COMPATIBILITY AND DEGRADABILITY OF KENAF-FILLED LINEAR LOW DENSITY POLYETHYLENE/POLYVINYL ALCOHOL COMPOSITES

PANG AI LING

UNIVERSITI SAINS MALAYSIA

2018

COMPATIBILITY AND DEGRADABILITY OF KENAF-FILLED LINEAR LOW DENSITY POLYETHYLENE/POLYVINYL ALCOHOL COMPOSITES

by

PANG AI LING

Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

August 2018

ACKNOWLEDGEMENT

First and foremost, I would like to express my greatest appreciation to my supervisor, Prof. Dr. Hj. Hanafi Ismail for his valuable guidance, support and consistent encouragement during my study in USM. It is a great opportunity to complete my doctoral programme under his supervision. I would also like to express my gratitude to my co-supervisor, Prof. Madya. Dr. Azhar Abu Bakar, who always support and spending his precious time to teach and help me during my research study.

Most of the results presented in this thesis would not have been accomplished without a close collaboration with few laboratories. Hence, I would like to take this opportunity to thank the technical staffs from laboratories namely, Mr. Shahril, Mr. Suharudin, Mr. Mohamad Hassan, Mr. Rashid, Mr. Khairi, Mr. Faisal, Mr. Shahrizol, and Mr. Azrul. My humble regards to other whose names are not mentioned here for their kind assistance. Furthermore, I wish to thank Dean of the School of Materials and Mineral Resources Engineering (SMMRE), and all administrative as well as technical staffs of SMMRE, who has been kind enough to advise and help me in completing my study.

I am also thankful to my friends especially Dr. Mohsen Ahmadipour, Dr. Norshahida, Dr. Mathialagan, Dr. Sam Sung Ting, Dr. Ooi, Dr. Rohani, Dr. Dalina, Amin Lotfi, Ahmad Fikri, Nurulaizan, Nur Fasihah, for their personal and scholarly interaction. Nice knowing all of you and thanks. Last but not least, my special thanks to my parents and families for their endless care, love and supports.

TABLE OF CONTENTS

Page

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: MATERIALS AND METHODOLOGY

CHAPTER FOUR: RESULTS AND DISCUSSION

LIST OF PUBLICATIONS

LIST OF TABLES

- Table 4.7 TGA parameters of LLDPE/PVOH/KNF composites with untreated and EFCA-treated KNF at 10 and 40 phr KNF loadings 117
- Table 4.8 TG-DTG parameters of LLDPE/PVOH.KNF composites with untreated and $Cr_2(SO_4)_3$ -treated KNF at 10 and 40 phr loadings 131
- Table 4.9 TGA parameters of LLDPE/PVOH/KNF composites with untreated and lysine-treated KNF at 10 and 40 phr KNF loadings 146

LIST OF FIGURES

Page

different KNF loadings

loadings after subjected to natural weathering for 3 and 6 months

- Figure 4.20 Tensile strength of LLDPE/PVOH/KNF composites at different KNF loadings, before and after subjected to soil burial test for 3 and 6 months 75
- Figure 4.21 Tensile modulus of LLDPE/PVOH/KNF composites with different KNF loadings, before and after subjected to soil burial test for 3 and 6 months 76
- Figure 4.22 Elongation at break of LLDPE/PVOH/KNF composites with different KNF loadings after subjected to soil burial test for 3 and 6 months 78
- Figure 4.23 FTIR spectra of LLDPE/PVOH/KNF composites (at 40 phr KNF) before, after 3 and 6 months of soil burial exposure 80
- Figure 4.24 SEM micrographs of LLDPE/PVOH/KNF composites with (a) 0 81
- $(a)-(f)$ phr KNF (b) 10 phr KNF (c) 40 phr KNF after 3 months of soil burial exposure and (d) 0 phr KNF (e) 10 phr KNF (f) 40 phr KNF after 6 months of soil burial exposure at magnification of 1000X
- Figure 4.25 DSC thermograms (melting) of LLDPE/PVOH/KNF composites (at 40 phr KNF) before, after 3 and 6 months of soil burial exposure 83
- Figure 4.26 DSC thermograms (cooling) of LLDPE/PVOH/KNF composites (at 40 phr KNF) before, after 3 and 6 months of soil burial exposure 84
- Figure 4.27 Weight loss of LLDPE/PVOH/KNF composites with different KNF loadings after subjected to soil burial for 3 and 6 months 86
- Figure 4.28 Comparison of processing torque of LLDPE/PVOH/KNF composites with untreated and TMS-treated KNF at 10 and 40 phr KNF loading, respectively 87

xiv

- Figure 4.42 Equilibrium water absorption of LLDPE/PVOH/KNF composites With untreated and TMS-treated KNF at 10 and 40 phr KNF loadings 103
- Figure 4.43 Processing torque of LLDPE/PVOH/KNF composites with untreated and EFCA-treated KNF at 10 and 40 phr KNF loadings 104
- Figure 4.44 Stabilization torque of LLDPE/PVOH/KNF composites with untreated and EFCA-treated KNF at 10 and 40 phr KNF loadings 105
- Figure 4.45 Tensile strength of LLDPE/PVOH/KNF composites with untreated and EFCA-treated KNF at different KNF loadings 107
- Figure 4.46 Proposed possible mechanism during pre-treatment of KNF with EFCA 108
- Figure 4.47 Proposed possible mechanism between EFCA-treated KNF, PVOH and LLDPE 108
- Figure 4.48 Tensile modulus of LLDPE/PVOH/KNF composites with untreated and EFCA-treated KNF at different KNF loadings 109
- Figure 4.49 Elongation at break of LLDPE/PVOH/KNF composites with untreated and EFCA-treated KNF at different KNF loadings 111
- Figure 4.50 $(a)-(b)$ FTIR spectra of LLDPE/PVOH/KNF composites with (a) 40 phr untreated and (b) 40 phr EFCA-treated KNF 112
- Figure 4.51 SEM micrographs of fractured surfaces of LLDPE/PVOH/KNF 114
- $(a)-(f)$ composites with (a) 10 phr untreated KNF (b) 10 phr EFCA-treated KNF (c) 20 phr untreated KNF and (d) 20 phr EFCA-treated KNF (e) 40 phr untreated KNF and (f) 40 phr EFCA-treated KNF at magnification of 200x
- Figure 4.52 TG thermograms of LLDPE/PVOH/KNF composites with untreated and EFCA-treated KNF at 10 and 40 phr KNF loadings 115
- Figure 4.53 DTG thermograms of LLDPE/PVOH/KNF composites with 116

untreated and EFCA-treated KNF at 10 and 40 phr KNF loadings

- Figure 4.54 Water absorption of LLDPE/PVOH/KNF composites with untreated and EFCA-treated KNF at 10 and 40 phr KNF loadings 118
- Figure 4.55 Equilibrium water absorption of LLDPE/PVOH/KNF composites with untreated and EFCA-treated KNF at 10 and 40 phr KNF loadings 119
- Figure 4.56 Processing torque of LLDPE/PVOH/KNF composites with untreated and $Cr_2(SO_4)$ ₃-treated KNF at 10 and 40 phr KNF loadings 120
- Figure 4.57 Comparison of stabilization torque of LLDPE/PVOH/KNF composites with untreated and $Cr_2(SO_4)$ ₃-treated KNF at 10 and 40 phr KNF loadings 121
- Figure 4.58 Tensile strength of LLDPE/PVOH/KNF composites with untreated and $Cr_2(SO_4)$ ₃-treated KNF at different KNF loadings 122
- Figure 4.59 Proposed possible reactions that occurred during $Cr_2(SO_4)_3$ Treatment of KNF 123
- Figure 4.60 Tensile modulus of LLDPE/PVOH/KNF composites with untreated and $Cr_2(SO_4)_3$ -treated KNF at different KNF loadings 124
- Figure 4.61 Elongation at break of LLDPE/PVOH/KNF composites with untreated and $Cr_2(SO_4)_3$ -treated KNF at different KNF loadings 126
- Figure 4.62 FTIR spectra of LLDPE/PVOH/KNF composites with (a) 40 phr 127
- $(a)-(b)$ untreated and (b) 40 phr $Cr_2(SO_4)$ ₃-treated KNF
- Figure 4.63 SEM micrographs of fractured surfaces of LLDPE/PVOH/KNF 129
- $(a)-(f)$ composites with (a) 10 phr untreated KNF (b) 10 phr $Cr_2(SO_4)_{3-}$ treated KNF (c) 20 phr untreated KNF (d) 20 phr $Cr_2(SO_4)$ ₃-treated KNF (e) 40 phr untreated KNF and (f) 40 phr $Cr_2(SO_4)$ ₃-treated KNF at magnification of 200x
- Figure 4.64 TG thermograms of LLDPE/PVOHKNF composites with untreated and $Cr_2(SO_4)$ ₃-treated KNF at 10 and 40 phr KNF loadings 130
- Figure 4.65 DTG thermograms of LLDPE/PVOH/KNF composites with untreated and $Cr_2(SO_4)_3$ -treated KNF at 10 and 40 phr KNF loadings 131
- Figure 4.66 Water absorption of LLDPE/PVOH/KNF composites with untreated and $Cr_2(SO_4)_3$ -treated KNF at 10 and 40 phr KNF loadings 132
- Figure 4.67 Equilibrium water absorption of LLDPE/PVOH/KNF composites with untreated and $Cr_2(SO_4)_3$ -treated KNF at 10 and 40 phr KNF loadings 133
- Figure 4.68 Processing torques of LLDPE/PVOH/KNF composites with untreated and lysine-treated KNF at 10 and 40 phr KNF loadings 134
- Figure 4.69 Stabilization torques of LLDPE/PVOH/KNF composites with untreated and lysine-treated KNF at 10 and 40 phr KNF loadings 135
- Figure 4.70 Tensile strength of LLDPE/PVOH/KNF composites with untreated and lysine-treated KNF at different KNF loadings 137
- Figure 4.71 Proposed possible reaction between KNF and lysine 138
- Figure 4.72 Proposed possible reaction between lysine-treated KNF and LLDPE/PVOH matrices 138
- Figure 4.73 Tensile modulus of LLDPE/PVOH/KNF composites with untreated and lysine-treated KNF at different KNF loadings 139
- Figure 4.74 Elongation at break of LLDPE/PVOH/KNF composites with untreated and lysine-treated KNF at different KNF loadings 140
- Figure 4.75 FTIR spectra of LLDPE/PVOH/KNF composites with (a) 40 phr 141

untreated and (b) 40 phr lysine-treated KNF

 $(a)-(b)$

Figure 4.76 SEM micrographs of fractured surfaces of LLDPE/PVOH/KNF 143

- (a)-(f) composites with (a) 10 phr untreated KNF (b) 10 phr lysine-treated KNF (c) 20 phr untreated KNF (d) 20 phr lysine-treated KNF (e) 40 phr untreated KNF and (f) 40 phr lysine treated KNF at magnification of 200x
- Figure 4.77 TG thermograms of LLDPE/PVOH/KNF composites with untreated and lysine-treated KNF at 10 and 40 phr KNF loadings 145
- Figure 4.78 DTG thermograms of LLDPE/PVOH/KNF composites with untreated and lysine-treated KNF at 10 and 40 phr KNF loadings 146
- Figure 4.79 Water absorption of LLDPE/PVOH/KNF composites with untreated and lysine-treated KNF at 10 and 40 phr KNF loadings 147
- Figure 4.80 Equilibrium water absorption of LLDPE/PVOH/KNF composites with untreated and lysine-treated KNF at 10 and 40 phr KNF loadings 148

LIST OF ABBREVIATIONS

AFTA ASEAN Free Trade Area APTES 3-aminopropyltriethoxysilane ASTM American Society for Testing and Materials COCA Coconut oil coupling agent DSC Differential Scanning Calorimetry DTG Derivative thermogravimetric EFCA Eco-friendly coupling agent EVA Ethylene vinyl acetate FESEM field emission scanning electron microscope FTIR Fourier transform infrared HDPE High density polyethylene **KCF** KNF Kenaf core fiber Kenaf bast fiber KF Kenaf fiber KP Kenaf powder LDPE Low density polyethylene LLDPE Linear low density polyethylene MAPE Maleated polyethylene NaHCO₃ Sodium hydrogen carbonate NaOH Sodium hydroxide NKTB National Kenaf and Tobacco Board NR Natural rubber PA Phthalic anhydride PALF Pineapple leaf fiber PE Polyethylene

LIST OF SYMBOLS

KESERASIAN DAN KEBOLEHDEGRADASI KOMPOSIT POLIETILENA BERKETUMPATAN RENDAH LINEAR/POLIVINIL ALKOHOL TERISI KENAF

ABSTRAK

Penyelidikan berkaitan komposit polimer gentian semula jadi sedang meningkat dengan cepat disebabkan permintaan tinggi pada produk polimer yang mesra alam dengan harga yang berpatutan. Usaha-usaha yang berterusan adalah tertumpu untuk meningkatkan sifat-sifat komposit ini. Di dalam kajian ini, adunan polietilena berketumpatan rendah linear (LLDPE)/polivinil alkohol (PVOH) telah digunakan sebagai matrik polimer dengan komposisi yang telah ditetapkan pada 60/40 (wt. %), manakala gentian kenaf bast (KNF) digunakan sebagai pengisi. Kesan pembebanan pengisi dan pelbagai rawatan kimia terhadap pengisi semula jadi tersebut ke atas ciriciri pemprosesan, sifat-sifat tensil, struktur, morfologi, termal dan biodegradasi komposit LLDPE/PVOH/KNF telah dikaji. Komposit LLDPE/PVOH/KNF mengandungi pembebanan KNF yang berbeza (0, 10, 20, 30 and 40 phr) telah disediakan menggunakan pencampuran leburan dan pengacuanan mampatan. Didapati bahawa peningkatan pembebanan KNF, tork pemprosesan, modulus tensil, kestabilan termal dan penyerapan air komposit telah meningkat. Walau bagaimanapun, kekuatan tensil dan pemanjangan pada takat putus komposit telah didapati menurun. Ini menunjukkan lekatan antara muka yang lemah di antara matrik LLDPE/PVOH dan KNF sebagaimana dibuktikan dalam kajian SEM. Pencuacaan semula jadi dan penanaman di dalam tanah telah memberikan kesan negatif kepada sifat-sifat komposit LLDPE/PVOH/KNF, sebagaimana ditunjukkan oleh

kemerosotan di dalam sifat-sifat tensil, kerosakan permukaan yang terdedah, dan peratusan kehilangan berat yang lebih tinggi. Seterusnya, keputusan daripada spektra FTIR mengesahkan kehadiran degradasi dengan kemunculan puncak karbonil yang jelas. Kehadiran perawatan kimia ke atas KNF telah meningkatkan sifat-sifat tensil, morfologi, sifat terma dan juga mengurangkan penyerapan air komposit LLDPE/PVOH/KNF. Perawatan kimia KNF telah disahkan melalui spektroskopi FTIR. Berdasarkan keputusan yang diperolehi, didapati penambahan KNF terawat 3- (trimetosisilil)propil metakrilat (TMS) ke dalam matrik LLDPE/PVOH telah meningkatkan tork pemprosesan, kekuatan tensil, modulus tensil, kestabilan terma dan mengurangkan penyerapan air komposit. Ini dibuktikan dengan peningkatan lekatan antara muka di antara KNF terawat TMS dan matrik LLDPE/PVOH melalui analisis SEM. Penambahan KNF terawat dengan agen pengkupel mesra alam (EFCA), kromium (III) sulfat dan lisin ke dalam matrik LLDPE/PVOH juga didapati meningkatkan tork pemprosesan, sifat-sifat tensil, kestabilan terma dan mengurangkan penyerapan air komposit. Keputusan daripada analisis SEM menunjukkan peningkatan di dalam lekatan antara muka di antara KNF terawat dan matrik LLDPE/PVOH. Keputusan FTIR juga mengesahkan pembentukan ikatan kimia di antara agen-agen pengkupel dan KNF, seterusnya menghasilkan pautan di antara KNF and matrik LLDPE/PVOH.