THE EFFECT OF FILLERS LOADING ON PROPERTIES OF MWCNT/HIPS REINFORCED NANOCOMPOSITES

BY

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ABSTRACT

A new high impact polystyrene/multiwall carbon nanotubes (HIPS/MWCNTs) nanocomposite has been successfully developed. The mechanical, rheological, thermal and water absorption performances have been improved. The experimental design included one way MANOVA test to validate the significance of changes in HIPS due to 0.1wt%, 0.5wt%, 1wt%, 2.5wt%, 5wt%, 7.5wt% and 10wt% loadings of MWCNTs. An independent analysis for the different HIPS/MWCNTs nanocomposite was carried out. The improvement in Young's modulus ranged between 1.79% and 31.78% which confirmed that the load has been transferred successfully from the HIPS to the MWCNTs. There was an initial improvement of 4.24% in the impact strength at 0.1wt% of MWCNTs loading level, beyond which the value of the impact strength falls down. Thus an inverse relationship between the MWCNTs loading level and the impact strength was identified. The viscosity was found to be directly proportional to MWCNTs' loading, as it went up to five times the value of pure HIPS at loading level of 7.5wt% of MWCNTs. The water absorption resistance was found to be directly related to MWCNTs loading with improvement between 24% and 72.5% following the increase in MWCNTs loading. The MWCNTs loading also demonstrated an effect on the glass transition temperature with values ranging from 0.8% decrease and 1.4% increase. The HIPS/MWCNTs nanocomposite with 0.1 wt% of MWCNTs loading had yielded the best results in terms of Young's modulus, izod impact energy, viscosity, Tg, and water absorption. Further loading MWCNTs found to result in lower performance in one or more properties of the HIPS/MWCNTs nanocomposite. The cost of producing the new product at the optimum loading of 0.1wt% of MWCNTs was found to be 25% higher compared to the price of HIPS.

خلاصة البحث

تم بنجاح تطوير بولي ستايرين عالي المقاومة للصدمات معزز بأنابيب الكربون النانوية ذات الجدران المتعددة. جيث تم تطوير الاداء من النواحي الميكانيكية والريوليجية و الحرارية ومقاومة إمتصاص المياه . كذلك هدفت الدراسة لتقييم تأثير تكلفة مثل هذا التعزيز على التكلفة الكلية للبوليمر. تضمن تصميم التجارب تحليل المانوفا المتعددة بمتغير واحد للتحقق من مصداقية النتائج وفاعلية تأثير تغيير نسب التعزيز بمقدار (0.1%، 0.5%، 1%، 2.5%، 5%، 7.5%، 10%) على الاداء ومن ثم تبع ذلك بتحليل مستقل للاداء لمختلف مركبات النانو من البولي ستايرين العالي المقاومة للصدمات والمعزز بأنابيب الكربون النانوية ذات الجداران المتعددة. التحسن في معامل يونج تراوح بين 1.79% و 31.78% بما يثبت ان الحمل تم تبادله بنجاح بين البوليمر وأنابيب الكربون النانوية المتعددة الجدران. كان هنالك تحسن مبدئي بنسبة 4.24% في مقاومة الصدمات عند مستوى تعزيز 0.1% تبع بإنحدار متواصل في الاداء بما يثبت أن هنالك علاقة عكسية بين مستوى التعزيز بأنابيب الكربون ذات الجدران المتعددة والقدرة على مقاومة الصدمات. مستوى اللزوجة تبين ان له علاقة طردية بنسب التعزيز حيث أنه زاد الى مافوق خمس اضعاف مستويات البوليمر الغير معزز عند مستوى تعزيز 7.5%. بينما اظهر مركب البوليمر النانوي الجديد تحسنا في مقاومة إمتصاص الماء بقيم تفاوتت بين 24% و 72.5% تبعا لزيادة نسب التعزيز وعليه فعلاقته كانت طردية لتلك الزيادة. أظهرت أنابيب الكربون ذات الجدران المتعددة تأثيرا على درجة حرارة التحول الزجاجية فقد شهدت تغيرا بنسب تفاوتت بين إرتفاع بمقدار0.8% و إنخفاض بمقدار1.4%. أظهرت النتائج أن نسبة التعزيز بمقدار0.1% من أنابيب الكربون النانوية ذات الجدران المتعددة قد أعطت نتائج إيجابية في إختبارات معامل يونج ومقاومة الصدمات بالاضافة الى اللزوجة و درجة الحرارة الزجاجية ومقاومة إمتصاص الماء وأن أي نسبة تعزيز تتعدى ذلك فسيكون لها تأثير سلبي على الاداء في واحدة أو اكثر من خصائص البولي ستايرين العالي المقاومة للصدمات والمعزز بانابيب الكربون النانوية ذات الجدران المتعددة. كما قدر أن تكلفة تعزيز البولي ستايرين بمستوى 0.1% من أنابيب الكربون النانوية ذات الجدران المتعددة ترفع قيمة البولي ستايرين العالي المقاومة للصدمات بنسبة 25% .

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 is fully adequate, in scope and quality, as a thesis for the degree of Master of Science in Manufacturing Engineering.

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DECLARATION

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

Ahmed Salem A. AL-Ghamdi

Signature …………………………………… Date …………………..

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To my parents, wife, Baker, and Omar

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Al_2O_3	Aluminum oxide
ANOVA	Analysis of Variance
CNFs	Carbon nanofibers
CNT	Carbon nanotubes
CVD	Chemical Vapor Deposition
HIPS	High Impact Polystyrene
JIC	Jubail Industrial College
JTI	Jubail Technical Institute
KFUPM	King Fahd University of Petroleum and Minerals
MANOVA	Multivariate Analysis of Variance
MCNT S	Multiwall carbon nanotubes
MFR	Melt flow rate
MMT	Montmorillonite organoclays
MWCNTs	Multiwall carbon nanotubes
NC	Nanocomposites
N-silica	Nanosilica
PE	Polyethelene
POSS	Polyhedral oligomeric silsesquioxane
PS	Polystyrene
RCJ	Royal Commission in Jubail
SABIC	Saudi Arabian Basic Industrial Company
SEM	Scanning Electron Microscope
SWCNTs	Singlewall nanotubes
TEM	Tunneling Electron Microscope
TiO_2	Titanium Oxide

LIST OF SYMBOLS AND UNITS

%	Percentage
l_c	Capillary length
m_w	Piston and dead weight mass
$\dot{\gamma}$	Shear rate at capillary
Δp	Pressure gradient measured on capillary length
Å	Angstrom
A_0	Original cross-sectional area through which the force is applied
As	Cross section area
d	Capillary diameter
E	Young's modulus
E_B	Breaking energy
E_I	Impact energy for the test
E_L	Loss Energy
GPa	Giga Pascal
kJ/m^2	Kilojoules per meter square
L_0	Original length of the object
m^2/g	Squared meter per gram
MPa	Mega Pascal
nm	Nanometer
Q	Volumetric rate of flow
rpm	Revolution per minute
t	Time of MFR measurement
T	Thickness of specimen
T_g	Glass Transition Temperature
USD	US Dollars
W	Width of specimen
ΔL	Amount by which the length of the object changes
µm	Micrometer
ρ	Density
D	Diameter of plastometer cylinder
F	Force acting on melt
g	Acceleration of gravity
τ	Shear stress on capillary

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

The current age is the age of plastics, as they are dominating the manufacturing world with their excellent properties and are being used in many versatile applications. They are light in weight, cheap to buy, and easy to process compared to other metallic materials such as steels, copper, and aluminium (Brewer, 2010).

Nevertheless, plastics or polymers possess number of properties that can be improved further to suit more challenging applications. This improvement can be accomplished in many ways and the most effective one is the reinforcement process. This process usually results in new composite with unique or enhanced properties that are superior to the properties of the constituent materials. In the past years researchers extensively studied the materials that can be used to reinforce polymers, thus, special forms of carbon fiber, fiberglass, aramid came to existence. The size, length and the orientation of such fiber are crucial factors that can affect the properties of the new composite (Bacon's, 2010; Harris, 2009).

Moreover, with the tremendous advancement of nanotechnology, many recent studies had focused on the incorporation of carbon nanotubes (CNTs) to enhance the properties of polymers, so better material for more challenging applications can be achieved. For example, the new carbon based Boeing 787 (Figure 1.1) was the first airplane that changed its fuselage structure from metal to polymer/carbon composites which have helped to eliminates 1,500 aluminium sheets and 40,000 to 50,000 fasteners. This was possible as easy processing of polymer/carbon composites allowed the structure to be built in one piece rather than many parts that are joined together.

Furthermore, the light weight of its composite structure allowed the 787 also to fly using 20 percent less fuel per passenger than similarly sized airplanes. This achievement would have not been possible without extensive research work on polymers reinforcement with CNTs and other materials (Boeing, 2011).

Figure 1.1: Boeing 787 the carbon based airplane (Boeing, 2011)

An excellent polymer high impact polystyrene (HIPS), which is discussed in details in chapter 2, is one type of polymer that is widely used in many versatile applications, due to its balanced mechanical performance, ease of processing and low cost. Yet, there is still a need for detailed examination of its reinforcement possibilities with CNTs by studying the changes in the mechanical, thermal, rheological, and water absorption properties due to the CNTs loading. This overall evaluation is mandatory to confirm the balanced enhancement of the resulting nanocomposite without compromising any of the desirable properties of the original polymer. Otherwise the development process of the nanocomposite cannot be considered successful. For example, in recent attempts to load HIPS with multiwall carbon nanotubes

(MWCNTs), using melt mixing method, good dispersion with enhanced electrical conductivity was reported at loading level of 5 wt% of MWCNTs. However, the results of such high loading level on the overall performance in terms of mechanical properties, viscosity, glass transition temperature (Tg) and water absorption were lacking. Therefore, successful development of new material cannot be reported with such limited information (McClory et al., 2010; Andrews et al., 2002).

Furthermore, it is very important during the development of new product that an evaluation of the economical benefit and safe use of the product to be reported in details. Information on the performance parameters in terms of Young's modulus, impact strength, Tg, viscosity and water absorption can be vital to judge the success or failure of the newly developed material. For example, the space shuttle Challenger disaster that has happened in 1986 was due to an improper use of rubber O-ring that was used below its Tg point. This caused the O-ring to fail to serve its objectives and thus leading to fuel leakage that resulted in the space shuttle explosion shortly after launching (NASA, 1986).

1.2 PROBLEM STATEMENT AND ITS SIGNIFICANCE

The need for lighter materials with enhanced performance to serve in application such as aviation and aerospace had driven the research efforts to concentrate on the development of polymer/CNTs nanocomposites. However, HIPS is one polymer that is still not yet been investigated in details to enhance its overall performance through MWCNTs loading. The previous research attempts to load HIPS with MWCNTs focused more on the electrical properties and/or tensile strength individually. Yet, Young's modulus, impact strength, viscosity, Tg, and water absorption which are considered important performance criteria were lacking or partially reported in the surveyed literature. Thus, there is a great possibility of imbalanced enhancement of performance in previous attempts, as improving one property was found to deteriorate other few properties.

Furthermore, detailed analyses have not been done to identify the changes that have taken place for several important properties due to the material reinforcement. Hence, the possibility of HIPS/MWCNTs nanocomposite to serve in higher order applications can be considered an active area of research. In addition, experimental investigation is needed to identify the MWCNTs loading levels that would provide ease of process ability and at the same time will provide an optimum value for most of the performance criteria.

1.3 RESEARCH OBJECTIVES

The main objective of the research is to develop a new nanocomposite with enhanced mechanical, rheological, thermal and water absorption performances, by manipulating the MWCNTs loading levels and then studying the influence of such loading on each property. Therefore, the objectives would be to determine the influence of each MWCNTs' loading level on the overall performance of HIPS through number of specific objectives that can be arranged as follows;

1. To evaluate the mechanical performance based on;
   i. The Young's modulus test.
   ii. The impact resistance test.
2. To evaluate of the rheological performance experimentally by identifying the melt flow rate and the viscosity.
3. To analyse the glass transition temperature (Tg) using differential calorimetric scanning (DCS) analysis.

4. To identify the water absorption rate by conducting the standard water absorption test.

1.4 RESEARCH METHODOLOGY

Seven types of HIPS/CNTs nanocomposites with 0.1wt%, 0.5wt%, 1wt%, 2.5wt%, 5wt%, 7.5wt% and 10wt% loadings of CNTs, representing low, medium and high concentrations of CNTs, were prepared using melt mixing method. The design of the experiment was such a way that one way Multivariate analysis of variance (MANOVA) was used to test the significance of each CNTs loading level, including the pure HIPS, as fixed independent variables on five dependant variables, namely; Young's modulus, impact strength, viscosity, Tg, and water absorption percentage. Each experiment was repeated six times to give a total of 240 experiments (8 Levels represents the loading levels × 5 Variables represents the tested properties× 6 Replicates represents number of samples).

Furthermore, the normality of the 240 readings of tests results and the significance of the correlation among, within and between the tests were analyzed. The newly developed HIPS/CNTs nanocomposite results were also analyzed and discussed. Finally, a summary of the findings, cost analysis and recommendations for future research were given. The flow charts in Figure 1.2 demonstrate the overall experiment.

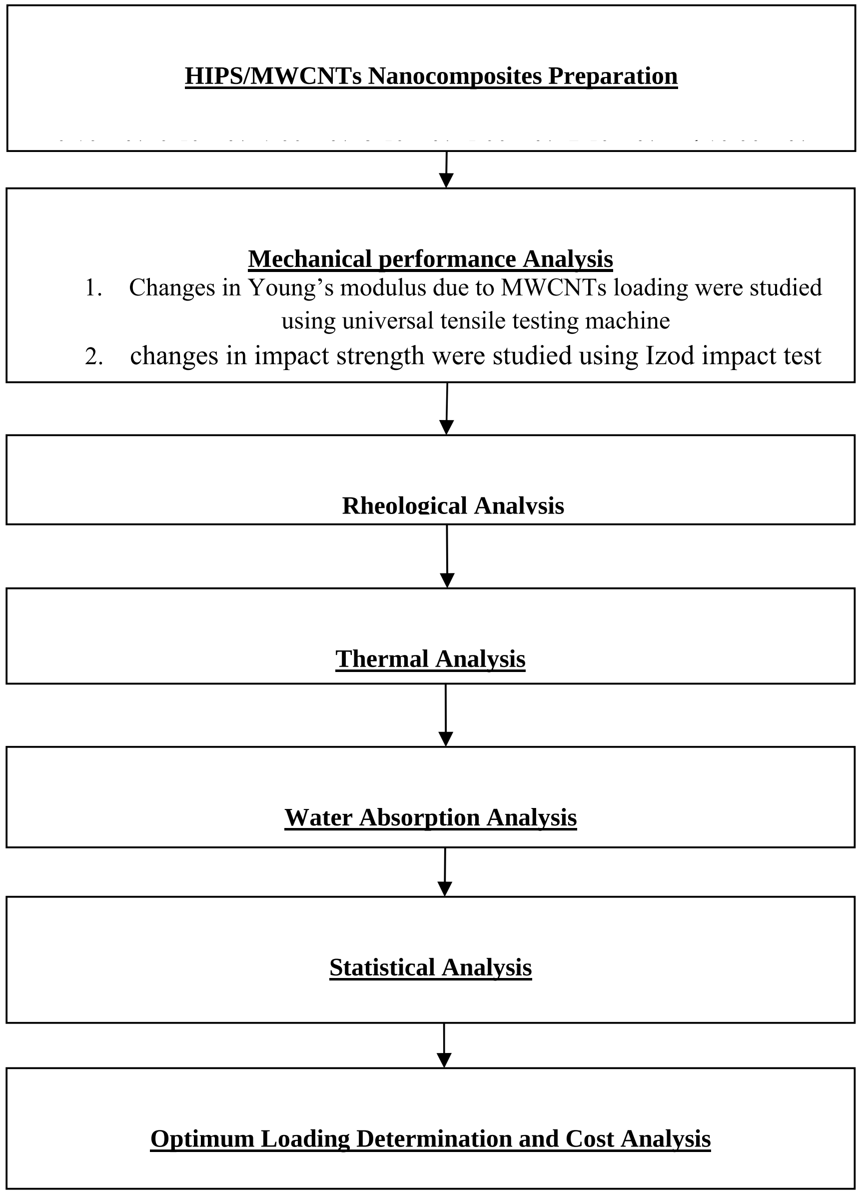

Figure 1.2: Flow chart of the overall experiment

1.5 RESEARCH SCOPE

The scope of the research is to prepare a HIPS/MWCNTs nanocomposite with balanced performance in terms of mechanical properties, viscosity, Tg, and water absorption. This will be achieved through, analyzing the changes in the specified areas experimentally and with the use of statistical tools to ensure the appropriateness of the results.

1.6 DISSERTATION ORGANIZATION

The dissertation arrangement is in five chapters. Chapter 1 consists of introduction, problem statement, then the research objectives, methodology and its scope. Chapter 2 provides a review of the available literatures. It starts with an introduction, then an overview of polymers nanocomposites and an overview of polymers reinforcement. S

Then finally, the chapter concludes with a summary. Chapter 3 covers the methodologies used in the research, with detailed explanation of the experimental work. Chapter 4 lays out the results from the experimental work and provides a detailed discussion. Finally chapter 5 concludes the work by giving a summary of the important findings and recommendations on future works.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Carbon nanotubes are considered to be the stiffest and the strongest fibers ever produced. The Young's modulus of the nanotubes can be as high as 1000 GPa, approximately five times higher than steel, while their tensile strength can be up to 63 GPa, around 50 times higher than steel. Thus, these properties coupled with their light weight, gives CNTs a huge potential in a whole new wide range of applications (Harris, 2009). These properties had driven the current research efforts to highly concentrate on CNTs production, enhancement, and reinforcement possibilities to other materials matrices, therefore, these innovated and advance nanocomposites (NCs) can be produced to serve in more challenging applications that had never been possibly to be served by any other traditional materials (Coleman et al., 2006; Kim et al., 2007).

Moreover, polymers with their attractive processing abilities and low cost had become excellent candidates for reinforcement with CNTs. Thus, the performance of HIPS, which is one type of polymers that is used in huge number of applications, could be enhanced further with the addition of CNTs according to preliminarily researches done on HIPS (McClory et al., 2010; Andrews et al., 2002). Therefore, in order to understand the issues related to the development of HIPS/MWCNTs nanocomposite it was necessary first to study the relevant literature of the polymers nanocomposites, CNTs and HIPS/CNTs, which was reviewed and summarized in the coming sections of this chapter.