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Date of birth : 1st MAY 1988

Title : TENSILE AND THERMAL PROPERTIES OF ELATERIOSPERMUM TAPOS SEED SHELL FILLED RECYCLED POLYPROPYLENE ECO-COMPOSITES

Academic Session : 2013/2014

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TENSILE AND THERMAL PROPERTIES OF ELATERIOSPERMUM TAPOS SEED SHELL FILLED RECYCLED POLYPROPYLENE ECO-COMPOSITES

by

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A thesis submitted in fulfilment of the requirements for the degree of

Master of Science in Materials Engineering

School of Materials Engineering
UNIVERSITI MALAYSIA PERLIS

Year

2015

ACKNOWLEDGEMENT

In the name of God, most Gracious, most Compassionate.

May the Peace, Mercy and Blessing of Allah be upon you.

Alhamdulillah, all praises to the all mighty Allah for blessing me with love, guidance, healthiness and strength in completing this task. There's no God that worthy of worship except you, ALLAH.

First of all, thank you very much to my awesome supervisor, Assoc Prof Ir Dr Salmah Husseinsyah for her hard work and patience in guiding me to complete the thesis for my master programme. Thank you to my kind co-supervisor, Assoc Prof Dr Hakimah Osman.

To my beloved parents, Nor Aisah binti Abd Ghaffar and Lotfi bin Mohamad, thank you so much for the consistence love, moral and financial supports during the progress of my studies. To all my lovely sisters, Nurul Liyana, Nurul Hanisah and Nurul 'Ain, thank you for your calls and patience. Thank you for having me as your brother.

To all my friends out there, Fuadi, Syahmie, Amri, Seong, Phua, Meor, Wan Zakaria, Izuddeen, Abduh, Khalis, Shahrir, Zuki, muslims or non-muslims, Malaysians, lecturers, ikhwah, housemates, usrah-mates, juniors, technicians, postgraduates students of University Malaysia Perlis. Last but not least, thanks to all the staffs from University Malaysia Perlis especially those from School of Materials Engineering.

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LIST OF ABBREVATIONS

ETSS	*Elateriospremum Tapos* Seed Shell
MA	Maleic Acid
PDMS	Polydimethysiloxane
OSL	Organosolv Lignin
rPP	Recycled Polypropylene
FTIR	Fourier Transform Infrared
ASTM	American Society For Testing And Materials
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
SEM	Scanning Electron Microscope
PKS	Palm Kernel Shell
LDPE	Low Density Polyethylene
DTG	Derivative Thermogravimetric Analysis
PP	Polypropylene
PLA	Polylactic acid
LDPE	Low density polyethylene
php	Part per hundred polymer
MFI	Melt Flow Index

LIST OF NOMENCLATURES

C	Carbon
C=O	Carbonyl
H_2SO_4	Sulphuric Acid
C=C	Ethylene (IUPAC name: Ethene)
C-O-C	Ether
Si	Silicone
OH	Hydroxyl
CH_2	Methylene
CH_3	Methyl Group

LIST OF SYMBOLS

°C	Degree Celsius
ΔH^o_f	Heat of Fusion for 100% Crystalline PP
ΔH_f	Heat of Fusion for PP
%	Percentage
μm	Micrometer
cm^{-1}	Reciprocal Wavelength (wavenumber)
cm^3	Centimetre cubic
% v/v	Volume / Volume Percentage
% w/v	Weight / Volume Percentage
X_c	Degree of Crystallinity
Wv	the loss of ignition
Wr	the residue of ignition
Ma	the mass of empty crucible
Mb	the mass of crucible containing the mass of ETSS
Mc	the mass of crucible containing the ignited mass of ETSS

Sifat-sifat Tegangan dan Terma Eko-komposit Polietilena Kitar Semula Terisi Kulit Biji *Elateriospermum Tapos*

ABSTRAK

Kesankulit biji *elateriospermum tapos* (KBET) dan modifikasi kimia terhadap sifat-sifattegangan, morfologi dan terma eko-komposit polietilena kitar semula (PKS) telah dikaji. Eko-komposit PKS/KBET disedia menggunakan Brabender EC-PLUS pada suhu 180 °C dengan kelajuan rotor 50 rpm. Tiga jenis modifikasi bahan kimia telah digunakan iaitu; asid maleik (AM), polidimetilsiloksan (PDMS) dan lignin organosolv (LOS). Didapati bahawa penambahan KBET ke dalam eko-komposit PKS telah mengurangkan kekuatan tegangan, pemanjangan pada takat putus dan darjah penghabluran (X_c). Modulus elastisiti dan kestabilan terma dalam eko-komposit telah meningkat dengan peningkatan kandungan PKS di dalam eko-komposit tetapi takat putus pemanjangan menunjukkan penurunan yang ketara. Kajian morfologi terhadap eko-komposit telah menunjukkan interaksi yang lemah diantara pengisi KBET dan matrik PKS. Modifikasi kimia terhadap KBET telah meningkatkan sifat-sifat tegangan dan terma dalam eko-komposit. Kekuatan tegangan dan elastisiti modulus eko-komposit PKS/KBET yang dimodifikasi dengan AM, PDMS dan LOS adalah lebih tinggi daripada eko-komposit yang tidak dimodifikasi. Darjah penghabluran dan kestabilan terma dalam eko-komposit yang telah di modifikasi adalah lebih tinggi berbanding eko-komposit yang belum dimodifikasi. Interaksi antaramuka diantara KBET dan PKS dalam eko-komposit yang telah dimodifikasi, adalah lebih baik telah dibuktikan melalui kajian Mikroskop Electron Pengimbasan (MEP). Analisa FTIR spektra membuktikan terdapat perubahan kepada kumpulan berfungsi di dalam KBET yang dimodifikasi. Eko-komposit yang dimodifikasi dengan AM menunjukkan kekuatan tegangan dan kestabilan terma yang paling tinggi dibandingkan dengan eko-komposit modifikasi yang lain. Walaubagaimanapun, eko-komposit yang dimodifikasikan dengan PDMS menunjukkan elastisiti modulus dan darjah penghabluran yang paling tinggi, diikuti modifikasi dengan LOS dan AM.

Tensile and Thermal Properties of *Elateriospermum Tapos* Seed Shells Filled Recycled Polypropylene Eco-Composites

ABSTRACT

The effects of *elateriospermum tapos* seed shell (ETSS) and its chemical modification on tensile properties, morphology and thermal properties of recycled polypropylene (rPP) eco-composites were investigated. The rPP/ETSS eco-composites were prepared using Brabender EC-PLUS at 180°C temperature and rotor speed 50 rpm. Three types of chemical modification were used; maleic acid (MA), polydimethylsiloxane (PDMS) and organosolv lignin (OSL). It was found that the addition of ETSS in rPP eco-composites have decreased the tensile strength, elongation at break and degree of crystallinity of the eco-composites. The modulus of elasticity and thermal stability of eco-composites increased with increasing of ETSS content but the elongation at break was significantly dropped. Morphology study of eco-composites showed the poor interaction between ETSS filler and rPP matrix. The chemical modification of ETSS has increased the tensile and thermal properties of eco-composites. The tensile strength and modulus of elasticity of rPP/ETSS eco-composites with MA, PDMS and OSL were higher than unmodified eco-composites. The degree of crystallinity and thermal stability of modified eco-composites was also higher than unmodified eco-composites. The better interfacial interaction between modified ETSS and rPP has been proven by scanning electron microscope (SEM) studied. Spectra FTIR analysis has proven the changes of functional group of modified ETSS. The modified eco-composites with MA showed the highest tensile strength and thermal stability compared to the other modified eco-composites. However, the modified eco-composites with PDMS indicated highest modulus of elasticity and degree of crystallinity followed by modification with OSL and MA eco-composites.

CHAPTER 1

INTRODUCTION

1.1 Research background

For the last couples of decades until present, the researchers have growth interest upon the making of the green or environmental friendly materials composites due to the increasing demands on it (Mohanty et al., 2000; Joshi et al., 2004; Lau et al., 2009). On the other hand, it were also popularly known as the bio-composites, eco-composites, natural fibre composites, biodegradables composites and many more depending on the specific material combined to produce the composites and the specific performance of it (John et al., 2007). However, all of this shows the efforts of the researchers towards the making of the more environmental friendly materials.

Eco-composites were known for materials that made out of the natural based fillers where from plant or nature that combined with the polymeric materials (Bogoeva-Gaceva et al. 2007; Sarki et al., 2011; Kim et al., 2013). The applications of these materials widen into several industries from packaging, automotive, marine, interior construction to the aerospace (Mallick et al., 1993; Suppakarn et al., 2009; Bourmaud et al., 2013). Instead of being biodegradables, renewable and cheap (Monteiro et al., 2009), another important advantages that push this sector further was because of it releasing non-toxic gases during combustion plus reuse the agro waste like plant waste (Yang et al., 2004). On the other hand, eco-composits also includes low density, high toughness, comparable specific strength properties, reduction in tool wear, low energy consumption in fabrication, and carbon dioxide (CO_2) neutrality (Mohanty et al., 2000).

Recently, there were a lots of studies made by the researchers involved PP filled plant based filler such as, PP with hemp fibres (Pracella et al., 2006; Beckermann et al., 2008; Etaati et al., 2014), kenaf (Feng et al., 2001; Hao et al., 2014), wood (Kazayawoko et al., 1999; Zhang et al., 2012), pineapple leaf fibres (Arib et al., 2006; Biswal et al., 2009), flax (Zafeiropoulos et al., 2002), jute (Ranganathan et al., 2015; Gassan et al. 2000; Doan et al., 2007), coconut shell (Sarki et al., 2011; Chun et al., 2013), chitosan (Salmah et al., 2011; Salmah et al., 2012), pine fibre (Gironès et al., 2007) and palm kernel shell (Salmah et al., 2013). All of these natural based materials strongly related with the lignocelluloses because it was a major part in most of the natural based material. Thus, and it played a huge role on the performance of the eco-composites when it was used as a filler in the polymer matrix (Nishino et al., 2004).

ElateriospermumTapos or in Southeast Asian popularly known as perah or pogoh nut (Malaysia), kedui or tapos (Indonesia) and look-kra or look-pra (Thailand). The plant is one of the Malaysian canopy species tree in the tropical rainforest (Osada et al., 2003). Researchers reported it can be found in Peninsular Malaysia (MohdHasmadi et al., 2008; Osada et al., 2003), Brunei (Chumkiew et al., 2007), Peninsular Thailand (Ngamriabsakul&Kommen, 2011) and the land of Java (Sosef et al., 1998). The tree is about 80-140 ft high with the red colour of young leaves. The perah fruit are about 2-2.5 inch long, buff colour hanging on the singly on stalk and the seeds are about 1.75 inch long in shining brown shell (Yong et al., 2006) like the rubber seed in oblong size. The study has been reported the usage of the seed oils *elateriospermumtapos* (Yong et al., 2006; Ling et al., 2006; Choonhahirun, 2013).

Polypropylene (PP) has been one of the most important commodity polymers which widely used in the packaging, textile and automobile industries because of its good processibility and great recyclability (Zebarjad et al., 2004). It also commonly used as a polymer matrix in the making of eco-composites (Bismarck et al., 2001; Zafeiropoulos et al., 2002; Doan et al., 2007; Beckermann et al., 2008; Amar et al., 2011). However, it also has been one of the plastics that became a huge part in the plastics waste stream as reported by Hernández-Sánchez et al., 2001. This polymer material has worldly known as a non-degradable material which cannot be dump away in land filled. Thus recycling has become one of the ways to avoid the abundances of this material on the land filled area for a very long period of time. The interests upon the usage of the recycled material growth, for an example recycled polypropylene which favour in the making of the automotive products. However the drawback factors in using these recycled materials was the source of the material. The collected recycled materials normally were the combination of many types of product grades which leads to the material impurities. This problem will leads to the inconsistencies of the product properties (Gupta et al., 2012). Several methods have been studied to counter this issue (Żenkiewicz& Kurcok, 2008), but also does not totally solving the main problem.

Therefore, the researchers still forced to make a studies solve this problem. Thus there were a few ways have been inspired and applied to counter the abundance of these non-biodegradable polymeric materials in our environment, such as the mechanical crushing, pyrolysis and incineration. However, every method that has been implemented has its pros and cons. Even though it reduced the amount of plastic waste in the environment, but the cost of the production was high. This is because the plastic waste taken from the nature required sorting and bleaching process which increased of the selling cost of the products. This has made the recycled materials hard to compete with the price of the normal plastic materials (Marco et al., 2002).

The global production of plastic waste has become very well-known. Instead just for the sake of environment, all of these recycled industries were able to survive due to the demands from the industries of automotive packaging and electrical. Many studies have been made involving the recycled plastic products (Hernández-Sánchez et al., 2001; Chun et al., 2013). Javierre et al., (2007) reported that PP has become one of the highest polymer recycled among the others recyclables polymer.

On the other scope of studies, researchers have also focused on the making of the natural based composites materials as mention before. However, the plant based filler material could exhibit high moisture absorption due to the hydrophilicity of it. The characteristic of the plant based filler has leads to the compatibility problems between the natural filler and hydrophobic polymer matrix. Both of it has different polarity, thus the combined materials may lead to the reduction of the composites performances because the filler has weak adhesion to the polymer matrices (Sgriccia et al., 2008). Many reported that, the interaction between these two major parts played a very significant role on determining the final properties of the eco-composites. All of this will determine the stress transfer ability of the composites which will leads to the mechanical performances of the eco-composites (Jarukumjorn&Suppakarn, 2009); Ares et al., 2010).

There were many ways has been studies to counter the incompatibility issues. Many researchers have done various methods to solved this problems such as using chemical treatment (Kazayawoko et al., 1999; Ghali et al. 2009; Cao et al., 2006; Alix et al. 2009; Kalia et al., 2013; Nam et al., 2011; De Rosa et al., 2011), surface modification (George et al., 2001; Sreekala et al., 2003; Corrales et al., 2007; Vilay et al., 2008; John et al., 2008; Sreekumar et al., 2009). The surface modification can modify the filler surface and improving the compatibility between the polymer and the filler (George et al., 2001; Sreekala et al., 2003; Demir et al., 2006; Corrales et al., 2007; Vilay et al., 2008; John et al., 2008; Sreekumar et al., 2009).

The used of coupling agent (Demir et al., 2006). The team reported that the usage coupling agent upon the luffafiber filled polypropylene composites enhanced the mechanical properties of the composites by improving the adhesion between organic filler and PP. This was happening due to the existence of the new covalent and hydrogen bond when the process was done. Most of the studies using the coupling agent were reporting the same factor (Pickering et al., 2003;Gironès et al., 2007; Gironès et al., 2008; Li et al., 2007; Xie et al., 2010; Franco-Marquèsa et al., 2011). Franco-Marquès, et al., 2011 reported that the tensile and flexural properties of the PP reinforced recycled fiber increased after the usage of the maleated polypropylene (MAH-PP) as a coupling agent. The presence of coupling agent has improved the chemical mechanism between the MAH-PP and the fibers which involved the enstablishment of the ester bonds between –OH groups between MAH-PP and fibers.

1.2 Problem Statement

The increasing numbers of the consumers' needs upon the environmental friendly materials was due to the raising of the non-degradable plastic waste on the water streams and as well as the landfill. It shows that the awareness upon the post-consumer plastics waste has become the main focus in the environmental pollution issues. The major polymeric materials of these plastic found in waste streams were the polyethylene (PE), polypropylene (PP), polyvinyl chlorides (PVC) and polyethylene terephtalate (PET). The issues have pushed the researchers to take the responsible upon the making of the materials that could decompose naturally in the environment condition. Reproducing the materials out of the recycled plastic could also be the alternative to counter these issues. The recycled polypropylene has been used in this study because the waste of it has become one of the highest plastic waste products.

The addition of the inorganic filler such as glass fibre or carbon in the polymer composite can cause harm and hazardous to the human by polluting the environment due to the non-degradable characteristic that it possessed. Furthermore, it also released the toxic gases after combustion. One of the purposes of selecting the *elateriospermumtapos*seed shell (ETSS) as new organic filler is to replace the traditional synthetic filler reinforcement. It is an agro-waste made by the industries. The mechanical performance of the organic fillers was possible to achieve equally the same as synthetic filler plus it also biodegradable and cost saving. The usage of the waste by product of the agriculture also will increase the value of the plant waste.

The previous study reported about the using of natural filler in thermoplastic composite, but the utilization of ETSS in thermoplastic not yet reported. The main problem about the eco-composites was the incompatibility between the hydrophobic recycled polypropylene and the hydrophilic ETSS. In this study, compatibility issues between the matrix and filler interactions have becomes a huge impact. Thus to improve the adhesion between both materials, the chemical modifications were used. The modification will enhance the mechanical performance of the rPP/ETSS eco-composites.