UTILIZATION OF CARBON NANOTUBE TOWARDS THE IMPROVED PROPERTIES OF POLYAMIDE 6 NANOCOMPOSITES

by

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Thesis submitted in fulfilment of the requirements
For the degree of
Doctor of Philosophy

June 2015

ACKNOWLEDGEMENT

First and foremost, I would like to offer my most profound thanks to my supervisor, Professor Dr. Abdul Rahman Bin Mohamed, for his patience, guidance, motivation, support and generous encouragements all through my study. Without his financial and emotional support, I would not be able to proceed and bring this research to completion. I have been extremely lucky to have a supervisor who cared so much about my work and life. His support and patience in the most difficult moments of my life is exemplary.

I would like to express my special gratitude to Professor Dr. Zainal Arifin Mohd Ishak, my co-supervisor, for his invaluable guidance, helpful recommendations, patience, enthusiastic encouragement and useful critiques concerning the interpretation and analysis of the data.

I would also like to express my special gratitude to Professor Dr. Azlina Bt Harun @ Kamaruddin, the dean of School of Chemical Engineering, for her kind concern regarding my academic requirements. My gratitude also goes to Professor Dr. Abdul Latif Bin Ahamd, the former dean of School of Chemical Engineering.

I am particularly grateful for the assistance given by Dr. Yeoh and Dr. Phua for their contribution to this project, especially during CNT production and data analysis.

I would also like to thank all the laboratory technicians and administrative staff, for the assistance they rendered to me particularly, Mr. Mohd Khairul Nizam B Mohd Zuhan, Mr. Segar, Mr. Faizal, Mr. Shahril, Mr. Arif, Mr. Fadzil, Ms. Aniza, Ms. Normie, Ms. Nurul, Ms. Fatimah and Ms. Rohaya.

My gratitude is extended to my beloved parents, family members for their support and encouragement. In addition, I dedicate my special appreciation to my beloved wife who always has been patient and encouraged me.

Last but not least, I would like to extend my sincerest gratitude to my friends, particularly Dr. Mazaheri, Dr. Rezaei, Mr. Adeli, Dr. Lahijani, Dr. Mohammadi, Mr. Eshghabadi and others whom I am not able to address here.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
ATR-IR	Attenuated Total Reflectance Infrared
CCNT	Commercial carbon nanotube
CCVD	Catalytic Chemical Vapor Deposition
CNT	Carbon Nanotube
DMTA	Dynamic Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
DTG	Differential Thermogravimetry
FTIR	Fourier transform infrared spectroscopy
HDT	Heat deflection temperature
MFI	Melt Flow Index
PA6	Polyamide 6
PCNT	As-produced carbon nanotube
PE	Polyethylene
RAMAN	Raman Spectroscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

LIST OF SYMBOLS

A	Pre-exponential Arrhenius factor (min^{-1})
α	Conversion rate (dimensionless)
β	Heating rate (K/ min)
ΔH_f^0	Fusion heat of 100% crystalline polymer (J/g)
ΔH_f	Fusion heat of sample (J/g)
d	Spacing between diffraction lattice plane (interspacing)
ε_b	Elongation at break
E_A	Apparent activation energy (kJ/mol)
E	Young modulus (MPa)
E'	Storage modulus
E''	Loss modulus
$f(\alpha)$	General expression of kinetic model
g	gram
$g(\alpha)$	Integral form of kinetic model (d $f(\alpha)$/dt)
Hz	Hertz
k	Arrhenius rate constant
kPa	kilo Pascal
min	minute
m_i	Sample weight at t=0
m_f	Sample weight at $t=\infty$
m_t	Sample weight at t=t
nm	nanometre

n	kinetic exponent
ºC	Degree Celsius
R	Universal gas constant (8.314 J/mol. K)
tan δ	Loss factor
t	time
T	Absolute temperature (K)
T_c	Crystallization temperature (°C)
T_d	Decomposition temperature
T_g	Glass transition temperature (°C)
T_m	Melting temperature (°C)
w%	Weight percent
Wt.%	Weight percent
X_c	Degree of crystallinity
θ	Diffraction angle
σ	Tensile strength

PENGGUNAAN TIUB NANO KARBON DALAM MENINGKATKAN SIFAT-SIFAT BAHAN NANOKOMPOSIT POLIAMIDA 6

ABSTRAK

Polimer/nanokomposit CNT adalah bahan dengan ciri-ciri yang unik untuk pelbagai aplikasi serta mempunyai masa depan yang baik. Interaksi permukaan di antara CNT dan matriks polimer memainkan peranan penting dalam sifat akhir nanokomposit. Objektif utama kajian ini adalah untuk meningkatkan kesan interaksi ini ke atas matriks polimer.

Nanotiub karbon berdinding lapisan (MWCNT) yang berasaskan pemangkin dwilogam Co- Mo/MgO dihasilkan menggunakan kaedah pemendapan wap bahan kimia bermangkin (CCVD). Gas metana digunakan sebagai sumber. Pembelauan sinar-X (XRD), mikroskop elektron pancaran (TEM), analisis Termogravimetri (TGA) dan spektroskopi Raman membuktikan pembentukan nanotiub karbon dengan diameter di antara 10-20 nm. Kesan sifat mekanikal, morfologi, haba dan sifat reologi PA6 nanotiub karbon (PCNT) yang tidak diubahsuai, yang telah diubahsuai dan nanotiub karbon (CCNT) komersial dengan diameter yang sama pada telah dikaji.

Penulenan dan pengoksidaan CNT dilakukan dengan beberapa cara bagi mendapatkan keadaan tindak balas yang terbaik iaitu masa, suhu dan kepekatan asid. Rawatan CNT dalam asid hidroklorik (HCl) berkepekatan 12 M pada suhu 70° C selama 6 jam dapat menghilangkan kira-kira 95% daripada bendasing CNT . Asid nitrik, campuran asid sulfurik dan asid nitrik , dan larutan piranha digunakan untuk menulenkan dan mengoksidakan CNT dan untuk memasukkan kumpulan karboksil, hidroksil dan keton ke atas CNT. Kehadiran kumpulan berfungsi pada permukaan CNT disahkan spektroskopi inframerah transformasi Fourier (FTIR), TGA dan spektroskopi Raman. Etilenadiamina (EDA), heksametilenadiamina (HDA) dan oktadekilamina (ODA) telah berjaya digraf di permukaan CNT.

Komposit PA6 mengandungi CNT yang tidak diubahsuai dan diubahsuai telah disediakan dengan muatan CNT yang berbeza dengan pencampuran peleburan mudah. Corak XRD semua nanokomposit menunjukkan CNT mengubah bentuk struktur kristal rapi PA6 dari bentuk α/γ kepada struktur fasa-α yang memiliki termodinamik yang lebih stabil. Thermogram kalorimetri pengimbasan pembezaa (DSC) menggambarkan CNT yang tidak diubahsuai dan perubahan suhu penghabluran beralih kira-kira 10-15 °C kepada suhu yang lebih tinggi disebabkan oleh kesan penukleusan nanotiub. Tambahan pula, darjah penghabluran meningkat sebanyak lebih daripada 50% dalam beberapa komposit. Thermogram TGA menunjukkan peningkatan permulaan degradasi terma nanokomposit untuk sampel yang mengandungi CNT yang difungsikan. Mekanisme degradasi tak sesuhu nanokomposit dikaji menggunakan kaedah Coats - Redfern dan Horowitz - Metzger. Tenaga pengaktifan dan praeksponen faktor Arrhenius untuk degradasi terma nanokomposit dalam udara dan nitrogen dianggarkan menggunakan kaedah ini.

Keputusan menunjukkan bahawa kekuatan tegangan dan modulus nanokomposit meningkat (kira-kira 43 hingga 55%) dengan peningkatan kandungan CNT yang diubahsuai sehingga ke tahap yang tertentu, bergantung kepada jenis CNT. Kekakuan dan kemuluran meningkat dengan peningkatan kandungan CNT .

Kelikatan lebur nanokomposit meningkat pada muatan CNT yang tinggi kerana kekusutan antara pengisi-matriks.

UTILIZATION OF CARBON NANOTUBE TOWARDS THE IMPROVED PROPERTIES OF POLYAMIDE 6 NANOCOMPOSITES

ABSTRACT

Polymer/CNT nanocomposites are promising materials with unique properties for wide range of applications. Interfacial interaction between CNTs and polymer matrix play a key role in final properties of nanocomposite. The major objective of this study was to increase this interaction to achieve more impact on polymer matrix.

Multi-walled carbon nanotubes (MWCNTs) based on bimetallic Co-Mo/MgO catalyst were produced by chemical catalytic vapour deposition method (CCVD). The source gas was methane. X-ray diffraction (XRD), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and Raman spectroscopy proved carbon nanotube formation with the diameter of 10-20 nm. Effect of unmodified and modified as-produced carbon nanotubes (PCNTs) and commercial ones (CCNTs) with same diameter on mechanical, morphological, thermal and rheological behaviour PA6 was investigated.

Purification and oxidation of CNTs carried out with several routes to standardize the best reaction conditions i.e. time, temperature and acid concentration. Treatment of CNTs in 12 M hydrochloric acid (HCl) at 70 °C and 6 hr removed about 95% of impurities of CNTs. Nitric acid, mixture of sulphuric acid and nitric acid, and piranha solution used to purify and oxidize CNTs and to introduce carboxyl, hydroxyl and keton groups on the CNTs. Presence of functional groups on the surface of CNTs approved by Fourier transform infrared spectroscopy (FTIR), TGA and Raman spectroscopy. Ethylenediamine (EDA), hexamethylenediamine (HDA) and octadecylamine (ODA) were successfully grafted on the surface of CNTs.

PA6 composites containing unmodified and modified CNTs prepared at different CNT's loading by simple melt mixing. XRD patterns of all nanocomposites showed CNTs changed the crystalline structure of neat PA6 from α/γ form to more thermodynamic stable α-phase structure. Differential scanning calorimetry (DSC) thermograms depicts unmodified and modified CNTs shifted crystallization temperature about 10-15 °C to higher temperatures due to the nucleating effect of nanotubes. Furthermore, degree of crystallinity increased by more than 50% in some composites. TGA thermograms revealed onset of thermal degradation of nanocomposites increased for samples containing functionalized CNTs. Non-isothermal degradation mechanism of nanocomposites studied using Coats-Redfern and Horowitz-Metzger methods. Activation energy and pre-exponential Arrhenius factor for thermal degradation of nanocomposites under air and nitrogen estimated by these methods.

The results indicate that the tensile strength and modulus of nanocomposites increased (about 43 and 55%) with increasing modified CNTs content up to a certain level, depending on the type of CNTs. Stiffness and ductility increased by CNT contents.

Nanocomposites melt viscosity increased at high CNTs loading due to the filler-matrix entanglements.

CHAPTER 1 - INTRODUCTION

1.1 Introduction

Better life forced humankind to innovate new materials for many applications such as aircrafts, bridges and power plants. Thus, scientists tried to introduce modern materials such as polymer, steel and other metal alloys to actualize their dreams. However, in some cases, these materials do not cover the performance for planned target. Therefore, the scientist tried to find new materials, and their experience led them to composite materials. The idea of combination of two or more materials (composite) for new application and improved properties of continues phase (matrix) was used from a long time ago (Hsu et al., 2011). Several types of composites have been made and have been used in different areas. Stability over time, versatility of use, capacity to be shaped, high specific strength (strength to weight ratio) and lightweight are the main characteristic of traditional composite materials. Of these, lightweight can reduce energy consumption. Due to the better corrosion resistance of composite materials to the metal (i.e. aluminium) alloys, the maintenance operation of resulting parts can be reduced. In some cases, composite materials have more cost than other materials, but lower production costs, reduction in weight, higher performance and lower waste materials can balance high price of composite materials.

As an example, fuel consumption of Boeing 787 (Figure 1-1) is about 20% less than fuel consumption of its competitors only by changing of aluminium parts to the composite materials (Galiotis, 2011; Ng et al., 2013).