STUDY ON THE EFFECT OF CLAY LOADING UNDER NORMAL AND AUTO-THERMAL EXTRUSION TO THE MORPHOLOGY STRUCTURE AND THERMAL PROPERTIES OF NYLON 6 NANOCOMPOSITES

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KAJIAN KESAN KANDUNGAN TANAH LIAT MENGGUNAKAN SISTEM KONVENSIONAL DAN AUTO-TERMA TERHADAP STRUKTUR MORFOLOHI DAN SIFAT TERMA KOMPOSIT NANO NILON 6

ABSTRAK

Dalam kajian ini, pengaruh penyemperitan auto-terma terhadap kestabilan terma dan morfologi polyamide6 (PA6) nanocomposites dengan muatan tanah liat dan kelajuan skru yang berbeza dibincangkan. Sistem penyemperitan tanpa kesan haba terhadap kadar degradasi haba organic polimer dan tanah liat nano organic merupakan focus utama kajian ini. Komposit nano polimer berasaskan daripada polyamide6 (PA6) dan Cloisite®20A, tanah liat nano yang organic yang telah diubahsuai dikomersilkan, telah disediakan dengan menggunakan sistem auto-terma dan konvensional penyemperitan. Ciri-ciri morfologi telah ditentukan melalui permohonan pembelauan sinar-X (XRD) dan mikroskop electron pengimbas (SEM). Kestabilan terma komposit nano PA6/C20A yang disebatikan telah ditentukan dengan menggunakan analisis termogravimetri (TGA). Kandungan tanah liat dan kelajuan skru penyemperit yang menentukan kualiti komposit nano PA6/C20A dan bukannya sistem auto-terma atau konvensional itu sendiri sahaja. Penyemperitan auto-terma mempengaruhi kestabilan haba komposit nano yang diproses dengan membenarkan pengagihan tenaga haba di seluruh sebatian lebur. Walaubagaimanapun, ia mempunyai kesan yang sangat sedikit pada struktur morfologi komposit nano PA6/C20A. Selain itu, kelajuan skru daripada penyemperit juga member kesan terhadap degradasi sampel yang dihasilkan.

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ABSTRACT

In this research, the influence of auto-thermal extrusion on the thermal stability and morphology of fabricated polyamide6 (PA6) nanocomposites with varying clay loading and screw speed is discussed. The effect of zero-heat transferred extrusion systems on the thermal degradation rate of organic polymer and inorganic nanoclay is the main focus of this research. A polymer nanocomposite based from polyamide 6 and Cloisite® 20A, commercialized organic modified nanoclay, was prepared by using auto-thermal and conventional melt extrusion system. The morphological characteristics were determined through the application of X-ray diffraction (XRD) and scanning electron microscope (SEM). The thermal stability of compounded PA6/C20A nanocomposite was conducted using thermogravimetric analysis (TGA). The clay content and screw speed of the extruder dictates the quality of the PA6/C20A nanocomposites as well as the auto-thermal or conventional extrusion system itself. The auto-thermal extrusion affects the thermal stability of the melt-processed polymer nanocomposites by allowing even distribution of heat energy throughout the molten compound. However, it has very little effect on the morphology structure of PA6/C20A nanocomposites. As an addition, the screw speed of the extruder also affects the onset degradation temperature of samples produced.

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Polymers are macromolecule consisting of long and repeating chain of smaller units called monomer. Polymer consists of natural and synthetic polymer. Natural polymers are most commonly found in plants and animal such as proteins, enzymes, starches, and cellulose. However, synthetic polymer would be plastic, and fiber materials(Callister & Rethwisch, 2008). The main material used in this research would be a type of plastic. However, its features do not merely portray a normal plastic but instead as an enhanced material which can be used widely.

It is a known fact that a diverse of field such as transportation, construction, electronics and consumer products uses composites widely. The composites used consist of a variety of combination in terms of stiffness, strength and weight that are rather difficult to acquire in individual components (Giannelis, 1996). Whereby, in this research the focused would be on the Polyamide 6 and organoclay nanocomposites. The dispersion of nano-particle such as the organoclay in the matrices of polymer would further improve the properties of Polyamide 6.

Furthermore, the method of fabrication is also correlated towards the quality of material produced. The method of fabrication is crucial due to the varying effects it has on the material itself as certain method of compounding the material would degrade the material at the same time Therefore, the method proposed in this research would be melt compounding.

Among the polymer composites most frequently used in the industry includes polyamide 6 (PA6) or more commonly known as Nylon 6. The first successfully commercialized polymer/clay nanocomposites that have been studied widely is the polyamide 6/ organoclay (Fujiwara, et al., 1993; Usuki, et al., 1993). Nylon 6 is in fact a type of thermoplastic which is produced by polymerization of pure ε-Caprolactam. The properties of Polyamide 6 have been enhanced with the addition of various kinds of additives as mentioned by many researchers previously.

1.2 Problem Statement

Polymer composites often undergo polymer degradation when being compounded; this is initiated by the high strength stress of screw and resulting in the reduction of molecular weight of polymer. It is most possible that the thermal stability of polymer is affected which leads to degradation of polymer in terms of exfoliation property of the polymer itself. Therefore, study on the thermal stability of polymer nanocomposites is important to learn on the process and the relationship between structure and polymer degradation.

1.3 Research Objectives

1.3.1 To fabricate polyamide 6 and organoclay nanocomposites using normal clay loading and adiabatic condition.

1.3.2 To study the dispersion of montmorillonite (MMT) in the morphological structure of polyamide 6

1.3.3 To study the thermal stability of PA6/MMT nanocomposites under normal clay loading and autothermal clay loading

1.4 Scope of Proposed Study

In order to achieve these objectives, the following scopes are designated;

1.4.1 Fabrication of nylon6 organoclay nanocomposites by combining polyamide 6 and Cloisite® 20A which is the commercially available natural montmorillonite that has been modified with a quaternary ammonium salt using melt intercalation method by means of extrusion process.

1.4.2 Characterization of the nylon6 nanocomposites samples using x-ray diffraction analysis (XRD), transmission electronic microscopy (TEM) and thermogravimetric analysis (TGA).

1.4.3 Study the morphological and thermal effect of extrusion with a twin screw extruder at normal clay loading and auto thermal condition.

1.5 Significance of Proposed Study

The significance of this proposed study is to determine the control of processing conditions that affects degradation in the polymer material as well as to produce an enhanced PA6 material which exhibits mixed intercalated/exfoliated morphology which can be beneficial for the use of the industry.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Nanotechnology is an expanding field of study in both academic and industry currently. Nanotechnology is in fact the study and control of matter at the dimensions of an estimation of 1 to 100 nanometers (nm) which has been discovered decades ago and has been growing ever since. Hence, the usage of the term nanotechnology to describe any practical application that is of such. From Raj Bawa et al. (2005), a more precised meaning of nanotechnology was proposed and clearly defined as:

> "The design, characterization, production, and application of structures, devices and system via a controlled manipulation of size and shape at the nanometer range (atomic, molecular, and macromolecular scale) that produces structures, devices, and systems with at least one novel or superior characteristic or property."

As a new branch of materials, nanophase and nanomaterials has attracted a great deal of attention due to their potential applications in areas such as electronics, optics, catalysis, ceramics, and magnetic data storage and polymer nanocomposites (Koo, 2006). Therefore, nanotechnology is growing at an increased pace due to the potential it portrays to a wide range of industries.

When nanotechnology is involved, the most common application of nanotechnology would be in the polymer industry. In fact, polymer nanocomposites (PNC) have been the topic for numerous researches in a number of previous publications and extensive inquisition work. A detailed examination was conducted by Toyota researchers (Fujiwara, et al., 1993; Usuki, et al., 1993) and brought upon an outburst of interest in academic, government and industrial laboratories. A wide coverage has been done to improve its structural formation, degree of exfoliation and mechanical strength.

Material degradation is unavoidable when mechanical mixing of PNC by an extruder is conducted. This is due the interruption that could have occurred by numerous factors during the processing of composite. Hence, this research focus on material

degradation during fabrication of polyamide 6 nanocomposites with a twin-screw extruder, in which is the most important part of the experiment whereby the study on the effects of organoclay, loading, and screw speed on the thermal and morphological properties are observed.

2.2 Polyamide 6

Polyamides are polymer containing monomers of amides joined together by peptide bonds. Polyamides consist of aliphatic polyamides, polyphthalamides and aromatic polyamides. Nylon 6 or polyamide-6 falls in the aliphatic polyamides family. Polyamide 6 is a class polymer in which molecular chains are formed by the regular spacing of amide groups (-CONH-) (Trossarelli, 2010). Polyamide 6 is also known as polycaprolactam which is a polymer developed by Paul Schlack from pure ε-Caprolactam.

2.2.1 Synthesis of Polyamide 6

Polyamide 6 is synthesized from pure ε-Caprolactam by polymerization at 533K and with the presence of inert Nitrogen for a few hours, followed with the peptide bond

in each caprolactum molecule being broken and the active groups on each side reform two new bonds where as the monomer part of the polymer would become the polymer backbone. The illustration of the reaction can be obtained from Figure 2.1.

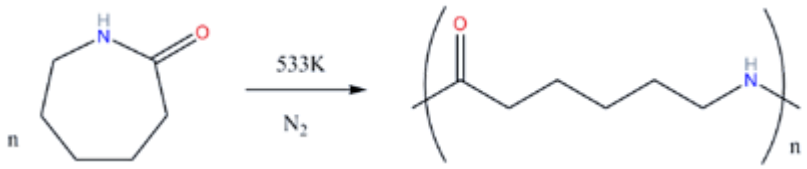

Figure 2.1 Polymerization of ε-Caprolactam to form monomers of polyamide 6.

(**Source:** Wikipedia the Free Encyclopedia, 2012)

Numerous studies have been conducted on PNCs based on polyamide. As mentioned by Chow and MohdIshak (2006), polyamide 6-clay hybrids display a high modulus, high distortion temperature and good barrier properties of gas and water. This shows that polyamide 6 is a good material for conducting experiment involving high stresses in terms of mechanical, rheological and physical stress.

It is also reported that the synthesis of polyamide 6- clay hybrid via montmorillonite (MMT) with ε-Caprolactam revealed in the X-ray diffraction that the chain axes of ε-Caprolactam were paralleled to the montmorillonite plates (Kojima et al., 1993). This would mean that the silicate layers of polyamide 6-clay hybrid was

distributed in the matrix and the clay was intercalated with the ε-Caprolactam. However, the better results would be that the structure of the Nylon 6-clay hybrid was of the exfoliated structure.

2.3 Nano Clay

Clay minerals are promising nanofiller reinforcement for polymers due to their unique layered structure, ability to intercalate chemically and its availability at low cost for the manufacturing of low-cost, light weight and high performance polymer nanocomposites. The three types of clay minerals includes 2:1 type, 1:1 type and layered silicic acids which are summarized in Table 2.1.

For the purpose of this study, the organoclay used is montmorillonite (MMT) which has already been modified by organic treatments to increase the affinity and compatibility of the platelet to be more compatible with the organic polymer (Dennis, et al., 2001). Previous research has already addressed on the effectiveness of the processing and a sample preparation technique greatly affects the degree of dispersion of the MMT in the polymer matrix (Liu et al., 2006).

Table 2.1 Clay minerals used for polymer nanocomposites.

Type of Clay	Formula	Origin	Substitution	Layer Charge
2:1 Type				
MMT	$M_x(Al_{2-x}Mg_x)Si_4O_{10}(OH)_2.nH_2O$	N	Octahedral	Negative
Hectorite	$M_x(Mg_{3-x}Li_x)Si_4O_{10}(OH)_2.nH_2O$	N	Octahedral	Negative
Saponite	$M_xMg_3(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$	N	Tetrahedral	Negative
Fluorohectorite	$M_x(Mg_{3-x}Li_x)Si_4O_{10}F_2.nH_2O$	S	Octahedral	Negative
Laponite	$M_x(Mg_{3-x}Li_x)Si_4O_{10}(OH)_2.nH_2O$	S	Octahedral	Negative
Fluoromica (Somasif)	$NaMg_{2.5}Si_4O_{10}F_2$	S	Octahedral	Negative
1:1 Type				
Kaolinite	$Al_2Si_2O_5(OH)_4$	N	-	Neutral
Halloysite	$Al_2Si_2O_5(OH)_4.2H_2O$	N	-	Neutral
Layered Silicic Acid				
Kanemite	$Na_2Si_4O_9.5H_2O$	N/S	Tetrahedral	Negative
Makatite	$Na_2HSi_2O_5.7H_2O$	N/S	Tetrahedral	Negative
Octasilicate	$Na_2Si_8O_{17}.9H_2O$	S	Tetrahedral	Negative
Magadiite	$Na_2Si_{14}O_{29}.10H_2O$	N/S	Tetrahedral	Negative
Kenyaite	$Na_2Si_{20}O_4.10H_2O$	S	Tetrahedral	Negative

(**Source:**Zeng et al., 2005)

2.3.1 Layered Structure

In the fabrication of polymer nanocomposites, layered silicates and modified layered silicates are most commonly used by manufacturer due to the cost of

nanofillerper weights and accessibility. It has been found that polymer layered silicates exhibits distinctive improvements in many properties compared to the conventional macro or micro composites.

The properties of the materials are found to be enhanced drastically with the incorporation of layered silicates at fairly low concentrations (Pandey et al., 2005). This shows that the presence of the layered silicates in the nanofiller aids to the properties of the materials even in a small amount. Thus, for this study the amount of clay loading used varies from 1wt% to 5 wt%.

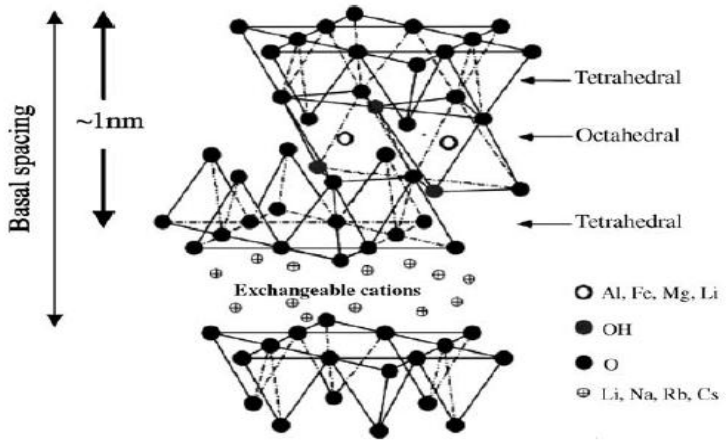

Figure 2.2 Structure of 2:1 phylosillicates

(**Source:**Sinha Ray & Okamoto, 2003)

As shown in Figure 2.2 is the arrangement of atoms in the crystal structure of 2:1 layered silicates in which shows the two dimensional layers and central octahedral alumina sheets fixed to two external silica tetrahedral sheets. The thickness of each layer is approximately 1 nanometer (nm) where as the lateral dimensions may vary from 30 nm to several microns or larger, depending on the particular layered silicates (Sinha Ray & Okamoto, 2003). The layered silicates structure serves an important role in enhancement to the polymer nanocomposites when added.

2.4 Polymer Nanocomposite

For almost two decades ago, Toyota Central Research and Development produced a group of polymer-clay complexes or composites, which are currently known as polymer-layered silicate nanocomposites or polymer nanocomposites. These polymer nanocomposites are in fact a polymer matrix with a reinforced phase containing one dimensional nano-sized particle.

The advantages of this successfully introduced polymer nanocomposites are such as the significant improvement of mechanical, thermal, chemical and barrier properties of nanocomposites as mentioned by Chow and MohdIshak (2006). Therefore, the change in characteristics of polymer nanocomposites with the presence of

nanofillerin the fabrication of polymer nanocomposites would be explained further later in the study.

2.4.1 Types of Nanocomposite

From the structural point of view, polymer nanocomposites can be categorized according to its nature and interaction of its components as well as on it preparation technique being used. The nature and interaction refers to the type of silicate material and organic material used to render the hydrophilic silicates organophilic and the nature of the polymer matrix. Whereas the preparation technique associates with the mechanical factors that aids the penetration or intercalation of polymer chains into the layers of silicate.

The types of nanocomposite consist of phase separated micro composite, intercalated nanocomposite and exfoliated nanocomposite. From the three mentioned, the most desired interaction of layered silicates and polymer would be the exfoliated nanocomposite. As mention before in previous research, exfoliated nanocomposites shows improvement in properties such as the increase in tensile properties, along with an enhanced barrier properties, decreased solvent uptake, an increase in thermal stability and flame retardance (Okada and Usuki, 1995; Giannelis, 1996).