Palm Kernel Shell, Nanosilica and Palm Kernel Shell/ Nanosilica Filled Polypropylene Hybrid Composites

by

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LIST OF SYMBOLS, ABBREVIATIONS OR NOMENCLATURES

AA	Acrylic Acid
AO	Antioxidant
ASTM	American Society for Testing and Materials
ATRP	Atom Transfer Radical Polymerization
BB	Beech Bark
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetric
EFB	Empty Fruit Bunch
ΔH_f	Enthalpy of fusion of the system
ΔH°_f	Enthalpy of fusion of perfectly (100%) crystalline polymer
iPP	Isotactic polypropylene
LDPE	Low Density Polyethylene
LGF	Long Glass Fiber
MA	Maleic anhydride
MAPP	Maleinated Polypropylene
MDF	Medium Density Fiberboard
MFI	Melt Flow Index
MFR	Melt Flow Rate
PET	Poly(ethylene Terephthalate
PGMA	Poly(glycidyl Methacrylate)
PKS	Palm Kernel Shell
PMMA	Poly(methyl methacrylate)

POFA	Palm Oil Fatty Acid Additives
POME	Palm Oil Effluent
PP-B	Block Copolymer Polypropylene
PP-G-MA	Polypropylene grafted Maleic Anhydride
$PP\text{-}G\text{-}NH_2$	Aminated Polypropylene
PP-H	Homopolymer Polypropylene
PP	Polypropylene
PP-R	Random Copolymer Polypropylene
Q_t	Molar Sorption
Q_∞	Equilibrium Water Uptake Values
RH	Rice Husk
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analyzer
T_m	Melting Temperature
W	Weight of sample
X_{com}	Percentage of Crystallinity of Composite

KOMPOSIT HIBRID POLIPROPILENA TERISI TEMPURUNG KELAPA SAWIT, NANOSILIKA DAN TEMPURUNG KELAPA SAWIT / NANOSILIKA TERISI

ABSTRAK

Kajian terhadap komposit hibrid polipropilena (PP) terisi tempurung kelapa sawit (PKS) dan nanosilika terbahagi kepada empat bahagian. Fasa pertama kajian mengutamakan siasatan terhadap kesan penambahan PKS sebagai pengisi tunggal ke atas sifat-sifat mekanikal, penyerapan air, morfologi dan terma PP. PKS (berat pengisi 10-40%) telah disebatikan dengan polipropilena menggunakan pencampur dalaman Brabender Plastograph pada suhu proses 180°C dan kelajuan rotor 50 rpm. Keputusan menunjukkan penurunan terhadap kekuatan tensil, kekuatan hentaman dan pemanjangan pada takat putus dengan peningkatan berat pengisi tetapi meningkatkan modulus Young dan penyerapan air. Kajian morfologi yang menggunakan mikroskop elektron pengimbas (SEM) menunjukkan interaksi interfasa yang lemah antara pengisi PKS dan PP dengan peningkatan berat kandungan pengisi. Tambahan pula, didapati PKS mengurangkan penghabluran komposit dalam kajian terma. Fasa kedua kajian adalah untuk mengkaji kesan penambahan nanosilika terhadap sifat-sifat mekanikal PP. Nanosilika (berat pengisi 1-5%) telah disebatikan dengan PP menggunakan pencampur dalaman pada suhu proses 180°C dan kelajuan rotor 50 rpm. Sifat-sifat mekanikal PP terisi nanosilika komposit telah dibandingkan bagi menentukan pengimbangan sifat-sifat mekanikal yang terbaik dimana ianya akan digunakan sebagai asas untuk kajian komposit hibrid PP di bahagian yang ketiga. Keputusan menunjukkan pada berat pengisi yang rendah, komposit mempamerkan kekuatan tensil dan pemanjangan pada takat putus yang tinggi tetapi dengan peningkatan berat pengisi, kekuatan dan pemanjangan mula menurun. Fasa ketiga kajian melibatkan penggunaan formulasi komposit PP terisi nanosilika yang terkuat, iaitu PP terisi nanosilika dengan berat pengisi 2%, sebagai asas untuk mendapatkan formulasi komposit hibrid yang optimum. Justeru itu, semua komposit hibrid dengan berat pengisi 2% akan digunakan untuk kajian ini. Komposit hibrid disebatikan menggunakan parameter yang sama dengan komposit PP terisi PKS. Penggunaan dua jenis pengisi di dalam PP matriks didapati meningkatkan kekuatan tensil, pemanjangan takat putus dan kekuatan hentaman tetapi menurunkan modulus Young dan penyerapan air PP komposit. Kajian terma menunjukkan peningkatan pada kebolehan penghabluran oleh pengisi hibrid menyumbang kepada peningkatan sifat-sifat mekanikal komposit tersebut. Fasa terakhir kajian ini melibatkan penggunaan penyerasi "polypropylene grafted maleic anhydride" (PP-g-MA) ke atas komposit yang mempunyai pengisi tunggal dan komposit hibrid. Kesan modifikasi kimia terhadap komposit yang mempunyai pengisi tunggal dan komposit hibrid oleh PP-g-MA telah meningkatkan kekuatan tensil, modulus Young, kekuatan hentaman dan penghabluran tetapi menurunkan pengambilan air. Kajian morfologi menunjukkan interaksi yang lebih baik antara pengisi dan matriks dengan penggunaan berat PP-g-MA 2%.

PALM KERNEL SHELL, NANOSILICA AND PALM KERNEL SHELL/ NANOSILICA FILLED POLYPROPYLENE HYBRID COMPOSITES

ABSTRACT

The research on palm kernel shell (PKS) and nanosilica filled polypropylene (PP) hybrid composites consists of four parts. The first part is mainly to investigate the effect of incorporating PKS as single filler on the mechanical, water absorption, morphology and thermal properties of PP. PKS (10-40 weight % filler loading) was compounded with polypropylene using Brabender Plastograph internal mixer at processing temperature 180°C and rotor speed 50 rpm. Preliminary results show that the tensile strength, impact strength and elongation at break decreased with the increasing of filler loading but increased the tensile modulus and water absorption. The morphology study using scanning electron microscopy (SEM) shows poor interfacial interaction between PKS and PP with the increasing of filler content. In addition, PKS was found to be a poor nucleating agent in thermal studies. The second part of the research is to study the effect of incorporation of nanosilica on mechanical properties of PP. Nanosilica (1-5 weight %) were mixed with PP using internal mixer at processing temperature 180°C and rotor speed 50 rpm. The mechanical properties of nanosilica filled PP composites were compared to determine the best balance in mechanical properties which would be used as platform for the study of hybrid PP composites in the third part of the research. The results show that at low filler loading the composite exhibit high tensile strength and elongation at break but with the increasing of filler loading, the strength and elongation started to deteriorate. The third part of the research would be to use the strongest nanosilica filled PP composite formulation, i. e. nanosilica filled PP with 2 weight % filler loading, to act as benchmark for the determination of the optimum hybrid composite formulation. Subsequently, all the hybrid composites in the studies were to have 2 weight % of nanosilica loading. The hybrid composites were compounded using similar parameters as in PKS filled PP composites. The usage of two types of filler in PP matrix was found to enhance the tensile strength, elongation at break and impact strength but reduced the tensile modulus and water absorption of the PP composites. Thermal studied confirmed that the improved nucleating ability of the hybrid fillers contributed to the superb mechanical properties of the hybrid composites. The final part involved subjecting the single-filler and hybrid filler PP composites to polypropylene grafted maleic anhydride (PP-g-MA) compatibilizer. The effect of chemical modification of single-filler and hybrid composites with PP-g-MA improved tensile strength, tensile modulus, impact strength and crystallinity but decreased water uptake. The morphology study shows better interaction between filler and matrix with the usage of 2 weight % of PP-g-MA.

CHAPTER 1

INTRODUCTION

1.1 Research Background

An attraction of people toward polymer composites has increase every year especially in automotive industry. In order to pursue the enhancement of the polymer composites properties to be more suits in this application, continuous advancements are required time by time. These advancements are emphasis on strength, durability, fracture toughness, etc. Consequently, by manipulated polymer composites, scientists come out with the idea of hybrid system (Karian, 2003).

Hybrid composites are the composites whereby reinforcing two or more reinforcement in a single matrix to create the diversity in its properties (Li *et al.*, 2000). However, these hybrid composites must be design judiciously in order to provide linear additive properties unavailable in single or binary phase composites and multiplicative enhancement for interaction of different constituents (Shonaike & Advani, 2003).

Some researchers have done on thermoplastic reinforced by two different fillers which is hybrid composites. Thermoplastics have been mixed with wood flour and recycled glass fiber (Valente *et al.*, 2011), short glass fiber and calcite (Fu *et al.*, 2002), long glass fiber and calcium carbonate (Hartikainen *et al.*, 2005), talc and calcium carbonate (Leong *et al.*, 2004) glass fiber and wollastonite (Joshi & Purnima, 2010). Not much works have been done in hybrid composites which involve the nano size of fillers so far.

Nanoparticle is well known by its size advantage which gives high surface contact area to the matrix. However, the use of nanoparticle in polymer composites is taking up the challenges for material engineer to ensure that the homogenous dispersion of inorganic nanoobjects into a polymer matrix. This is the natural behavior of nanoparticle which has a tendency to form agglomeration (Wu *et al*, 2005; Zhou *et al*, 2008) even worse than microparticle in polymer composites. Agglomeration of filler will lead to material deteriorate and decrease performance of polymer composites in mechanical and thermal properties.

Other filler that attract materials engineer in recent years is lignocellulosic materials. These lignocellulosic materials consist of lignin, hemicellulose and cellulose and become an alternative over conventional filler like glass fiber, calcium carbonate and others. This is due to its environmentally friendly because lignocellulosic materials are derived from plants. Palm kernel shell (PKS) is one of the lignocellulosic materials which are derived from palm oil plants. PKS are being considered as agricultural waste because only its kernels were extracted for palm oil that used for daily cooking.

Polypropylene play important role in composite whereby it protect the fillers from environment threat. The usage of polypropylene in plastic manufacturing industrial increased every year compared to other low cost polyolefins because of its high temperature resistance, easy to process and high crystallinity (Peacock & Calhoun, 2006)

However, compatibility of polymer matrix with filler should be deliberated and well managed to get optimum performance of composite. Since polypropylene is well-known for its versatility, it can be modified in many ways in order to achieve wide variety of end-use applications. For example, people created cost-effective mechanical properties of polymer by the addition of various fillers and reinforcements. Both mechanical and thermal properties can be improved with the addition of fibrous materials such as tensile, flexural strength, heat deflection temperature and impact strength as well. Fillers normally used for reducing final material cost while enhanced stiffness and impact of the material. However, most fillers or reinforcements and polymer matrix are not compatible to each other. Polymer modification can be implementing to overcome this problem (Karian, 2003).

Polymer modification involved the polymer grafted with polar molecules such as maleic anhydride (Bikiaris *et al.*, 2005) and NH_2 (Chen *et al.*, 2009). Compare to fibre modification which involves with solvent based processes, polymer modification come out with swift and effective method to provide interfacial adhesion between polymer matrix and filler or reinforcement (Pracella *et al.*, 2006).

There is limited literature base on the palm kernel shell filled thermoplastic composites. Thus, the research work prepared in this thesis emphasis on the study of palm kernel shell/nano-SiO_2/polypropylene hybrid composites by modified the polypropylene with polypropylene grafted maleic anhydride.

1.2 Problem Statement

The awareness of ecological issues burgeoning whereas many governments or leaders of the countries in the world try to introduced green technology to people. Since Malaysia become one of the biggest palm oil producer country in the world (Alengaram *et al.*, 2011), this country produce many tons of wastes include empty fruit bunches (EFB), palm kernel shell, pericap and palm oil effluent (POME) which worsening the disposal issues in Malaysia. In order to reduce this problem, PKS waste can be used to combine with nanoparticle and polymer to form hybrid composites.

However, a homogenous dispersion of PKS and nano-SiO_2 in a polymer is often difficult to achieve due to the strong tendency of the fillers to agglomerates. In order to overcome this problem, PP-g-MA copolymer was employed as compatibilizer which can formed boundary layer between the filler and matrix thus, improved the adhesion of the filler with matrix.

1.3 Objective of Study

The purpose of this research is to prepare and characterize palm kernel shell/nano-SiO_2 filled polypropylene hybrid composites. The purposes for this research are to:

1) Determine the optimum loading Palm Kernel Shell (PKS) in polypropylene in order to achieve good balance in mechanical properties, thermal properties and water absorption properties.
2) Determine the optimum loading of nanosilica in polypropylene in order to achieve good balance in tensile strength.
3) Study the hybridizing effect on the mechanical properties, thermal properties and water absorption properties of polypropylene composites.
4) Study the effect of polypropylene grafted maleic anhydride (PPMAH) on the mechanical properties, thermal properties and water absorption properties of PKS/ nanosilica filled polypropylene hybrid composites.

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CHAPTER 2

LITERATURE REVIEW

2.1 Particulate Filled Polymer Composites

Particulate is one type among the filler family which are being used for various application. In this project, particulate have been choose as filler to form composites. Particulate fillers are trusted to improve processing, control density, control of thermal expansion and properties such as stiffness, hardness, abrasion and tear resistance. In some cases, particulate fillers also use for enhancing magnetic properties, flame retardancy, thermal conductivity and optical effects (Karian, 2003).

2.1.1 Particulate Filled Thermoplastic Composites

In automotive application, well balanced of stiffness and impact strength of composites are very important in order to produce durable transport especially car. Particulate filled thermoplastic composites have ability to achieve these requirements. High temperature resistance ability can be offer by particulate filled thermoplastic composites whereby it essential for underhood and automotive interior parts. This type of composite shows high potential towards global uses as dependable material and many material engineers spend their time to create better particulate filled thermoplastic composites (Karian, 2003).

This proved by Baral *et al*., (1999) who examined thermoplastic polyurethane-mica composites by investigating its thermal properties. They found that the addition of mica in the thermoplastic polyurethane will enhanced the thermal stability of the composites by improved its decomposition temperature, thus longer the degradation process of the composites. For automotive interior parts, this advantage helps them to resist high temperature from heat created by sunlight especially when the car parked at roofless parking lots or travelled for long journey.

In addition, Rusu *et al*., (2001) investigated the mechanical and thermal properties of high density polyethylene composites filled with zinc powder. They found that zinc powder has improved the hardness, density and thermal stability of the high density polyethylene composites. However, the usage particulate fillers also gave negative impact to the thermoplastic composites. The addition of zinc powder into the high density polyethylene decreased the mechanical properties of the composites such as tensile strength.

Verbeek (2003) studied the influence of interfacial adhesion, particle size and size distribution on the predicted mechanical properties of particulate thermoplastic composites. He discovered that there was no effect or limited effect to the Young's modulus when varying the particle size between 60 and 300 μm. In addition, particles which were smaller than 240 μm will reduce the tensile strength. All these pros and cons provide chance to scientist to explore more about particulate filled thermoplastic composites and use them wisely for many applications in this world.

2.2 Nanosilica Filled Polymer Composites

Although they have been recognized for a long time, silica reinforced nanocomposites have until recently been minor commercial interest. However, in research scope, this type of composites attracted many researchers to study and evaluate the ability of nano-SiO_2 filled polymer composites. According to Wu *et al.*, (2002), the addition of nanoparticles into polypropylene composites has reinforced and toughens the composites. They explained that the significant improvement of tensile strength of the composites due to the chain interdiffusion and entanglement between the macromolecules of the grafting polymers and the matrix. Then, when increased the amount of nanoparticles, grafting polymer chains raised and interfacial stress transfer efficiency will decreased. In addition, Jacob *et al.*, (2010) examined the reinforcing effect of nanosilica on polypropylene-nylon fibre composites. They discovered that the presence of nanosilica in the polypropylene-nylon fiber composites has slightly enhanced the crystallization temperature and improve the thermal stability of composites.

Nano-SiO_2 is well known for its high aspect ratio and surface area where 1% and 2% of nano-SiO_2 filler loading is assumed to be comparable to 10% and 20% of micro-SiO_2 filler loading. Therefore, only small amount of nano-SiO_2 required enhancing the properties of composite compared to conventional method which used silica in micro size as reinforcement (Leng *et al.*, 2007). The statements that mention above also supported by Garcia *et al.*, (2007) whereby they investigated the role of nano-SiO_2 particle surfaces in the thermal degradation of nano-SiO_2 -poly(methyl methacrylate) (PMMA) solution-blended nanocomposites. They had successfully prepared homogeneous nanocomposite by a dispersion solution casting procedure. It was reported that low amount of nano-SiO_2 give better properties to the composites compared to high amount of nano-SiO_2. According to Figure 2.1, they explained that at low silica loading, labile chain ends are trapped by the silica particles and stabilized at the interface with the silica particle while at high silica loading, the interface is composed of a lesser concentration of labile chain ends. This increased the rate of random scission propagation, thus destabilize the polymer chain.

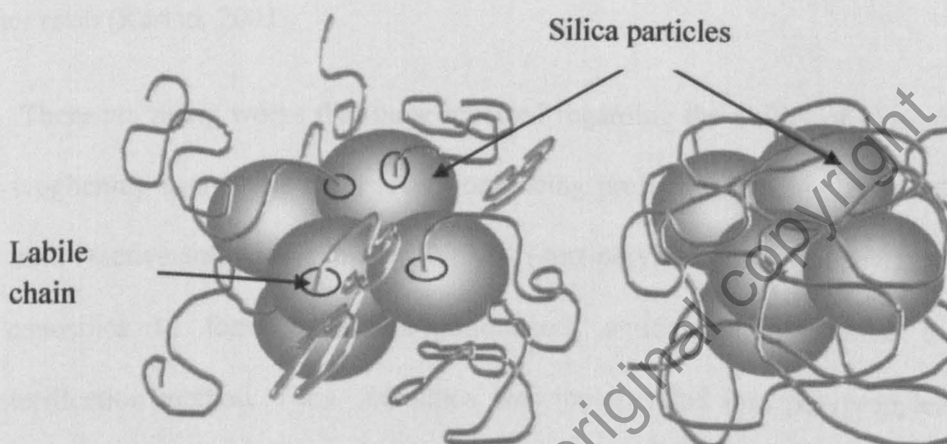

Figure 2.1: Nature of the interface PMMA/silica in low silica loading nanocomposites (Left). Nature of the interface PMMA/silica in high silica loading nanocomposites (Right)(Garcia *et al.*, 2007).

Nevertheless, the extremely small materials in this case in nano size will undergo through dispersion problem whereas the particles will stick to each other and form agglomeration (Liu & Kontopoulou., 2006; Aso *et al.*, 2007). This problem can be solving by the treatment of the fillers, polymer matrix or both, polymer matrix and fillers.

2.2.1 Nanosilica Filled Polypropylene Composites

From section 2.2, there are many researches have been done in nanosilica reinforce polymer especially thermoplastic. Polypropylene attracted world with combination of low cost, low density and high heat distortion temperature. However, there always exist certain shortcomings that can limit universal use of any given polymer resin (Karian, 2003).

There are many works that have reported regarding the ability of nanosilica to act as toughening agent. The most recent one being presented by Chen *et al.*, (2011), which used reactive antioxidant, methyl 3-(3,5-di-tert-butyl-4-hydroxy-phenyl), to react with nanosilica to form nanosilica-immobilized antioxidant, AO-silica through transesterification method. Then, AO-silica was incorporated into polypropylene via melt compounding. It was observed that AO-silica was homogeneously dispersed into the matrix polypropylene, thus improve the reinforcing effect of nanosilica toward polypropylene.

Meanwhile, Zhou *et al.*, (2007) had studied the effect of reactive compatibilization on the mechanical properties of nanosilica reinforced polypropylene composites. The nano-particles were grafted with poly(glycidyl methacrylate) (PGMA) through solution free-radical polymerization and then, melt blended together with polypropylene matrix and aminated polypropylene (PP-g-NH_2). PP-g-NH_2 played role as reactive compatibilizer in the composites. It was reported that the composites with reactive compatibilization enhanced the interfacial interaction between matrix and nano-particles thus, improved tensile strength, young's modulus and impact strength of nanosilica reinforced polypropylene composites.