THERMODEGRADATION OF MEDIUM-CHAIN-LENGTH POLY(3-HYDROXYALKANOATES), AND ASSESSMENT OF THE BIOPOLYESTERS AND OLIGOESTERS AS PLASTICIZER FOR POLY(VINYL CHLORIDE)

SIN MEI CHAN

FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR, MALAYSIA

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SIN MEI CHAN

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~~Registration~~/Matric No: SHC 080034

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ABSTRACT

Medium-chain-length poly(3-hydroxyalkanoates) (mcl-PHA) are natural polyesters of hydroxyl fatty acids, composed of monomers with 6 to 14 carbon atoms length. These biopolyesters are primarily synthesized by fluorescent pseudomonads under nutrient imbalance, as carbon and energy storage compounds. In this study, mcl-PHA were produced by *Pseudomonas putida* PGA1 using oleic acid (OA) and saponified palm kernel oil (SPKO) as carbon source in shake flasks and fed-batch fermentations. From thermogravimetric analysis (TGA), the mcl-PHA derived from oleic acid (PHA_{OA}) showed a drastic decomposition at temperature above 183 ℃, while mcl-PHA derived from saponified palm kernel oil (PHA_{SPKO}) above 196 ℃. Therefore thermal degradation of the PHA_{OA} was carried out at temperatures of 160 ℃, 170 ℃ and 180 ℃; whereas thermal degradation for the PHA_{SPKO} was performed at temperatures of 160 ℃, 170 ℃, 180˚C and 190°C, respectively. Changes in the polymer structures and properties before and after thermal treatments were studied by TGA, Differential Scanning Calorimetry (DSC), Gel Permeation Chromatography (GPC), Gas Chromatography (GC), Fourier Transform Infrared (FTIR) Spectroscopy, 400-MHz Proton Nuclear Magnetic Resonance (^{1}H-NMR) Spectroscopy, and end group analysis.

Acid values obtained from end group analysis showed that mcl-PHA heat-treated at higher temperatures had higher concentration of terminal carboxylic acids and lower number average molecular weight (M_n). Based on GC, FTIR and ^{1}H-NMR spectroscopic analyses on the thermal degradation products, it is suggested that the thermal degradation mechanism of mcl-PHA involved random α-chain scission *via* hydrolytic ester bond cleavage, producing a mixture of lower molecular weight oligomeric hydroxyacids. Heating above 180˚C in the acidic environment would lead to the dehydration of some hydroxyl terminal groups to produce alkenoic acids. These low molecular weight oligoesters possess functional terminals and could be used as natural-based plasticizers in

PVC compounds. While the common PVC plasticizers, particularly phthalates, are known to be detrimental to the environment and human health, the mcl-PHA and its oligoesters have the potential to be alternative eco-friendly plasticizers for PVC. On this premise, a series of solution-cast blends of poly(vinyl chloride)-poly(3-hydroxyalkanoates) (PVC-PHA) were prepared to assess whether mcl-PHA and its oligoesters could be acted as compatible plasticizers for PVC. Scanning Electron Microscopy (SEM), FTIR, ^{1}H-NMR, DSC and Dynamic Mechanical Analysis (DMA) were conducted to study the microstructure, film morphology, miscibility and viscoelastic properties of the PVC-PHA blends.

SEM micrographs of PVC/PHA films showed that plasticization of PVC involved the PHA penetrated in some of the porous structures of PVC, and interfused with PVC polymer segments. Both FTIR and ^{1}H-NMR spectroscopic analyses suggested the PVC-PHA miscibility was possibly due to the specific interactions between the ester C=O group of PHA with the $^{\alpha}$H and local dipoles of chlorines of PVC. TGA study was used to investigate the thermal stability and thermo-dynamic parameters of the plasticized PVC films. Both measurements of DSC and DMA gave consistent results of a single T_g for the blends, indicating that mcl-PHA was highly miscible with PVC. Results from DMA also showed that mcl-PHA and its oligoesters could reduce the T_g of PVC, imparting elasticity to the PVC compounds and therefore decreasing the stiffness of the polymer.

ABSTRAK

Poli(3-hidroksialkanoat) dengan rantai sederhana panjang (mcl-PHA) adalah asid lemak hidroksil poliester semulajadi, terdiri daripada monomer yang mempunyai 6 hingga 14 atom karbon. Biopoliester ini terutamanya disintesis oleh *Pseudomonads* berpendarfluor di bawah ketidakseimbangan nutrien, sebagai komponen simpanan karbon dan tenaga. Dalam kajian ini, mcl-PHA telah dihasilkan oleh *Pseudomonas putida* PGA1 menggunakan asid oleik (OA) dan minyak isirung sawit tersaponin (SPKO) sebagai sumber karbon dalam proses penapaian menggunakan kelalang goncang dan kaedah suapan kelompak. Daripada analisis *thermogravimetric* (TGA), mcl-PHA yang diperolehi daripada asid oleik (PHA_{OA}) menunjukkan dekomposisi drastik pada suhu melebihi 183 ℃, sementara mcl-PHA yang diperolehi daripada minyak isirung sawit tersaponin (PHA_{SPKO}) melebihi 196 ℃. Oleh yang demikian, degradasi termal bagi PHA_{OA} dijalankan pada suhu 160 ℃, 170 ℃ dan 180 ℃; manakala degradasi termal bagi PHA_{SPKO} dijalankan pada suhu 160 ℃, 170 ℃, 180 ℃ dan 190 ℃, masing-masing. Perubahan dalam struktur dan sifat-sifat polimer sebelum dan selepas rawatan termal telah dikaji menggunakan TGA, *Differential Scanning Calorimetry* (DSC), *Gel Permeation Chromatography* (GPC), *Gas Chromatography* (GC), *Fourier Transform Infrared* (FTIR) *Spectroscopy*, 400-MHz *Proton Nuclear Magnetic Resonance* (^{1}H-NMR) *Spectroscopy* dan analisis *end group*.

Nilai asid yang diperolehi daripada analisis *end group* menunjukkan mcl-PHA yang dipanas pada suhu yang lebih tinggi mempunyai kepekatan terminal asik karbosilik yang lebih tinggi dan bilangan purata berat molekul (M_n) yang lebih rendah. Daripada analisis GC, FTIR dan ^{1}H-NMR ke atas produk degradasi termal, ini mencadangkan bahawa mekanisme degradasi termal bagi mcl-PHA melibatkan pemotongan α-rantaian secara rawak melalui potongan terhidrolisis pada ikatan ester, menghasilkan campuran asid hidroksi oligomer yang mempunyai berat molekul yang lebih rendah. Pemanasan

melebihi 180℃ dalam persekitaran berasid mungkin menyebabkan dehidrasi bagi sesetengah terminal kumpulan hidroksi dan menghasilkan asid alkenoik. Oligoester yang mengandungi berat molekul yang rendah ini mempunyai terminal yang berfungsi dan dapat digunakan sebagai *plasticizer* semulajadi dalam kompaun PVC. Plasticizer PVC yang umum, terutamanya *phthalates*, diketahui membawa mudarat kepada alam sekitar dan kesihatan manusia, mcl-PHA dan oligoesternya mempunyai potensi sebagai alternatif *plasticizer* yang mesra alam kepada PVC. Pada premis ini, satu siri 'solution-cast' campuran terdiri daripada poli(vinyl kloride)-poli(3-hidroksialkanoat) (PVC-PHA) telah disediakan untuk menilai sama ada mcl-PHA dan oligoesternya boleh bertindak sebagai 'compatible plasticizer' bagi PVC. *Scanning Electron Microscopy* (SEM), FTIR, ^{1}H-NMR, DSC dan *Dynamic Mechanical Analysis* (DMA) telah dijalankan untuk mengkaji mikrostruktur, morfologi filem, keterlarutcampuran dan sifat-sifat 'viscoelastic' bagi campuran-campuran PVC-PHA.

SEM mikrograf bagi PVC/PHA filem menunjukkan bahawa 'plasticization of PVC' melibatkan penebusan PHA ke dalam struktur berpori PVC, dan menyatu dengan segmen polimer PVC. Analisis spektroskopi FTIR dan ^{1}H-NMR mencadangkan keterlarutcampuran PVC-PHA mungkin disebabkan oleh interaksi khusus antara kumpulan ester C=O daripada PHA dengan $^\alpha$H dan 'local dipoles' antara klorin daripada PVC. Kajian TGA telah digunakan untuk menyelidik kestabilan termal dan parameter-parameter termo-dinamik untuk filem *plasticized* PVC. Kedua-dua ukuran daripada DSC dan DMA memberi keputusan konsisten, iaitu nilai T_g yang tunggal bagi campuran-campuran ini, menunjukkan bahawa mcl-PHA adalah sangat 'miscible' dengan PVC. Keputusan daripada DMA juga menunjukkan bahawa mcl-PHA dan oligoesternya dapat menurunkan T_g PVC, memberikan keanjalan kepada kompaun PVC, oleh itu mengurangkan keteguhan polimer.

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LIST OF SYMBOLS AND ABBREVIATIONS

AN	Acid number
ASTM	American Society for Testing and Materials
BBP	Benzyl butyl phthalate
$CDCl_3$	Deuterated chloroform
DBP	Dibutyl phthalate
DEHP	Di-2-ethyl hexyl phthalate
DIDP	Diisodecyl phthalate
DIHP	Diisoheptyl phthalate
DINP	Diisononyl phthalate
DMA	Dynamic Mechanical Analyzer
DOP	Dioctyl phthalate
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetry
E	Elastic modulus
E'	Storage modulus
E''	Loss modulus
E_d	Degradation activation energy
FTIR	Fourier Transform Infrared
$\Delta G°$	Standard Gibbs free energy change
GC	Gas chromatography
GPC	Gel permeation chromatography
ΔH_m	Enthalpy of fusion
3HB	3-hydroxybutyric acid
3HD	3-hydroxydecanoic acid
3HDD	3-hydroxydodecanoic acid
$3HH_x$	3-hydroxyhexanoic acid
$3HH_xD$	3-hydroxyhexadecanoic acid
3HO	3-hydroxyoctanoic acid

3HTD	3-hydroxytetradecanoic acid
K_a	Acid dissociation constant
M_n	Number average molecular weight
M_w	Weight average molecular weight
mcl-PHA	Medium-chain-length poly(3-hydroxyalkanoates)
MSDS	Material Safety Data Sheet
NMR	Nuclear Magnetic Resonance
PDI	Polydispersity index
PHA	Poly(3-hydroxyalkanoates)
$\mathrm{PHA_{OA}}$	Poly(3-hydroxyalkanoates) derived from oleic acid
$\mathrm{PHA_{SPKO}}$	Poly(3-hydroxyalkanoates) derived from saponified palm kernel oil
PHB	Poly(3-hydrobutyrate)
PHBV	Poly(3-hydrobutyrate-*co*-valerate)
phr	Parts per hundred parts resin
PKO	Palm kernel oil
pO_2	Partial pressure of oxygen
PORIM	Palm Oil Research Institute of Malaysia
ppm	parts per million
P. putida	*Pseudomonas putida*
PS	Polystyrene
PVC	Poly(vinyl chloride)
$\mathrm{PVC/degPHA_{OA}}$	Polymer blend consisted of poly(vinyl chloride) and oligomeric poly(3-hydroxyalkanoates) derived from oleic acid
$\mathrm{PVC/degPHA_{SPKO}}$	Polymer blend consisted of poly(vinyl chloride) and oligomeric poly(3-hydroxyalkanoates) derived from saponified palm kernel oil
$\mathrm{PVC/degPHA_{OA\text{-}2.5}}$	Polymer blend consisted of poly(vinyl chloride) and 2.5 phr oligomeric poly(3-hydroxyalkanoates) derived from oleic acid
$\mathrm{PVC/degPHA_{OA\text{-}5}}$	Polymer blend consisted of poly(vinyl chloride) and 5 phr oligomeric poly(3-hydroxyalkanoates) derived from oleic acid
$\mathrm{PVC/degPHA_{SPKO\text{-}2.5}}$	Polymer blend consisted of poly(vinyl chloride) and 2.5 phr oligomeric poly(3-hydroxyalkanoates) derived from saponified palm kernel oil

PVC/degPHA$_{\text{SPKO-5}}$	Polymer blend consisted of poly(vinyl chloride) and 5 phr oligomeric poly(3-hydroxyalkanoates) derived from saponified palm kernel oil
PVC/PHA	Polymer blend consisted of poly(vinyl chloride) and poly(3-hydroxyalkanoates)
PVC/PHA$_{\text{OA}}$	Polymer blend consisted of poly(vinyl chloride) and polymeric poly(3-hydroxyalkanoates) derived from oleic acid
PVC/PHA$_{\text{SPKO}}$	Polymer blend consisted of poly(vinyl chloride) and polymeric poly(3-hydroxyalkanoates) derived from saponified palm kernel oil
PVC/PHA$_{\text{OA-2.5}}$	Polymer blend consisted of poly(vinyl chloride) and 2.5 phr polymeric poly(3-hydroxyalkanoates) derived from oleic acid
PVC/PHA$_{\text{OA-5}}$	Polymer blend consisted of poly(vinyl chloride) and 5 phr polymeric poly(3-hydroxyalkanoates) derived from oleic acid
PVC/PHA$_{\text{SPKO-2.5}}$	Polymer blend consisted of poly(vinyl chloride) and 2.5 phr polymeric poly(3-hydroxyalkanoates) derived from saponified palm kernel oil
PVC/PHA$_{\text{SPKO-5}}$	Polymer blend consisted of poly(vinyl chloride) and 5 phr polymeric poly(3-hydroxyalkanoates) derived from saponified palm kernel oil
rpm	Revolutions per minute
rRNA	Ribosomal RNA
RT	Retention time
ΔS	Entropy of activation
scl-PHA	Short-chain-length poly(3-hydroxyalkanoates)
SEM	Scanning Electron Microscopy
SPKO	Saponified palm kernel oil
T_{g}	Glass transition temperature
T_m	Melting temperature
T_{onset}	Temperature at onset degradation
T_p	Temperature at fastest degradation
tan δ	Loss angle tangent
TG	Thermogravimetry
TGA	Thermogravimetric Analysis