPE based nanocomposites with various nanoparticles like nanoclays such as montmorillonite (MMT) and carbon nanotubes (CNTs). For example in Chang, Li, and Wu [2011], the increasing mechanical properties were found to have certainly improved after the proper MMT and MA grafted were added into LDPE matrix. In addition, The  $T_m$  and enthalpy of LDPE-g-MA group were also observed relatively lower. It is indicating that MMT would be easier to embed in polymer matrix through grafting with MA. The  $T_d$  values determined with TGA examinations revealed improvement in the thermal stability because of the presence of MA grafting [Chang, 2015]. In Sabet and Soleimani [2014], it was revealed that 10 wt% CNTs addition to LDPE increased young's modulus and tensile strength values of composites by 96% and 60%, respectively. Mechanical properties of pure LDPE augmented with CNTs addition too.

A great portions of published data on polymer/clay nanocomposites focused on lamellar layered silicates, especially on the intercalation and exfoliation of montmorillonite (MMT), whereas polymer/sepiolite nanocomposites have not been studied to that level [Fukushima, Tabuani and Camino, 2009]. Most of the literature regarding clay nanocomposites has been focused on platelet-like clays, such as MMT. The current research deals with sepiolite, which is a needle-like fibrous nanofiller with open channels extended longitudinally in the fiber direction with hydrated magnesium silicate having the unit cell formula,  $Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$ . It can have a very high surface area as high as  $200\text{-}300\text{ m}^2\text{g}^{-1}$ , lengths of  $0.2\text{-}4\text{ }\mu\text{m}$ , width of  $10\text{-}30\text{ nm}$  and thickness of  $5\text{-}10\text{ nm}$ . Sepiolite is also a member of the phyllosilicate mineral lineage. It

is hydrated magnesium silicate clay having microfibrinous morphology and its structure consists of an octahedral sheet of magnesia sandwiched between two tetrahedral silica sheets. The result of discontinuity of octahedral sheets in sepiolite exposes number of silanol groups ( $Si - OH$ ) on its external surface [Syafik, Yasin and Saeed, 2012].

It is expected that these fibrous nanofiller can be more simply scattered in polymer matrix because of its surface area compared to the platelet-like clays of the same aspect ratio. The relatively less contact surface area reduced the tendency to agglomeration which may result in better mechanical properties, thermal stability, flame retardancy and barrier properties of the polymers even at a very low level of filler loading [Bilotti, Fischer & Peijs, 2008; Zheng & Zheng, 2006; Fartaglione *et al.*, 2008]

Other than sepiolite, another filler that guarantees major enhancement to the LDPE is silica. Among the ordinarily utilized particulate reinforcement, silica particles reinforcement has increased much consideration nowadays because of its accessibility, cheap and stiffness [Ahmad and Mamat, 2012; Cho, Joshi and Sun, 2006]. Silica nanoparticles have turned out to be an applicable additive to polymers by enhancing durability, quality, and flexibility. Silica is utilized as an additive to enhance quality and workability of self-compacting and high performance concretes [Rizlan and Mamat, 2014; Saleh, Ibrahim and Salman, 2015].

A few efforts have been made by researchers to examine the effect of silica nanoparticles in polymer matrix. Both thermoset and thermoplastic polymer strengthened with silica nanoparticles have been accounted for in the literature. Zhu Z.K. *et al.* [1999] explored that silica particles size is reliant on its content in the composites. Since Young's modulus increases linearly with silica content, the particle

size effect is insignificant. Thus it is 100-200nm, 200-450nm and 1-2 $\mu$ m respectively for silica content of 5, 10 and 20wt%. Otherwise, the relationship will be non-linear.

In the earlier work [Oluyemi *et al.*, 2015], sol-gel process for the developing of submicron silica particles from rice husk ash (RHA) was explained and the effect of the silica particles on the mechanical properties of High Density Polyethylene (HDPE) was also showed. Energy dispersive x-ray spectrometer (EDX) and scanning electron microscopy (SEM) was used to determine the elemental composition and the morphology of the powder respectively. The EDX analysis confirmed the existence of silica in the composite to be 96.1%. The powder particle size was also proved by Horiba dynamic particle size analyzer. The average particle size was 0.5 $\mu$ m. The silica powder causes improvement in the mechanical properties of HDPE up to 4 wt.%.

Jordan *et al.* [2005] studied the effect of micron and nanosized silica particles incorporated in polyurethane matrix and spotted that the existence of micron sized silica particles further increased the overall density of the composites as compared to the nanosized incorporations. Tahir and Othman [2011] developed HDPE reinforced with silica nanoparticles. In their work, higher weight content of silica nanoparticles reduces the mechanical properties of the composite. Tahir, Othman and Rafiq [2013] studied the effect of silica nanoparticles on epoxy-based composites. They observed that 15 %wt. incorporation of silica nanoparticles enhances the Young's modulus of the composites. Decreasing in tensile strength was also observed due to incorrect mixing of the silica nanoparticles in the epoxy resin. The lack of any improvement in the tensile properties was due to particle clustering.

The key issue in LDPE/nanosepiolite and LDPE/nanosilica composites is to develop good compatibility between hydrophobic polymer and hydrophilic filler.

Because LDPE is a non-polar polymer, it is difficult to prepare LDPE/nanosepiolite and LDPE/nanosilica composites. Overall, two applicable ways are used to formulate LDPE/nanosepiolite and LDPE/nanosilica composites, in-situ polymerisation [Heinemann *et al.*, 1999; Rong *et al.*, 2001; Bergmann *et al.*, 1999] and melt intercalation [Wang *et al.*, 2001; Wang *et al.*, 2002; Gopakumar *et al.*, 2002].

Melt intercalation has been viewed as the most necessary for the thermoplastic polymers, by which the filler layers are direct scattered in the molten polymers by utilizing traditional melt processing procedures. The melt intercalation technique to make non-polar polyolefin/filler nanocomposites depends on the acquaintance of a compatibilizing agent to bond the hydrophilic filler surface and the hydrophobic polymers [Kawasumi *et al.*, 1997]. In LDPE, homogeneous dispersion of filler layers was recognized by using maleic anhydride-grafted polyethylene (MAPE) [Wang *et al.*, 2001; Wang *et al.*, 2002; Gopakumar *et al.*, 2002]. However, it should be noted that application of the right amount of compatibilizer and an appropriate process for blending is crucial to the properties of the final product [Thomas, Grohens, and Jyotishkumar, 2014; Thomas, Shanks, and Chandran, 2013].

Nevertheless, polyolefines are oxidation-vulnerable, particularly at high temperature. Antioxidant is the most suitable and effective agent introduced to prevent thermo-oxidative degradation of these materials. Irganox 1010 is a phenolic antioxidant and the most widely used polyolefin antioxidants. Its compatibility with polyethylene was investigated by several author. In Sekii, Ohno and Oguma [2004] finding, they found out that samples with absence of phenolic antioxidant has higher amount of oxidized substances comparing to the samples blend with phenolic antioxidant. In irradiated UHMWPE stabilized with several antioxidant, Irganox 1010 gave the highest thermal oxidation resistance in the oxidative stability because Irganox 1010 has the

highest OH-group concentration per gram (stabilization potency) and the highest molecular mass (reduced migration) [Wolf, Wannomae and Muratoglu, 2011]. Also a study shows that antioxidants were confirmed to be effective in improving the mechanical properties and water absorption of the biocomposites which specifies that the by adding antioxidants as additive improves the properties and the stability of recycled high density polyethylene reinforced with a hybrid of rice husks and sawdust [Ghani *et al.*, 2014].

There is no study has been reported on LDPE/sepiolite and LDPE/silica sand in greenhouse film. This research was conducted to study the influence of nanosepiolite and nanosilica content on mechanical properties of the films and the effect of thermal aging of the composites films.

## 1.2 Problem Statement

LDPE is a popular one amongst the most utilized materials in plasticulture and its usage as agriculture greenhouse covers is a typical application. The principle properties that have guaranteed its success are particularly its light-weight and transparency.

Sunlight is the main harmful cause in the degradation of greenhouse cover resulting in decrease the lifespan of the cover which will deteriorate the mechanical properties. The greenhouse plastic covers degrade slowly under the combination of effect of heat, solar ultraviolet UV radiation, mechanical stress and chemical agents [Mourad, 2010; Dehbi, Mourad and Bouaza, 2011]. The greenhouse plastics that made without adding any additives such as filler, UV absorber, colouring agent, light stabilizer, antioxidant are normally show lower properties when it is been used for outdoor application. Energy-rich solar radiation and heat radiation causes plastics to become brittle and easily failure when it made from purely polymer. This is because, without additives, the polymer chain can easily dissociate and undergoes photo-degradation and thermo-oxidative degradation.

Therefore, the improvement on the quality of the greenhouse film by adding mineral filler such as nanosepiolite and nanosilica ought to be consider to improve the durability of plastics, while meeting increasingly tough requirements with respect to the ecological effect of agriculture, water consumption and cost of materials. By enhancing the properties of the greenhouse plastics films, the durability of the plastics could be extend and reduced the cost of maintenance to the planter/farmer. Greenhouse films with outstanding characteristics such as high durability, long life span and high light

transmission with optional characteristics that transforms the film to an dynamic provider to plant shelter, growth and productivity.

### 1.3 Objective Research

The main goal of this study is to evaluate the effectiveness of developing a high durability greenhouse plastic cover by incorporating nanosepiolite and nanosilica as reinforced filler. The specific objectives are:

- i) To study the effect of nanosepiolite and nanosilica content on the mechanical and morphology properties of LDPE/nanocomposites.
- ii) To compare the mechanical properties, morphology, FTIR analysis and ageing of LDPE/nanosepiolite and LDPE/nanosilica.
- iii) To investigate the effect of MAPE to properties of LDPE nanocomposites.
- iv) To analyze the effect of Irganox 1010 content on thermal ageing of LDPE nanocomposites.

## 1.4 Outline of Research Study

Chapter 1 presented the overview of greenhouse cover in general knowledge and function. In this chapter, the potential of nanosepiolite and nanosilica sand as the reinforced filler, MAPE as compatibilizer and Irganox 1010 were briefly describe based from previous literature. This chapter also reviewed the objectives and problem statement in details.

Chapter 2 reviewed the literature of greenhouse structure, indicate the general information about greenhouse structure and also factors that affect the stabilization of the greenhouse covers. In addition, the details of the compounding ingredients such as LDPE as the polymer matrix, mineral filler, compatibilizer and antioxidant featured in details. Besides that, the mechanisms of compatibilizer and antioxidant were also explained.

Chapter 3 focus on the details of LDPE as raw material, nanosepiolite and nanosilica as the mineral filler, MAPE as the compatibilizer and Irganox 1010 as the antioxidant. In addition, the details on how compounding this ingredients were also explained. Testing and characterization also has been deliberated in this chapter.

Chapter 4 discussed the results and discussion based on the four (4) parameter proposed, namely; (1) the effect of different type of fillers on LDPE properties, (2) the effect of different compatibilizer loading on the LDPE properties, (3) the effect of different antioxidant loading on LDPE properties and (4) the effect of thermal aging on the LDPE/nanocomposites.

Chapter 5 mainly summarized the contribution of the theses and also recommendation for future and continuos work of the project.