MECHANICAL, MORPHOLOGICAL AND THERMAL PROPERTIES OF HYBRID KENAF FIBER/NANOCLAY REINFORCED POLYLACTIC ACID (PLA) BIOCOMPOSITE

BY

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A dissertation submitted in fulfilment of the requirement for the degree of Master of Science (Materials Engineering)

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SEPTEMBER 2012

ABSTRACT

The biocomposites based on polylactic acid (PLA), short kenaf fiber and nanoclay hybrid is prepared through different processing method. The processes used are single and double compounding method using twin screw extruder followed by injection moulding. The mechanical properties of blended biocomposites are studied through tensile, flexural and impact tests. The morphology of the composites were characterized by scanning electron microscopy (SEM) and transmission electrom microscopy (TEM). The thermal properties are characterized by using differential scanning calorimetry (DSC), thermogravimetry analysis (TGA) and dynamic mechanical analysis (DMA). Besides these X-ray diffraction (XRD) and fourier transform infra-red (FTIR) analysis was carried out to know the nanoclay dispersion, percentage of crystallinity and possible bond formation. The aim of this work is to hybridize nanoclay and short kenaf fiber in polylactic acid (PLA) by using double extrusion method and followed by mechanical, thermal and morphological characterization. Mechanical properties show improvement with nanoclay, specifically impact strength increases more than 50% than unreinforced PLA. Double extruded hybrid biocomposite shows 3-10% better tensile and flexural properties than the single extruded. Similarly, addition of nanoclay increases decomposition and melting temperature (T_m) from 198 ^oC to 225 ^oC and 152 ^oC to 155 ^oC respectively. Crystallization temperature (T_c) is however decreases with nanoclay from 116 ^oC to 106 ^oC and storage modulus (E') are increased by about 1GPa. These findings were also supported by scanning electron micrograph (SEM) and transmission electron micrograph (TEM) where in double extruded hybrid biocomposite better dispersion of nanoclay were observed. As for X-ray defraction (XRD) and Fourier transform infra-red (FTIR) spectroscopy, higher percentage of crystallinity and formation of new bonds respectively were seen with the addition of nanoclay, which indicates on enhancement in thermal and mechanical properties of PLA-based hybrid biocomposite.

ملخص البحث

مستعدة biocomposites يعتمد على حمض polylactic (جيش التحرير الشعبى الصينى)، قصيرة الألياف التيل والهجين nanoclay من خلال طريقة معالجة مختلفة. العمليات المستخدمة هي طريقة مفردة ومزدوجة يضاعف باستخدام التوأم برغي الطارد تليها حقن صب. يتم دراسة الخواص الميكانيكية للbiocomposites المخلوطة من خلال اختبارات الشد، وتأثير العاطفة. تميزت التشكل من المركبات عن طريق المسح الضوئي المجهر الإلكتروني (SEM) ونقل electrom المجهر (TEM). وتتميز خصائص الحرارية باستخدام المسح التفاضلي الكالوري (DSC)، وتحليل thermogravime try(TGA) وتحليل ديناميكية الميكانيكية (DMA). إلى جانب أجريت هذه حيود الأشعة السينية (XRD) وتحويل فورييه تحليل الأشعة تحت الحمراء (FTIR) إلى معرفة تشتت nanoclay، نسبة ممكنة من crystallinity وتشكيل السندات. والهدف من هذا العمل هو لهجن nanoclay وقصيرة الألياف التيل في حمض polylactic (جيش التحرير الشعبى الصينى) باستخدام طريقة البثق المزدوجة وتليها توصيف الميكانيكية والحرارية والمورفولوجية. الخواص الميكانيكية تظهر تحسنا مع nanoclay، وقوة تأثير على وجه التحديد يزيد أكثر من 50٪ من جيش التحرير الشعبى الصينى غير المدعومة. biocomposite الهجين المزدوج مقذوف يظهر الشد 3-10٪ أفضل وخصائص العاطفة من مقذوف واحد. وبالمثل، إضافة nanoclay يزيد تحلل وذوبان في درجة الحرارة (TM) من 198 درجة مئوية إلى 225 درجة مئوية ودرجة مئوية 152 حتي 155 درجة مئوية على التوالي. درجة حرارة التبلور (TC) ولكن هو يتناقص مع nanoclay من 116 درجة مئوية درجة مئوية إلى 106 و التخزين معامل (E ') وزاد بنحو GPa1. وقدم الدعم أيضا هذه النتائج صورة مجهرية الإلكترون عن طريق المسح الضوئي (SEM) وانتقال الإلكترون صورة مجهرية (TEM) حيث مزدوجة في مقذوف تشتت sitebiocompo أفضل مزيج من nanoclay لوحظت. أما بالنسبة للأشعة X defraction(XRD) وتحويل فورييه بالأشعة تحت الحمراء (FTIR) الطيفي، وارتفاع نسبة من crystallinity وتشكيل روابط جديدة على التوالي شوهدت مع إضافة nanoclay، مما يدل على تعزيز الخصائص الحرارية في والميكانيكية لجيش التحرير الشعبى الصينى، يعتمد biocomposite الهجين.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and fully adequate, in scope and quality, as a thesis for the degree of Master of Science in Materials Engineering.

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DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted for any other degrees at IIUM or other institutions.

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To my beloved parents

ACKOWLEDGEMENTS

In the name of Allah, Most Gracious, Most Merciful and Praise be to Allah, the Cherisher and Sustainer of the worlds for giving me chance to do this work. I would also like to convey my sincere salam to His messenger and our prophet, Mohammad (SAW).

I wish to express my sincere appreciation and gratitude to my supervisor Dr. Hazleen Binti Anuar, for her extremely helpful guidance, generous support and continuous encouragement with her wisdom, knowledge and experience. Her countless hours spent for guiding both my writing and research efforts have been extremely helpful for the successful completion of this dissertation. My appreciation also extends to her family. My gratitude also goes to my co-supervisors, Assoc Prof Dr. M. A. Maleque and Dr. S. B. A. Razak for their kind support and meaningful contributions.

I would also like to express my gratitude to all research members as well as the Department of Manufacturing and Materials Engineering with all our technical staff especially Br. Hairi, Br. Rahimie, Br. Hafiz, Br. Shamsul and Br. Sanadi, who directly and indirectly helped me in accomplishing this study, and also to Sr. Maizana from Malaysia Rubber Board Sdn Bhd.

I am also greatly indebted to Dr. Nurasikin Binti Samat for her encouragement and nice suggestions. My further appreciation goes to all my friends specially Noor Mohammad, Hasanul Banna, Asif Mahmud, Arifutzzaman Rahat, Khairul Islam Shaon, Aimi Nasir, Mohd Adlan, Nur hafiza and Faiza Fuad for their help and encouragement.

Finally, I would particularly like to acknowledge my father, mother, brother and many others for their affection and moral support. I will always be in their debt.

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LIST OF ABBREVIATIONS

ACRES	Affordable Composites from Renewable Resources
Al	Aluminum
ASTM	American Society for Testing Materials
CCD	Charge Coupled Device
DBTT	Ductile Brittle Transition Temperature
DE	Double Extrusion
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
et al.	(*et alia*): and others
etc.	(*et cetera*): and so forth
e.g	(example gratia) as for example
EFB	Empty Fruit Bunch
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infra-Red
g	gram
g/cm^3	gram per cubic centimeter
GPa	Giga-Pascal
HLC	Hybrid Laminated Composites
i. e	(id est) that is
KF	Kenaf Fiber
KFI	Kenaf Natural Fibre Industrie
kN	Kilo-newton
LC	Laminated Composites
Mg	Magnesium
mm	Millimetre
MPa	Mega-Pascal
Na	Sodium
PBAT	Aromatic copolyesters
PBSA	Aliphatic copolyesters
PCL	Polycaprolactone
PEA	Polyesteramide
PET	Polyethylene Terephthalate
PHA	Polyhydroxyalkanoate
PKN	PLA-kenaf-nanoclay
PLA	Polylactic Acid
PP	Polypropylene
PU	Polyurethane
rpm	Revolution per minute
SE	Single Extrusion
TEM	Transmission Electron Microscopy
TGA	Thermogravimetry Analysis
T_c	Crystallization temperature
T_f	Final decomposition temperature
T_g	Glass transition temperature

T_β	β-transition temperature
T_i	Initial decomposition temperature
T_m	Melting temperature
μm	Micrometer
V_f	Volume fraction
V%	Volume percent
wt%	Weight percent
XRD	X-ray Diffraction
^oC	Degree Celsius
%X	Percentage of crystallinity
%T	Percentage of infra red transmission
ρ	Density

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Light weight, high toughness and high ductility, better wear resistance, easy processing and low cost are among the advantages of polymer materials. The weakness, however are lower in strength, stiffness, flammable and high permeability to most of gases and solvent as compared to metals and ceramics. Lower electrical and thermal conductivity are also deemed to be disadvantages in some cases. Reinforcement with nano meter size fillers can overcome many of these drawbacks if nanoparticles are well dispersed in the polymer matrix. Most properties enhancements can be achieved at significantly smaller loadings than conventional micro sized reinforcements and resulted in "nanocomposites" that are light in weight.

Since they were pioneered by researchers at Toyota Motors in the late 1980's (Kojima et al., 1993; Zanetti et al., 2001) organically modified layered silicates (Okamoto et al., 2000) have been a main subject of interest for the reinforcing nano-material. Metal cations on negatively charged silicate surface (Yao et al., 2002) can be exchanged with organic modifiers such as alkylammonium surfactants, which increases the miscibility with polymers (Figure 1.1 (a)) (Pluta et al., 2002). Partial or complete dispersion of these layers in the matrix polymer leads to the "intercalated" or "exfoliated" nanocomposites, as depicted in Figure 1.1 (b) (Okamoto et al., 2000). Their key benefits are improvement in mechanical properties, (Nishino et al., 2003; Biagotti et al., 2004) dimensional stability, (Giannelis, 1996; Alexandre and Dubois, 2000) gas barrier, (Lagaro et al, 2005) and flame resistance (Gilman et al., 2000) of host polymers.

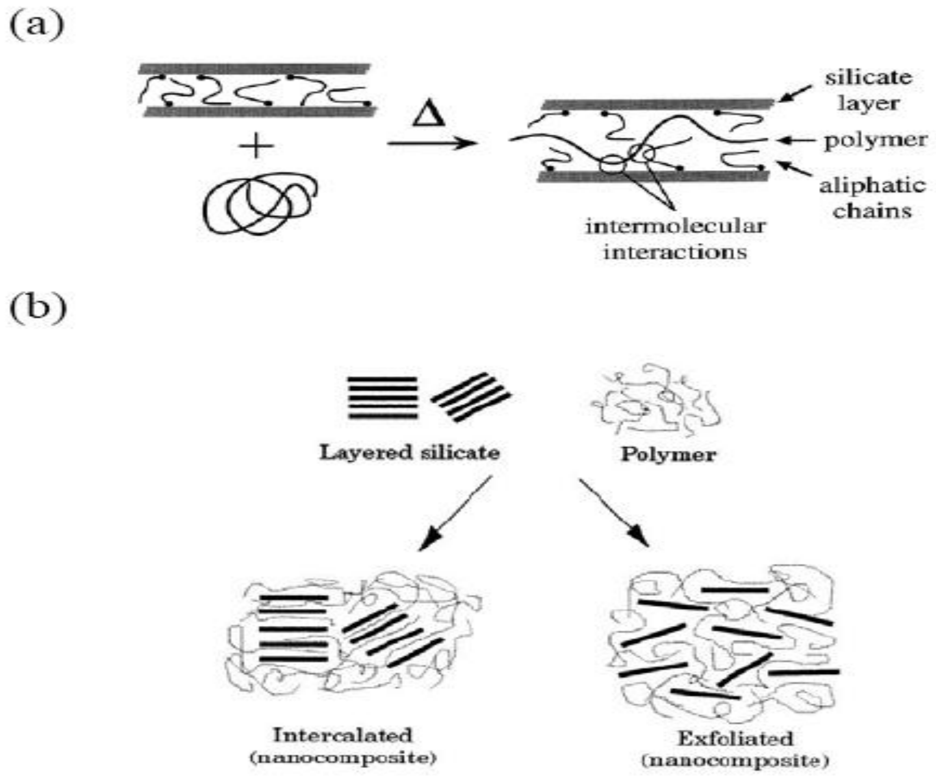

Figure 1.1: (a) Schematic diagram describing interaction between a polymer chain and layered silicates (Pluta et al., 2002). (b) Different stages of composites arising from dispersion of layered silicates in polymers: intercalated and exfoliated state (Okamoto et al., 2000)

Kenaf, *Hibiscus cannabinus, L. family Malvaceae*, is an herbaceous annual plant that can grow under a wide range of weather condition, especially in Asia and Central America and finds application as cordage and sack fiber. The excellent cellulose in the kenaf fiber (KF) source also made kenaf as a source for a large range of paper products. Moreover kenaf bast short fiber also attracted huge interest for their availability, renewability, better mechanical property and lower cost. Kenaf have been used for enhancement in mechanical properties, reducing the cost of the composite, and to make it commercially viable. Recently, researches have further increased the diversity of uses for kenaf by demonstrating its suitability in building materials, textiles, adsorbents, and fibers in new and recycled plastics (Nishino et al 2003). In addition, KF is available in large amounts, easy to get, low cost, non-abrasive during processing also exhibits high specific mechanical properties and biodegradability (Ray et al., 2002; Sydenstricker et al., 2003; Eichhorn et al., 2001; Sgriccia et al., 2007; Wambua et al., 2003). Hydrophilicity of natural fibers however results in better adhesion to hydrophilic matrix resins, specifically in polylactic acid (PLA).

An alternative composite material which is a mixture of micro bio-fiber and nanoclay with bio-polymer (such as polylactic acid) known as hybrid bio-composite has become a state of art in composite research and development. The bio-composite has been widely studied with different combinations for the application of secondary structure in automotive industry, packaging, aerospace, sports, armour products and others. The availability of natural fiber (such as kenaf fiber) makes the bio-composite competetively low in cost and feasible to be produced industrially for wide range of applications. However very few researches has been done on hybrid biocomposite (Amin et al., 2007; Anuar et al, 2008; Bakar et al., 2005; Cicala et al., 2009). The main objectives of this research are to fabricate and to study the performance of micro sized kenaf/nanoclay filled polylactic acid (PLA) hybrid bio-composite. It is hypothesized that the fabricated biocomposite will show better performance than PLA/ kenaf and PLA/ nanoclay composite.

1.2 PROBLEM STATEMENT AND ITS SIGNIFICANCE

In the UN millennium development goals from 2000, it was agreed to work for eradication of extreme poverty and hunger, and to ensure environmental sustainability (Jeffrey, 2005). These two goals are not easily met simultaneously. The fast economical growth in some developing countries that is seen lately will hopefully continue and spread. But there are some quite alarming obstacles for this positive development to persist: i) the demand for all kinds of products increases when economical welfare is increased but the world's resources remain limited, ii) world population is growing rapidly thus demand will continue to raise in all kinds of sectors and iii) this is all happening in a time when we experience climate changes which most likely are triggered by human activities, mainly the use of fossil resources, which will escalate due to the increased consumption, if we do not act. Mankind has a large challenge to deal with. Parts of the solution are a major redirection of our consumption habits in the Western world and an alteration from using fossil to renewable resources for energy production as well as in our products. Among lots of plastic products and plastic-based materials are responsible for depletion of fossil and environmental pollution for their diversified usage.

The increased use of plastics all over the world has resulted in an increase in plastic waste. For this reason the development of biodegradable polymers has been a subject of great interest in materials science for both ecological and biomedical perspectives. Bio-based plastics are sustainable, largely biodegradable and biocompatible. They reduce our dependency on depleting fossil fuels and are carbon dioxide (CO_2) neutral.

Different biodegradable polymeric materials like polycaprolactone (PCL), polyesteramide (PEA), aliphatic copolyesters (PBSA), aromatic copolyesters (PBAT), polyhydroxyalkanoate (PHA) and polylactic acid (PLA) were used to replace the conventional polymer. Among them, PHA and PLA are agro based polyester, which are the most promising to replace the conventional one. Between PLA and PHA, PLA shows better mechanical and thermal properties (Averous, 2004). Extensive research work has been done for the fabrication of biocomposite and nanocomposite with different natural fibers and nano fillers (John and Thomas, 2008; Robeson and Paul, 2008). Both biocomposite and nanocomposite have some merits and demerits. As for example PLA/ kenaf biocomposite shows better strength, stiffness, low cost and easy to be fabricated. This biocomposite however shows higher moisture absorption, less flame retardancy and low impact strength. On the other hand PLA/ nanoclay nanocomposite shows higher flame retardency, less moisture absorption and higher impact strength. Again the main drawback of nanocomposite is high in cost and difficult to be processed.

Therefore it is necessary to investigate the effect of adding nanoclay into biocomposite of PLA/ kenaf fibre. It is also necessary to find out the suitable process fabrication process for homogeneous distribution of fibres and fillers. This is necessary in order to fabricate an environmental friendly hybrid biocomposite and as well to replace the conventional polymer in terms of cost, availability and property.

1.3 RESEARCH OBJECTIVES

i. To investigate the effect of the incorporation of nanoclay into PLA/kenaf fiber on the mechanical and thermal properties of the biocomposite.
ii. To examine the effect of different processing sequence / method on the mechanical and thermal properties of the composites.
iii. To examine the morphology of the fracture surface of hybrid bio-composite.

1.4 SCOPE OF RESEARCH

In this research work, PLA-kenaf-nanoclay hybrid composite had been developed through extrusion process. During extrusion, two processing parameters involved were temperature and speed. The temperature was set between 180 to 190 ºC and the screw speed was 100 rpm. PLA, kenaf and montmorillonite (MMT) clay were the main materials involved in developing the hybrid biocomposite. For this reason, three different processes were developed which are identified as PLA-kenaf-MMT single extrusion, PLA-kenaf-MMT double extrusion (PLA and kenaf extruded first then MMT was added) and PLA-MMT-kenaf double extrusion (PLA and MMT extruded first then kenaf was added).

In this study, 3 wt% of MMT was used which is based on Usman's (2011) studies. In her work, she used single extrusion for fabricating hybrid biocomposite but this research concentrated two different processes to manufacture the hybrid biocomposite. This was done for the better dispersion of MMT, through increment in mechanical and thermal properties. Previous study showed that with addition of MMT and kenaf, tensile strength and stiffness were increased, whereas impact strength decreased significantly. Again previous study did not cover thermal characterization, internal bonding, crystalline behavior and morphological behavior to observe the dispersion of filler.

So the research scope of this work was to find out a suitable process to fabricate hybrid biocomposite for homogeneous dispersion of nanoclay and fibres which leads to better mechanical, thermal and morphological properties. Besides these, the crystallinity behavior and internal bonding behavior are also mandatory to be investigated in order to synchronize with mechanical and thermal properties. Finally, the fabricated hybrid biocomposite was compared with PLA-kenaf biocomposite, PLA-clay nanocomposite and with pure PLA.

1.5 THESIS ORGANIZATION

There are five main bodies created in this research work which are being classified as Chapter 1, Chapter 2, Chapter 3, Chapter 4 and Chapter 5. In chapter 1, the introduction and background of the research done were briefly discussed. This includes a brief idea about the definition of hybrid biocomposites as well as its comparison with other systems. The characteristics of the nano particles employed into the hybrid biocomposites that make this system unique was generally conversed. Moreover, the increasing tendency of using petroleum-based plastic materials and its demerits are precisely describe. Biopolymers and their composites and finally hybrid composites future and bright prospect has been concisely explained under the introduction part.

A problem or matter that resulted in unsatisfied or unbalanced properties of the final products was discussed under problem statement. Suggestions and ideas to overcome such problems were also stated under this part. Moreover, the aims of developing hybrid biocomposites and its characterization were concisely stated under research objectives. General information on the steps involved in fabricating hybrid biocomposites system was discussed under the topic of research methodology. Different processes and parameters that used during manufacturing of hybrid biocomposite were clarified in this part as well. Under the scope of research topic, the background regarding hybrid biocomposites systems was briefly discussed. In addition, the raw materials used, type of processing as well as parameters involved also was explained under this part.

Polymer matrix composite, biocomposite, theoretical background of the hybrid biocomposites, different processing techniques as well as the advantages and disadvantages of biocomposite and hybrid biocomposite were discussed under

Chapter 2 as literature review. In this chapter, each concept mentioned above was explained in details.

Chapter 3 explains the routes of experiment involved in details along with the flow chart and figures for better understanding. In this chapter, the types of material used, materials property, processing parameters (temperature and speed), different methods of fabricating hybrid biocomposite as well as characterization methods to evaluate the mechanical, thermal and morphological properties of the hybrid biocomposites systems were concisely explained. In addition, the theory and concept regarding the methods of characterizations were briefly listed.

Chapter 4 comprises of different testing methods to assess the properties of the fabricated hybrid biocomposites. Obtained results were then discussed extensive and tried to co-relate to each other. Moreover, different source of references used were revealed to support the results obtained from these characterization methods. Each results acquired from different techniques of characterization were then compared between the other available processes. Results were then compared with PLA/kenaf biocomposite and unreinforced PLA to investigate the effect of nanoclay. Finally the best process and composite was determined based on the obtained results.

Chapter 5 describes the concluding remarks of the whole research work and suggests future works which are difficult to conclude from this research.

Works of other researchers that were being referred to was put in order in bibliography section. Once all the data needed was completely compiled, a clean and concise abstract was introduced at the beginning of the thesis. Brief information on the problem statement, research methodology and the results attained were part of the main topic that should be discussed in this section so that an overview about the study can be comprehended.