

**THE DURABILITY OF MODIFIED  
SILICA/POLYPROPYLENE NANOCOMPOSITES:  
WEATHERING RESISTANCE AND CREEP BEHAVIOR**

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**UNIVERSITI MALAYSIA PERLIS  
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**The Durability of Modified Silica/Polypropylene Nanocomposites:  
Weathering Resistance and Creep Behavior**

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## LIST OF ABBREVIATION

Ag	argentum
APTES	aminopropyl triethoxysilane
ASTM	American Society for Testing and Materials
AWT	Accelerated weathering test
CaCO <sub>3</sub>	calcium carbonate
DSC	Differential Scanning Calorimetry
Fe <sub>3</sub> O <sub>4</sub>	Ferum oxide
FESEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier-Transform Infrared Spectroscopy
hr	Hour
MFI	melt flow index
NaOH	Sodium hydroxide
Ni	Nikel
nm	Nanometer
PE	Polyethylene
PMC	Polymer matrix composites
PP	Polypropylene
PP-g-MA	Polypropylene - grafted-Maleic Anhydride
PPMAN	polypropylene maleic anhydride
PP-POSS	Polypropylene -Methyl Polyhedral Oligomeric Silsesquioxanes
rpm	Rotation per minutes

SEM	Scanning Electron Microscopy
SiO <sub>2</sub>	Silica
TEM	Transition Electron Microscopy
TGA	Thermogravimetric Analysis
TiO <sub>2</sub>	Titanium oxide
TS	tensile strength
UHMWPE	Ultra high molecule weight polyethylene
UV	Ultra violet
YM	Young's modulus
Zn	Zinc
ZnO	Zinc Oxide

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## LIST OF SYMBOLS

m	Meter
m <sup>2</sup> /g	specific surface area
t <sub>cr</sub>	Creep time
Wt %	Weight percent
%X <sub>c</sub>	Percentage of Crystallinity
ΔH <sub>m</sub>	melting entropy
ΔH <sub>o</sub>	Enthalpy of 100% materials

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## **Kebolehtahanan Nanokomposit Modifikasi Silika/Polipropilena: Sifat Kerintangan Cuaca Dan Sifat Rayapan**

### **ABSTRAK**

Dalam kajian ini, modifikasi silika ( $\text{SiO}_2$ )/polipropilena (PP) nanokomposit telah disediakan. Sifat kerintangan cuaca dipercepatkan dan sifat rayapan nanokomposit dikaji. PP bersama 2% berat daripada nanosilika dan 3% berat daripada penserasi (aminopropil triethoxysilane (APTES), polipropilena dicantumkan anhidrida maleic (PP-g-MA) dan polipropilena-metil polyhedral silsesquixone oligomerik (PP-POSS)) telah dicair campur di dalam pengadun dalaman Brabender dengan kadar kelajuan 60 rpm selama 10 minit. Pencirian nanokomposit ditentukan oleh Fourier transform infrared analysis (FTIR) dan mikroskop imbasan elektron (FESEM). Manakala sifat-sifat mekanik nanokomposit telah ditentukan dengan menggunakan alat ujian tegangan mengikut ASTM D638 dan tingkah laku haba melalui analisis thermalgravimetric (TGA) dan kalorimeter pengimbangan perbezaan (DSC), masing-masing, sebelum dan selepas terdedah kepada ujian cuaca dipercepatkan (AWT). Sifat ketahanan telah diuji menggunakan mesin ujian rayapan mengikut ASTM D2990. Dari analisis FTIR, nanokomposit yang mengandungi PP-POSS menunjukkan kurang kumpulan karbonil yang dikaitkan dengan fenomena degradasi untuk bahan berbanding nanokomposit yang mengandungi APTES, PP-g-MA dan tanpa modifikasi. Selain itu, imej FESEM menunjukkan kurangnya keretakan dan ubah bentuk pada permukaan patah pada nanokomposit yang mengandungi PP-POSS mengesahkan kecekapan bahan penserasi. Manakala, kekuatan tegangan menunjukkan nanokomposit terluluhawa terutama dengan kehadiran PP-POSS diikuti oleh PP-g-MA dan APTES mempunyai kekuatan tegangan yang lebih tinggi tetapi pengurangan sederhana dalam pemanjangan pada takat patah daripada nanokomposit terluluhawa tanpa bahan penserasi. Dari segi tingkah laku haba, PP-POSS menunjukkan kestabilan terma yang baik berbanding dengan nanokomposit yang lain. Manakala semasa ujian ketahanan, kehadiran penserasi pada nanokomposit silika/PP menunjukkan sifat kerintangan rayapan yang baik. Namun, PP-POSS mempunyai sifat kerintangan rayapan yang lebih baik berbanding dengan kehadiran PP-g-MA, APTES dan tanpa bahan penserasi. Ini dapat disimpulkan bahawa bahan penserasi meningkatkan rintangan cuaca dan rintangan rayapan kepada nanokomposit.

## The Durability of Modified Silica/Polypropylene Nanocomposites: Weathering Resistance and Creep Behavior

### ABSTRACT

In this research, the modified silica ( $\text{SiO}_2$ )/polypropylene (PP) nanocomposites were prepared. The accelerated weathering and creep behavior of nanocomposites were investigated. Neat PP with 2 wt% of nanosilica and 3 wt% of modifiers (aminopropyl triethoxysilane (APTES), polypropylene grafted maleic anhydride (PP-g-MA) and polypropylene-methyl polyhedral oligomeric silsesquioxane (PP-POSS)) were melt blended in the internal mixer Brabender with rotor speed 60 rpm for 10 minutes. The nanocomposites characterizations were determined by Fourier transform infrared analysis (FTIR) and field emission scanning electron microscope (FESEM). While the mechanical properties of the nanocomposites were determined using a tensile test instrument according to ASTM D638 and thermal behavior through thermalgravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively, before and after exposure to accelerated weathering test (AWT). The durability behavior of nanocomposites was tested under creep test instrument according to ASTM D2990. From the FTIR analysis, weathered nanocomposites with the PP-POSS showed less carbonyl group which related to the degradation phenomenon to the material comparing to the nanocomposites with APTES, PP-g-MA and without modifiers. Moreover, FESEM images showed less cracking and deformation on the tensile fractured surface of weathered nanocomposites with PP-POSS validating the efficiency of the modifiers. While, from tensile results, the weathered nanocomposites especially with the presence of PP-POSS followed by PP-g-MA and APTES have higher tensile strength but moderate reduction in elongation at break than the weathered nanocomposites without the modifiers. In the terms of thermal behavior, PP-POSS showed good thermal stability compared to other nanocomposites. While for the durability test, the presence of modifiers in the modified silica/PP nanocomposites exhibited good resistance to the creep. PP-POSS provided better improvement creep resistance compared to the nanocomposites with PP-g-MA, APTES and without modifier. This can be concluded that the addition of modifiers improved the weather resistance and creep resistance of nanocomposites.

# CHAPTER 1

## INTRODUCTION

### 1.1 Polymer Nanocomposites

Polymer nanocomposites are polymer matrices reinforced with nano-scale fillers. This new class of composite materials has shown improved mechanical and physical properties (Tjong & Mai, 2010). The revolution of nanotechnology has been started at 21<sup>st</sup> century to exploit the novel properties, phenomena and functionalities, performance when played at the level of a few nanometers as opposed to hundred nanometers and above. Nanoscale fillers are well known as a remarkable material because their outcome qualitatively good in mechanical strength and thermal stability when contrast with the macroscopic filler (Sati et. al., 2008)

Nanocomposites by the meaning of filler have at least one dimension in the nanometer scales ( $10^{-9}$  m) (Fedullo et. al, 2007). The most common types of fillers used are nanostructured silicas, nanoceramics, nanocalcium carbonates and nanotubes (carbon based). Researchers found that, nano-filler can be competed and performed same or better just like macro and micro-filler. They found that the nanosilica is able to increase the mechanical properties in the polymer composites (Sati et. al., 2008 & Jacob et. al, 2010). While in the other reporting research works, nano-fillers exhibited better compression behavior, according to their yield strength, ultimate strength and stiffness compared to the micro filler size (Omar et. al., 2013). Other researchers reported that the nano-zinc oxide (ZnO) /ultra-high molecular weight polyethylene (UHMWPE) composites behave relatively uniform and smooth in transfer films as compared to neat UHMWPE and micro-

ZnO/UHMWPE composites (Chang et. al., 2013). Due to this potential, researchers have been made up so many experiments and try to analyze the optimum amount and condition of nano-filler to ensure better compatibility of the nano-filler in the polymer matrix. By exploring into the nanocomposites world makes people realize the advantages of nanocomposites to the industries. Thus, they can achieve better results neither the mechanical properties, nor the physical properties as required.

According to Sunil et. al., (2009) the scientific and technological concern for tailoring and modifying the polymer properties has been driving bright research on the nano-structured materials and nanoparticulate fillers. They usually will increase the properties of polymers at the very small amount of additive, in the range of 3 and 5% by weight. This is a way below than normally required from amount conventional micron-sized fillers to achieve similar properties. Yet, it is important that good interfacial adhesion could enhance and enabling good ultimate mechanical properties. The effectiveness of compatibilization is the devaluation of the amount of the polymer domains yet they are showing counterpoise against processing or annealing, and good mechanical behavior (Sabu et al., 2014<sup>a</sup>).

As reported by Palza et al., (2011), incorporation of the nanosilica into the PP matrix had increased the tensile strength of the composites. Despite that, a noticeable improvement in the tensile strength was observed by adding the compatibilizer. The improvement of the characteristics of nanosilica-filled polypropylene composites was ascribed to an excellent dispersion of nanosilica and increased the compatibility between silica and polypropylene matrix with the existence of PP-methyl POSS as compatibiliser (Lin et al., 2009<sup>a</sup>). This phenomenon happened due to the increasing of the interfacial surface area between the nanofiller and the polymeric material (Vladimirov et al, 2006).

Nevertheless, the importance of any material is relying on its degradability and durability. About ten years ago, the knowledge growth towards the use of nanocomposite materials in industries where the durability of the properties is required arose. The study of degradation and stabilization of polymers is an extra important area of the scientific and industrial believes. A better understanding of polymer degradation will assure the long life of the product as well as the study of the durability of thermoplastics (Jitendra et al., 2005; Sandrine et al., 2008 & Sabu et al., 2014<sup>b</sup>).

The service lifetime of a polymeric material strongly depends on the specifications of the application under consideration. Often, visible surface degradation, such as discoloration and loss in transparency and gloss, is apparent before significant changes in the bulk physical properties such as tensile strength, elongation, or electrical properties were observed. For the intention of increasing the durability of polymeric materials by preserving them from environmental factors or by slowing down the degradation rate, different stabilizers can be combined together into a polymer matrix (Sandrine et al., 2008, Sabu et al., 2014<sup>b</sup>).

## **1.2 Problem Statement**

Nanoparticles are well famous by its size advantage which gives the high surface contact area of the matrix. However, the use of nanofillers in polymer composites is taking up the challenges for material engineers to ensure that the homogenous dispersion of inorganic nano-objects into a polymer matrix. This problem will cause the agglomeration of filler. Consequently, it will lead to material deteriorate and decrease efficiency of polymer composites in mechanical and thermal properties. In addition, the performance becomes worse when they are exposed to the weather and cause low its durability behavior. In this

case, the nanoparticles have to be modified to reduce the agglomeration. The use of coupling agent such as aminopropyl triethoxysilane and compatibilizer such as polypropylene-grafted maleic anhydride and polypropylene methyl polyhedral oligomeric silsesquixane in achieving a silica/polypropylene nanocomposites profile which engenders strength and thermal stability is thereby, a novel and exciting field of exploration. It is anticipated that the incorporation of these systems will improve the dispersion of nanoparticles and the material properties will perform well as desired. Besides, this is believed that reducing the degradation rates and increasing the durability behavior of nanocomposites will enhance their performance in industries such as automotive and engineering parts.

### **1.3 Objectives**

- 1.3.1 To study the effect of modifiers on the tensile properties and thermal behavior of modified silica/polypropylene nanocomposites before and after accelerated weathering test.
- 1.3.2 To determine the effect of modifiers on the creep behavior of modified silica/polypropylene nanocomposites.

### **1.4 Scope of Study**

This research focuses on the influence of modifier on nanosilica filled polypropylene with the contribution of different types of modifier to enhance the nanocomposites accelerated weathering and creep behavior. Next, 3wt% of modifier (silent treatment, PP-g-MA and PP-POSS) was added in the nanocomposites. All the materials were produced by melt mixing process before they were tested for mechanical

testing (tensile testing for weathered and unweathered specimens), durability test (creep testing), thermal properties (Thermogravimetric Analysis). The morphology of the tensile fractured surface of the nanocomposites was closely observed using field emission scanning electron microscope (FE-SEM). Functionality of weathered and unweathered nanocomposites was characterized using Fourier transform infrared spectroscopy.

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## **CHAPTER 2**

### **LITERATURE REVIEW**

## 2.1 Polymer Nanocomposites: Concepts and Applications

Polymer nanocomposites have attracted extensively to the researchers in these recent years. The interest in the nanocomposites arises from the positive progress giving a new class of materials which are the nanoscale structures with unique morphology, modulus, strength, limited environmental impact and heat resistance at very low loadings of the nanosize of inorganic components (1-10 wt %) (Ghosh et. al., 2006 & Barbosa et. al.,2009). A polymer nanocomposite is an innovation of polymer composites incorporation of nano-sized fillers in polymer matrix. The polymer's properties are mostly change after adding the nanoparticles as reinforcement (Gacitua et. al. 2005).

The concept of nanocomposites is innovating huge interface between the nano sized-building blocks and the polymer matrix. Nevertheless, the important role properties of nanocomposites are not only persistent by the size of the interface, but also considered on structure and interactions. Nanocomposites technology was began by bio mineralization, which an organic element such as protein, peptide, or lipid interacts with an inorganic substance for example calcium carbonate and generates new materials with increased toughness(Gacitua et. al. 2005 &Ibeh 2011). While, Powell& Beall (2006) reported polymer/clay nanocomposites old day's story of development began from 1960s and early 1970s. They also informed that, clay filled in nylon 6 nanocomposites was exploited in timing belt cover for Toyota Camry was foundedby employeesfrom Toyota Central Research Laboratories.

Polymer nanocomposites had been applied in many fields such as electronic, medical devices, construction and aerospace industries (Tjong& Mai, 2010; Zailin et. al., 2014 &Njuguna et. al., 2012). Yet, very often the homogeneous distribution of the nano

sized particles is problematic. The expected large interface is uneasy task to created, but the proper interaction or coupling of the components may trigger the matter (Kutz& Myer, 2011).

## 2.2 Nanoparticles Reinforced Polymer Composites

Nanoparticles are the key of nanotechnology as an addition of the common particle but in very fine particle. They play a main role in the application of nanotechnology in various engineering and industrial fields. Nanoparticles create the exclusive properties of the materials which are completely different from others of genuine material. Yet, the significant of the properties is depending on the percentage of activated functional groups at the surface of a material. The connectivity between polymer and nanoparticle become higher comparing to the macro and micron particles (Masuo et. al., 2012).

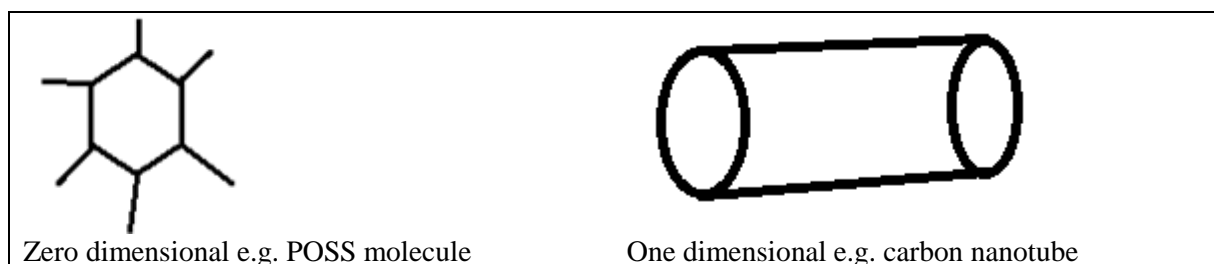
Nanoparticle might be in spherical, tubular, or irregularly shaped, and can be existed in fused, aggregated, or agglomerated forms. They are of two main types of nanoparticles as reported by Renato and co- authors, 2015 which are:

- **Non-engineered** nanoparticles present in the environment derive from natural events such as terrestrial dust storms, erosion, volcanic eruptions, and forest fires.
- **Engineered** nanoparticles are intentionally produced by man using many different materials, such as metals (including Ag, Zn, and Ni), metal oxides ( $\text{TiO}_2$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{SiO}_2$ ), non-metals (silica and quantum dots), carbon (nanotubes and fullerene), polymers (alginate, chitosan, hydroxymethylcellulose, polyhydroxyalkanoates, and poly-e-caprolactone and lipids (soybean lecithin and stearic acid).

The particle geometry will affect the characteristics of the nanocomposite materials. There are four dimensional of nanofillers which defined the geometry of nanoparticles (Gleiche, 2011):

- Zero dimension- filler material is incorporated like a building block on the molecular level for example Polypropylene methyl polyhedral oligomeric silsesquioxane(POSS) molecule.
- Quasi-dimensional – nanofillers in plate form are layered with thickness of one nanometer and the aspect ratio for other dimension for at least 25.
- Two dimensional - natural formation and representatives as two dimensional filler material are layered silicates or also known as nanoclays.
- Three dimensional – nanoparticles in the particles shape which were producing through either grinding, milling or precipitation techniques.

Figure 2.1 illustrates the different nanofiller geometries.



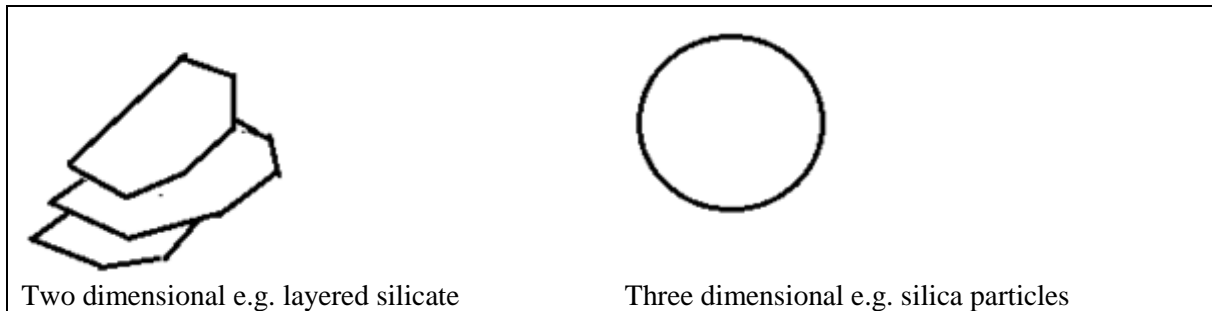


Figure 2.1: Nanofiller geometries.

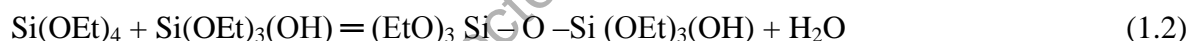
It is worth noting that the geometry of nanoparticle is important in achieving a certain properties. However, in this research work, three dimensional of silica has been focused and will be discussed in the following section.

### **2.2.1 Silica Nanoparticles: Synthesis, Characteristics and Their Thermoplastic Composites.**

Generally silica nanoparticles were divided into two types according to the method on how they were processed. According to Jal et. al. 2004, nanosilica is produced from sodium silicates solvent with sulphuric acid. In this process, either sodium silicate or silicon alkoxide or halide gets transformed to form a gel. Partial hydrolysis of orthosilicate occurs when it is assorted with water and ethanol. Condensation happens either between two hydroxyl groups or a hydroxyl and ethoxy group to form bridging oxygen either with water or ethanol. The annexation of acid or base wills stimulant the process. While the addition of an electrolyte or shifting in pH of sol forces the condensation process. Throughout silica synthesis by sol–gel process is depending on the situation like restriction of the gel growth, silica gets precipitated.

The preparation involves with the coagulation and precipitation from silica solution. The method of silica synthesis by precipitation technique, where, to acidified water (pH is

5–5.9) alkali metalsilicate solution and sulfuric acid were added together. The production of silica can be seen in formulation (1), (2) and (3). Silica precipitated silica dwell of porous particles with a main particle size of about 5-100 nm which forms large agglomerates of several micrometers. The specific surface area can be reached to 200m<sup>2</sup>/g (Jal et. al., 2004 & Gleiche, 2011). At the same times the fumed or pyrogenic silica is a form of non-crystalline silicon dioxide. It is assigned to as flame hydrolysis. It is initially outgrowth spherical particle sizes are between 5-30 nm which aggregate into larger agglomerates. These aggregates are branched, chain like structures and acceptable as fumed silica primary structure since the fusion process is irreversible. It can be sustained a fairly large specific surface area of 10-600 m<sup>2</sup>/g. In this work, we are using fumed silica.



Fume silica is in a fluffy white powder with a very low apparent density. It is universally used as surface improver and coagulating agent together with thixotropic property. It will be in liquid form when stirred or shaken but reoccurrence to normal state when motionless. It is also applied in paints, coatings, adhesives and sealants and be as a filler in plastics and rubber. Fumed silica is also used in thermal insulation material such as vacuum insulation panels (Wypych, 1999).

There are lots of studies on nanosilica in the polymer matrix. Chemically, thermoplastic resin is different from the thermoset resins. Thermoset resins depend on the