Faculty of Manufacturing Engineering

DEVELOPMENT OF CNT/SiO_2 FILLERS REINFORCED POLYESTER HYBRID COMPOSITES

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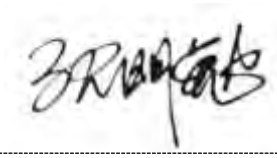
DECLARATION

I declared that this thesis entitled –Development of CNT/SiO2 Fillers Reinforced Polyester Hybrid Composites" is the results of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : 

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DEDICATION

To my beloved parents and siblings

ABSTRACT

With the progress of time, emphasis on friction and wear of polymer matrix composites is increasingly important. Modest attempt has been made to develop hybrid polymer composites reinforced micro- and nano- sized fillers. Silica (SiO_2) and carboxylic functionalized multi-walled carbon nanotube (MWCNT-COOH) are favored in friction and wear properties were added into polyester resin. This widely used micro-filler, SiO_2 were maintained at 10 wt. % while nano-filler, MWCNT-COOH were at 0.1 wt. %, 0.3 wt. % and 0.8 wt. %. Prior to the fabrication, ultrasonicator was used to assist the dispersion of SiO_2 and MWCNT-COOHinto unsaturated polyester resin. Elimination of voids was optimized by evacuation of the mixture in vacuum drying oven. Vacuum infusion technique was established to produce pin samples and resin casting method were applied to fabricate samples in rectangle size. Improvement of light weight properties was proven by measurement of density of each ready sample using densitometer. Investigation towards the stiffness and resistance to abrasion of the hybrid composites were performed by Vickers Hardness Test. The samples with only carboxylic functionalized multi-walled carbon nanotube at different loadings were investigated on the dispersion state by utilizing Transmission Electron Microscope. As received SiO_2 and MWCNT-COOH as well as dispersion state of ready samples were observed using Field Emission Scanning Electron Microscope.Spectrums were recorded by Attenuated Total Reflectance Fourier Transform Infrared to identify the relevant bonding or structural changes which show interaction in between fillers and matrix material. Dynamic mechanical analysis was able to provide maximum service temperature, glass transition temperature and viscoelastic behavior of hybrid polyester composites prior to dry sliding test. Pin-on-disc testerwas used to reveal tribological properties of this material. Wear parameters were at sliding speeds of 1.6 m/s, 2.8 m/s and 4.0 m/s as well as applied loads of 5 N, 10 N and 20 N. Wear and friction process were investigated at sliding speed of 4.0 m/s and applied load of 20 N for 2 hours at sliding interval of 15 minutes. Observation of wear surfaces and wear particles has been made using scanning electron microscope. At the optimum loadings, UPR/SiO_2/0.8, agglomerates were observed which has led to further increase of specific wear rates. Interaction in between fillers and matrix had regulated the decrease in specific wear rate and coefficient of friction. Wear and friction of sample pins were protected by transfer film formed after dry sliding. Further sliding has led to detached of transfer or wear particles whether from wear surface of transfer film. Different types of wear particles were observed when types of fillers varied. Sharp and edges wear particles were found on sample with MWCNT-COOH added whereas rounded and least edges wear particles were found in sample with SiO_2 added. The development of this advanced material will give significant implications on application requiring light and low coefficient of friction.

ABSTRAK

Dalam era maju ini, penegasan terhadap geseran dan kehausan komposit matriks polimer adalah semakin penting. Pelbagai percubaan telah dibuat untuk membangunkan komposit hibrid poliester bergabung dengan bahan pengukuhan mikro dan nano pengisi bersaiz. Sifat-sifat silika (SiO_2)dan MWCNT-COOH yang sesuai pada geseran dan kehausantelah digabung dengan resin poliester. Mikro-pengisi, SiO_2yang popular dikekalkan pada 10 wt. % manakala nano pengisi, MWCNT-COOH ialah pada 0.1 wt. %, 0.3 wt.%, dan 0.8 wt. %. Sebelum fabrikasi, ultrasonicator digunakan untuk membantu penyerakkan SiO_2 dan MWCNT-COOH ke dalam resin poliester. Penghapusan buih telah dioptimumkan dengan pengunaan ketuhar pengeringan vakum. Teknik infusi vakum telah ditubuhkan untuk menghasilkan sampel pin dan kaedah acuan resin telah digunakan menghasilkan sampel dengan saiz segi empat tepat. Ketumpatan telah dibuktikan oleh pengukuran ketumpatan setiap sampel bersedia dengan menggunakan Densitometer. Siasatan terhadap kekukuhan dan rintangan lelasan bagi komposit hibrid telah dijalankan oleh Vickers Hardness Test. Sampel dengan hanya MWCNT-COOH pada beban yang berbeza telah disiasat di negeri penyelerakan itu dengan menggunakan Transmission Elektron Microscope. SiO_2 dan MWCNT-COOH dan penyerakkan partikel dalam matriks telah diperhatikan menggunakan FESEM. Spektrum telah direkodkan oleh Attenuated Total Reflectance Fourier Transform Infrared untuk mengenal pasti ikatan yang berkaitan atau perubahan struktur yang menunjukkan interaksi di antara bahan pengukuhan dan bahan matriks. Dynamic mechanical analysismenghasilkansuhu perkhidmatan maksimum, suhu peralihan kaca dan kelakuan viskoelastik komposit poliester hibrid sebelum kering gelongsor ujian. Penguji Pin-on-disc telah digunakan untuk mengemukakan sifat tribological bagi bahan ini. Parameter gelongsor adalah pada kelajuan gelongsor 1.6 m/s, 2.8 m/s dan 4.0 m/s dan juga beban yang dikenakan 5 N, 10 N dan 20 N.Proseskehausan dan geseran telah dikaji pada kelajuan 4.0 m/s dan beban 20 N selama 2 jam dengan selang 15 minit.Permukaan kehausan dan partikel kehausan telah diperhati dengan menggunakan mikroskop elektron imbasan. Pada beban optimum, UPR/SiO_2/0.8, agglomerates ditemui telah mengakibatkan peningkatan kadar kehausanselanjutnya. Interaksi di antara bahan pengukuhan dan matriks telah mengakibatkan penurunan dalam kadar kehausan tertentu dan pekali geseran. Kehausan dan geseran pin sampel telah dilindungi olehfilem pemindahan yang dibentuk selepas kering gelongsor. Gelongsor yang selanjutnya telah menyebabkanpartikel kehausan atau pemindahan tertanggal daripadapermukaan kehausan dan filem pemindahan. Pelbagai jenis partikel kehausan diperhatikan apabila jenis bahan pengukuhanberlainan. Kehausan partikel yang petua dan bersudut dijumpai pada sampel dengan pergabungan MWCNT-COOH manakala kehausan partikel yang kurang petuaditemui pada sampel dengan pertambahan SiO_2. Pembangunan komposit hibrid poliester ini akan disesuaikan kepadaaplikasi memerlukan kurang berat dan pekali geseran yang rendah.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

ANOVA	-	Statistical analysis of variance
ATR	-	Attenuated Total Reflectance
COF	-	Coefficient of friction
DMA	-	Dynamic mechanical analysis
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared Spectroscopy
MEKP	-	Methyl ethyl ketone peroxide
MWCNT-COOH	-	Carboxylic functionalized multi-walled carbon nanotube
Pa	-	Pascal
PMC	-	Polymer matrix composite
PTFE	-	Polytetrafluoroethylene
SEM	-	Scanning Electron Microscope
SWCNT	-	Single-walled carbon nanotube
UPR	-	Unsaturated polyester resin
Tan δ	-	Tangent delta
TEM	-	Transmission Electron Microscope
E‘	-	Storage modulus
E”	-	Loss modulus
T_g	-	Glass transition temperature
μ	-	Coefficient of friction

W	-	Specific wear rate
wt. %	-	Weight percent

LIST OF PUBLICATIONS

Chong, M.M,Chang, S.Y., Muhammad, N., Mohd Rosli, Z., and Ahsan, Q, 2014.Effect of Nano- and Micro- Reinforced Agents on Dry Sliding Wear of Polyester Composites.*Sains Malaysiana*43(6), pp. 959-966.

Chong, M.M., Chang, S.Y., Mohd Rosli, Z., and Ahsan, Q, 2012.Effect of Carbon Nanotube Loading on the Tribological Behavior of Carbon Nanotube/Silica Reinforced Polyester Hybrid Composites.Proceeding in *International Conference on Design & Concurrent Engineering* 2012, pp. 442-447.

CHAPTER 1

INTRODUCTION

1.0 Background

Over the past decade, there has been an increasing emphasis on polymer matrix composites in various sectors that require friction and wear properties. The greater potential of employing these polymers based composites are due to their high strength, good wear resistance and self-lubrication properties. These encompass unique feature over other types of composites which can be varied by adding fillers with different weight percentages, shapes and sizes. Lin (2007) found that nano- or micro-sized inorganic fillers can be used to modify the properties of polymeric materials.

From the investigations of Kwon et al. (2008) and Kanchanomai et al. (2011), incorporation of silica particles were popular for applications involved in tribology. SiO_2 has been revealed that it significantly improves the tribological properties owing to its low thermal expansion coefficient which are required at the wear test. Utilization of micro-filler as reinforcing agent of polymer matrix often requires huge wt. % of the matrix, potential intrinsic defect arising therefrom (Renukappa et al., 2011). As a consequence, industries began to envision on the smaller scale fillers, CNTs which is a more suitable candidate in terms of weight, tribological and mechanical properties as documented in the following paragraphs.

Instead of adding micro-fillers, integration of nano-sized inorganic fillers has resolved the limitations of the conventional micro-sized fillers. This is agreed by Hossain et al. (2011) whereby integration of small amount of nano-sized fillers is able to contribute

significant improvement in properties of polymer composite due to its nano-fillers nature as reinforcement in polymer matrix. In comparison with the widely used conventional micro-fillers, nano-fillers especially CNTs possess a high tensile modulus and strength as high as 1 TPa and 200 GPa respectively (Lau and Hui, 2002 cited in Azeredo, 2009). The enhancement in strength implies that, for the same performance, replacing commercial carbon fibers with CNTs may lead to significant reduction in the density and volume of the composite parts. These nano- and micro- sized fillers reinforced polymer hybrid composites are regarded as attractive materials for most of the industries involving in tribological properties.

Literature works (Stachowiak and Batchelor, 2001;Larsen et al., 2008;Renukappa et al., 2011) pointed out that the formation of transfer film during wear lowers the friction and specific wear rate resulted from stabilization by presence of nano-fillers on the counter surface. In other words, it is added advantage in thermosetting polymer which does not form effective transfer films due to the cross linked molecular structure. CNT in combination with their high surface area and high aspect ratio, commonly causes significant agglomeration and prevents transfer of their superior properties to the matrix (Kumar et al., 2009;Ma et al., 2007;Prashantha et al., 2008, Spitalsky et al., 2010and Xie et al., 2005).This limits the CNTs reinforced composites fabricated for high performance structural materials. In order to obtain perfect dispersion of nano-fillers in polymer matrices, several methods have been applied to break down the clusters or agglomerates, including ultrasonic vibration (Lin et al., 2006;Huang et al., 2007), high shear energy dispersion process (Wetzel et al., 2006) and chemical treatments (Guadagno et al., 2011). Among these methods, ultrasonic vibration is the most widely used. In addition, under loading optimum stress transfer from matrix to CNTs may not occur as CNTs are almost of molecular size and may flow with molecular chains of molecule. Therefore, the application

of nano-sized fillers in polymeric matrices only is often not sufficient in regard to the improvement of mechanical strength or specific wear rate.

Hybrid materials are composedof more than one reinforcing fillers in a matrix provide an interesting approach to satisfy the demands by combining the properties of different fillers and even introduce synergisms. Recent studies on the hybridization by incorporating more than one filler are well-documented (Drubetski et al., 2005;Pavia et al., 2010; Sun et al., 2008). Thus, this research is important to establish the fundamental correlation between the structures, processing and final properties of CNTs based hybrid composites.

1.1 Problem statement

In the past, micro-filler, silica (SiO_2) particle was studied by Kwonet al.(2008) and Kanchanomai et al. (2011), low thermal expansion coefficient of silica tends to decrease material wear rate and made it a promising material for tribological product. With the progress of time, there is another key issue in automotive components industry that is lightweight. With addition of nano-fillers, lightweight material can be produced. Among the nano-fillers, CNT has been widely studied on the tribological and mechanical properties (Chen et al., 2007;Men et al., 2008;Montazeri et al., 2010;Nadler et al., 2009). Sun et al. (2008) investigated that wear resistant of nanocomposites has markedly increased as a result of great interactions between the small scale fillers and matrix. Transfer film formed by polymer matrix on countersurface is of paramount importance to add outstanding tribological properties to composite (Stachowiak, 2005). Previous research (Larsen et al., 2008) proved a stabilization of transfer film formed by composites with nano-fillers added. Nevertheless, beyond the critical loading of CNTs, the mechanical properties were deteriorated (Agnihotri et al., 2011). On account of these, the hybrid

approach of blending SiO_2 (micro-fillers) and carbon nanotubes (nano-fillers) can be viable approach for enhancing the tribological properties and mechanical properties.

According to criteria mentioned above, it is necessary to understand the tribological properties in terms of coefficient of friction and specific wear rate under specific condition. With the analysis of the above results, reference could be produced for future analysis in the relevant field. This is of paramount importance to produce analysis on the specific material and sliding condition due to wear is not a material property but system property. Results of the specific wear rate and wear mechanisms deviate with the addition of $SiO_2$and carbon nanotubes into unsaturated polyester resin. Prior to the analysis of tribological properties of the hybrid polyester composites, the interaction between fillers added and matrix material are determined through spectrum recorded using Fourier Transform Infrared Spectroscopy (FTIR). Another influential property on tribological properties in accordance to Archad wear equation. Therefore, microhardness of the material has to be produced. Similar to the maximum service temperature of the hybrid composites produced has to be known before the sliding tests.

The broad production of automotive components has made the fabrication process of component to be essentially economy wise. Hence, vacuum infusion, an efficient and lucrative technique, was adopted to achieve dimensional stability of product. An arduous problem emerges in dispersing CNTs in polyester matrix owing to its high specific surface areas and inert surfaces whereby entanglement of CNTs in matrix can affect the composites properties (Laurent and Peigney, 2004; Ahir and Terentjev, 2007;Liu et al., 2007;Seyhan et al., 2007). Homogeneous dispersion of CNTs can be achieved by chemical functionalization or impose mechanical force like ultrasonication. In an attempt to achieve uniform dispersion of fillers, a carboxylic functionalized multi-walled carbon nanotube (MWCNT-COOH) was chosen and followed by ultrasonication using ultrasonic horn.