

RICE HUSK DERIVED SILICA AEROGEL IN UNSATURATED POLYESTER
COMPOSITES

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DEDICATION

This thesis is dedicated to those who seek knowledge for the sake of knowledge. The author hopes pray for forgiveness, good things in this life and hereafter, if the reader found this thesis useful.

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ABSTRACT

Unsaturated polyester resins (UPR) are the most widely used thermosets for composite applications. Besides fiber materials, solid fillers are also used extensively with UPR as reinforcement to enhance thermal and mechanical properties. Recently, the use of high porosity solid such as silica aerogels (SA) in polymer resins is gaining interest. SA is a unique class of nano-porous material with extremely low bulk density and high specific surface area. The addition of SA in polymer resins had resulted in enhanced composite materials having excellent thermal insulation, heat resistance, flame retardancy and lightweight. However, there are two major problems which hindered the production of SA polymer composites on an industrial scale; Firstly, the high cost of conventional SA which depends on expensive chemicals as precursor and secondly, the problem of adsorption of polymer into the SA nano-pores which results to the loss of product properties. As solutions, two approaches were implemented in this study; first was to reduce the production cost via rice husk ash (RHA) as potential silica source for SA synthesis. Second, to prevent resin insertion into SA nano-pores, a novel coating method of the SA particles with polyvinyl alcohol was proposed to provide an impermeable layer to the structure of the SA. Through these approaches, this study aimed to investigate on how the physical, thermal and mechanical behaviours of the UPR composites are affected by changes in certain characteristics of the SA as the filler such as the porosity, particle sizes, surface coating and hybridization. As benchmarking, the amount of filler in UPR was fixed at 30% of volume fraction. The composites were characterized by various methods such as thermogravimetric analysis, differential scanning calorimetry, scanning electron microscopy, uniaxial tensile and compressive tests, dynamic mechanical analysis, hot-disk thermal analyzer and ASTM D635-14 standard for horizontal burning rate. Evaluation of the SA produced from RHA revealed comparable properties to the conventional SA with density of 0.07 g/cm^3 , surface area up to $600\text{--}700 \text{ m}^2/\text{g}$ and thermal conductivity as low as 0.04 W/mK . The coating of the SA particles of diameters around $2.5 \pm 0.5 \text{ }\mu\text{m}$ using a fluidized bed coating technique had resulted in closed-pores core-shell aerogel (CSA) particles with measured shell thickness of between $10\text{--}50 \text{ }\mu\text{m}$. For UPR composites filled with silica, the composite containing SA as porous filler was at least 23% and 55% lower in density and thermal conductivity than the composite filled with non-porous filler (precipitated silica) respectively. For the same volume fraction of SA, the improvement in composite's thermal insulation and thermal stability were found to be more for larger SA particles. However, increased in particle size also results in decreased of mechanical properties. For the same particle size, the composite with CSA particles showed a 50% higher of compressive strain and 10 to 12% lower for burning rate as compared to the composite with uncoated SA particles. The CSA particles show reinforcing effects on most of the properties studied, except tensile due to weak filler-matrix bonding. Finally, the combination of SA with alumina trihydrate (ATH) in UPR revealed a synergistic effect during thermal degradation as evidenced by higher thermal stability of the SA/ATH composite when compared to the composite containing only ATH.

ABSTRAK

Resin Poliester tak tepu (UPR) adalah termoset yang paling banyak digunakan bagi aplikasi komposit. Selain bahan gentian, pengisi pepejal juga digunakan secara meluas bersama UPR sebagai penguat bagi menambah baik sifat terma dan mekanikal. Kebelakangan ini, penggunaan pepejal berliang tinggi seperti silika aerogel (SA) dalam resin polimer semakin mendapat perhatian. SA adalah bahan nano berliang yang unik dengan ketumpatan rendah dan luas permukaan spesifik yang tinggi. Penambahan SA dalam resin polimer telah menghasilkan komposit diperhebat dengan penebatan haba, rintangan haba, rencatan api dan ringan. Namun, terdapat dua masalah utama yang menghalang penghasilan SA komposit polimer pada skala industri; pertamanya, kos tinggi bagi SA konvensional yang bergantung pada bahan kimia yang mahal sebagai bahan mula dan kedua, masalah penjerapan polimer ke dalam liang nano SA yang menyebabkan kehilangan sifat produk. Sebagai penyelesaian, dua pendekatan telah dilaksanakan dalam kajian ini; pertama adalah mengurangkan kos pengeluaran melalui abu sekam padi (RHA) sebagai sumber silika yang berpotensi untuk sintesis SA. Kedua, bagi menghalang kemasukkan resin ke dalam liang nano SA, satu kaedah salutan novel bagi partikel SA dengan polivinil alkohol telah dicadangkan bagi menyediakan lapisan tak telap kepada struktur SA itu. Melalui pendekatan tersebut, kajian ini bertujuan untuk menyelidik bagaimana kelakuan fizikal, haba dan mekanikal komposit UPR itu terkesan dengan perubahan ciri-ciri tertentu SA sebagai pengisi seperti keliangan, saiz partikel, salutan permukaan dan penghibridan. Sebagai penanda aras, kandungan pengisi di dalam UPR telah ditetapkan pada 30% pecahan isipadu. Komposit telah dicirikan dengan pelbagai teknik seperti analisis gravimetrik haba, imbasan kebezaan kalorimetri, mikroskop imbasan elektron, ujian ketegangan, mampatan, analisis mekanikal dinamik (DMA), analisis haba cakera - panas dan piawaian ASTM D635-14 untuk kadar pembakaran mendatar. Penilaian SA yang terhasil daripada RHA menunjukkan ciri yang setara dengan SA konvensional dengan ketumpatan 0.07 g/cm^3 , luas permukaan sehingga $600\text{-}700 \text{ m}^2/\text{g}$ dan keberaliran haba serendah 0.04 W/mK . Penyalutan partikel SA berdiameter $2.5 \pm 0.5 \text{ mm}$ menggunakan teknik salutan lapisan terbendalir telah menghasilkan partikel aerogel teras-cengkerang (CSA) yang berliang tutup dengan ketebalan cengkerang $10\text{-}50 \text{ }\mu\text{m}$. Untuk komposit UPR yang berisi silika, komposit mengandungi SA sebagai pengisi berliang adalah 23% dan 55% lebih rendah bagi ketumpatan dan keberaliran haba berbanding komposit berisi pengisi tak berliang (silika termendak). Bagi pecahan isipadu SA yang sama, peningkatan penebatan dan kestabilan haba dalam komposit dilihat lebih tinggi bagi partikel SA yang lebih besar. Namun peningkatan saiz partikel juga melemahkan sifat mekanikal. Bagi partikel bersaiz sama, komposit dengan CSA menunjukkan 50% lebih tinggi bagi terikan mampatan dan 10 hingga 12% lebih rendah untuk kadar pembakaran jika dibandingkan dengan komposit berisi partikel SA tak bersalut. Partikel CSA menunjukkan kesan penguatan pada kebanyakan sifat yang dikaji, kecuali ketegangan kerana ikatan lemah di antara pengisi dan matrik. Akhirnya, gabungan SA dengan alumina trihidrat (ATH) dalam UPR menunjukkan kesan sinergi semasa penguraian haba yang dibuktikan oleh kestabilan haba yang lebih tinggi oleh komposit SA/ATH apabila dibandingkan dengan komposit yang hanya mengandungi ATH.

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LIST OF ABBREVIATIONS

APD	-	Ambient pressure drying
ATH	-	Alumina trihydrate
ATR	-	Attenuated total reflectance
BET	-	Brunauer - Emmett, and Teller
CSA	-	Core – shell aerogel
DMA	-	Dynamic mechanical analysis
DSC	-	Differential scanning calorimetry
DTG	-	Differential thermogravimetric
EDX	-	Energy dispersive X-ray
FBC	-	Fluidized bed coating
FTIR	-	Fourier transform infra red
MEM	-	Modified Elshelby Method
PMC	-	Polymer matrix composite
PSD	-	Particle/pore size distribution
RH	-	Rice husk
RHA	-	Rice husk ash
SA	-	Silica aerogel
SCF	-	Supercritical fluid drying
SEM	-	Scanning electron microscopy
TGA	-	Thermogravimetric analysis
TEOS	-	Tetraethyl orthosilicate
TMOS	-	Tetramethyl orthosilicate
TMCS	-	Trimethyl chloro silane
UPR	-	Unsaturated polyester resin
UPSA	-	Unsaturated polyester / silica aerogel composites
XRD	-	X-ray diffraction

LIST OF SYMBOLS

E'	-	Storage modulus
E''	-	Loss modulus
$\tan \delta$	-	Damping factor
ε	-	Strain
ρ	-	Density
$p\text{-SiO}_2$	-	Precipitated silica
S_v	-	Volumetric shrinkage
W_{abs}	-	Water absorption %
T_g	-	Glass transition temperature
k	-	Thermal conductivity
a	-	Thermal diffusivity
C_p	-	Specific heat capacity
\emptyset	-	Particle diameter
η_a	-	Adsorption capacity

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Current market segments of polymer matrix composites (PMC) comprise of approximately 80% thermosetting resins or thermosets (Leon, Kim and Helga, 2017, p. 4). Thermosets are widely used for the production of permanent solid structure and dominated the high-temperature applications. Since 1930's, unsaturated polyester resins (UPR) have been intensively used in various sectors covering oil and gas industries, construction, transportation and consumer products owing to its low cost, ease of processing, chemical resistance and strong mechanical properties (Strong, 2008, p. 89). More recently, the development of reinforced UPR composites are gradually replacing steel and concrete in some segments of building and construction industry (Bagherpour, 2012, p. 158; Jabbar and Farid, 2018, p. 216). Due to its low density, a significant reduction in logistic cost can be achieved by using UPR composite materials. Besides, UPR is easier to be molded into intricate design as compared to cast steel, thus considerably reduced the labor cost and fabrication time. UPR market also has increased demands in transportation end-use industry on account of long service life and low maintenance (Gowda, Sanjay and Bhat, 2018, p. 5). Concurrently with this, the needs on improving the performance of UPR have become important in order to meet the requirements of current and future applications.

In general, there are two common approaches to improve the functional properties of polymer matrices. One is intrinsic modification by introducing new reactive species (i.e. monomers) into the polymer chain of the existing resin via co-polymerization process; the other way is additive type modification, which is by physically introduce non-reactive additives or fillers in the polymer resin (Zhang, Huang and Liu, 2011, p. 1768; Lin, Yu and Jin, 2016, p. 633). It is thought that the

former technique is more effective in enhancing the resin properties with little detrimental effects on the native properties of the resin. However, this technique showed major drawbacks such as high processing cost and a relatively complicated process. As an alternative, the use of particulate fillers to modify resin properties is often considered as cost-effective due to a variety of low-cost fillers available in the market with high processability. Thus, this area is one of considerable research activity by both industry and academia at the present time.

Regulations on the use of UPR in building and transportation requires deep consideration on human factors, therefore some features such as thermal comfort and fire safety are vital aspects in design (Troitzsc, 2013, p. 2). Currently, conventional UPR based composites often involves high amount of fillers such as sawmill, fumed silica and hollow glass micro balloons to improve thermal insulation, while halogenated compounds and hydrates are the most common material for flame retardancy (Schiavoni, Alessandro, Bianchi and Asdrubali, 2016, p. 990). Moreover, there were also fascinating research works on recycling biomass such as natural fibers as functional fillers in composite materials (Khan, Hameed and Ariffin, 2018, p. 770). Improving the composite performance as well as cost reduction is often thought as values added of using filler. However, cost reduction is not necessarily the case. Although most of the conventional fillers available are cheaper by weight than the resin, PMC fabrication (e.g. molding), however, is more concerned on filler-matrix volume fraction rather than weight (Rothon, 2003, p. 22). Thus, the use of higher density fillers means that volume costs are not reduced by as great an extent.

An effective method in reducing the specific density of a composite material is by the formation of structural pores during composite's fabrication or post-processing. To obtain porosity, the simplest method is by incorporating porous fillers in the polymer matrix itself. Two common characteristics sought after include; lighter weight and control of heat conduction. In this regard, highly porous materials such as silica aerogels (SA) have received an increasing interest in the last decades as filler in polymer composite. Unlike ordinary silica, SA is a special porous material with 3-dimensional mesoporous structure exhibiting many novel properties such as high surface area, ultra low density, excellent thermal insulation and high thermal

stability (Soleimani and Abbasi, 2008, p.10). SA is chemically inert and amorphous in nature. It can also be modified into hydrophobic for great dispersion in non-polar resin. Taking into account its unique properties, this study proposes the use of SA as potential filler for UPR with the aim of lightweight-composite materials for high-temperature applications.

1.2 Problems statements

In recent years, there has been growing interest in using SA as filler or reinforcement in polymer resins covering both thermosets and thermoplastics. The SA – polymer composites were characterized by good compressive strength, durability and the most important advantages – lightweight and improved thermal insulation (Salimian, Zadhoush and Naeimirad, 2017, p. 3385). Despite their potential for various applications, the development of the composites however is still far from commercialization due to the expensive cost of SA. Production of conventional SA involves expensive chemicals and energy intensive supercritical drying process. The SA available in the market are derived from silicon alkoxides such as Tetra-ethyl-ortho-silicate (TEOS) and Tetra-methyl-ortho-silicate (TMOS).

Apart from that, there is also a major problem of mixing the SA with liquid resins as intensive immersion of the resin into the porous structure will results in the loss desirable properties. Some studies have demonstrated a direct relationship between preservation of SA pores in the composite and thermal insulation of composites (Chang, Wang and Peng, 2014, p. 8; Kim, Noh and Yu, 2015, p. 40; Liu, Kim and Kwon, 2016, p.1705). To date, a number of methods have been proposed as solutions to prevent the intensive resin intrusion into the SA pores. These methods involve different techniques of polymer-filler mixing and curing but so far, no available study focus on the modification of the SA itself.

Formerly, SA was added in various thermosetting polymers in an attempt to raise the service temperature and insulation performance (Dourbash, Buratti and Belloni, 2017, p. 521; Maghsoudi and Motahari, 2018, p. 706; Guzel, Yilmaz,

Deveci, 2018, p. 2; Wang and Jin, 2018, p. 36; Mohamed, Mustaffa and Norizan, 2018, p. 18). However, the use of SA in UPR was only reported by a single group of authors (Mohamed et al, 2013, p. 600; Mohamed et al, 2018, p. 18). Besides, their studies were also limited on thermal stability and flammability of the composites.

In this thesis, economically viable form of SA for composite applications was produced using rice husk. Rice husk is rich silica and its ash can contains more than 85% of active silica by weight. As rice producing country, Malaysia generates more than half millions of tons of rice husks annually, thus can ensure a consistency in raw material. The novelty of this study lies on the approach designed to prevent intensive resin intrusion into the SA structure. Here, the produced SA particles were further coated with polymer into core-shell structure by using fluidized bed coating process. Based on the research gap identified from literatures, this research focuses on investigating the effects of SA on the properties of UPR.

1.3 Research objective and goals

The main objective of this thesis is to prepare and to characterize UPR composite materials using rice husk derived SA as fillers. Therefore this objective will be based on the following strategic goals:

1. To prepare SA particles from rice husk via sol-gel, surface modification and drying process and to characterize the SA particles for comparison with commercial SA.
2. To coat the SA particles with polymer solution into core-shell structured particles by using a bottom spray - fluidized bed coating process.
3. To investigate the effects of SA as fillers with different characteristics such as porosity, particle size, surface coating and hybridization on physical, chemical, mechanical, thermal and flammability properties of the UPR composites.

1.4 Research questions

Pertaining to the strategic goals, the following are the relevant research questions which need to be answered:

1. What are the advantages and disadvantages of rice husk derived SA over chemical derived (commercial) SA? Are their characteristics comparable?
2. What are the added values of modified SA over unmodified/plain SA? Is the proposed coating process feasible?
3. What are the reinforcement and deterioration effects of SA as filler materials on the properties of UPR composites?

1.5 Scope of study

The method of producing sodium silicate solution was based on a patented method (US 7,897,648 B2, Halimatun, 2011). Hydrophilic and hydrophobic SA having particles sizes of not larger than 3.0 μm were produced via supercritical and ambient drying method. Experimental variable in sol-gel process was limited to sol's pH. For a comparison, a high-grade TEOS based SA, was purchased from Cabot Aerogel, United States. Coating of the hydrophobic SA particles was carried out using a lab scale fluidized bed coating machine owned by Universiti Teknikal Melaka. Commercially available, ready to use polyvinyl alcohol (PVA) was used as the coating material and the parameters for coating process were based on optimized process. For polymer matrix, an industrial grade orthophthalic type of UPR was used. Experimental variables for composite blends are limited to the characteristics of the filler, such as porosity, particle size, surface coating and hybridization with filler volume fraction of 30%. As for material characterization, the properties studied are limited to density, morphology, chemical properties, tensile and compressive behaviour, dynamic mechanical properties, thermal degradation and thermal conductivity, curing shrinkage, water absorption and flammability.

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