UNIVERSITI PUTRA MALAYSIA

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By

MOHD NOR FAIZ B. NORRRAHIM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

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EVALUATION OF PROPERTIES AND CHEMICAL RECYCLABILITY OF POLYETHYLENE/POLY-(3-HYDROXYBUTYRATE-*co*-3-HYDROXYVALERATE) BLEND FOR SUSTAINABLE PACKAGING MATERIAL

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MOHD NOR FAIZ B. NORRRAHIM

January 2014

Chairman : Hidayah Ariffin, PhD
Faculty : Biotechnology and Biomolecular Sciences

Polyethylene (PE) is a great packaging plastic due to its low cost, high versatility and good processability. This polymer is however non-renewable and non-biodegradable which may cause serious environmental problem. The use of renewable, biodegradable and chemically recyclable plastic such as polyhydroxyalkanoates (PHA) is more advantageous from environmental perspective despite of its high price and inferior mechanical and thermal properties. In order to get the better of both plastics, blending of these two polymers was proposed for this research. In this research, PE was blended with poly (3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) ranging from 20 to 50 wt% of PHBV using melt blending techniques at 170^{o}C. The PE/PHBV blend films were then evaluated in term of their mechanical, morphological, thermal and permeability properties (oxygen transmission rate, OTR and water vapor transmission rate, WVTR).

It was found that the polymer blends consisted up to 30% of PHBV had a superior mechanical and permeability properties. OTR of the polymer blends containing 20 and 30% PHBV was reduced by 19 – 25% compared to that of neat PE, which indicated that PHBV functions as barrier for oxygen transmission. Meanwhile, WVTR value of PE/PHBV (70/30) increased by nearly 3-fold as compared to that of neat PE. These permeability properties may be suitable for packaging dried food products which require low OTR in order to maintain the shelf life of the products. Comparison of mechanical and permeability properties of the PE/PHBV blends with those of commercial plastics revealed that their properties are comparable.

Chemical recyclability of PHA in the form of polymer blends has never been tested previously. In this study, PE/PHBV blends were subjected for isothermal pyrolysis in glass tube oven at 310^{o}C for two purposes: i) to separate PHA from PE by exploiting their thermal stability differences, and ii) to chemically recycle PHA fraction. It was postulated that the difference in thermal stability of PHBV and PE is an advantage in this study as PHBV degraded as volatile matters at lower temperature and hence, can be

separated from PE. From the results, it was revealed that PE and PHBV can be completely separated from each other after the pyrolysis. GC-MS and ^{1}H-NMR analyses of the pyrolyzates confirmed that PHBV component in the polymer blend was successfully degraded into its volatile monomers (crotonic acid, CA and 2-pentenoic acid, 2-PA) and oligomers, suggested that chemical recycling of PHBV is possible.

All in all, PE/PHBV blends of up to 30% of PHBV exhibited properties which are within acceptable range for packaging application with additional advantage in terms of oxygen and water vapor permeability. Moreover, PHBV fraction can be separated from the polymer blend after its use through pyrolysis, as PHBV can be pyrolyzed into valuable volatile matters, *i.e.* monomers and oligomers. The pyrolyzates recovered can be utilized for making another polymer, or can be used as chemicals. Remaining PE can be either chemically or mechanically recycled for other useful products. Overall, the characteristics of PE/PHBV blends presented herewith are in line with sustainable packaging principles and cascade utilization of polymeric materials proposed herewith may contribute positively to the economic and social.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENILAIAN CIRI-CIRI DAN KEMAMPUAN KITAR SEMULA SECARA KIMIA BAGI POLIMER CAMPURAN POLIETILINA/POLI-(3-HIDROSIBUTIRAT-*co*-3-HIDROSIVALERAT) UNTUK BAHAN PEMBUNGKUSAN LESTARI

Oleh

MOHD NOR FAIZ B. NORRRAHIM

Januari 2014

Pengerusi : Hidayah Ariffin, PhD
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Polietilena (PE) adalah plastik pembungkusan yang mampan disebabkan kos penghasilannya yang rendah serta mempunyai cirri-ciri yang pelbagai, dan mudah untuk diproses. Polimer ini bagaimanapun tidak boleh diperbaharui dan tidak boleh dilupuskan yang di mana akan membawa kepada masalah alam sekitar yang serius. Penggunaan plastik yang boleh diperbaharui,dan lebih mesra alam serta boleh dikitar semula secara kimia seperti polyhidrosialkanoat (PHA) adalah sangat berfaedah dari perspektif alam sekitar walaupun harganya yang tinggi dan mempunyai sifat-sifat mekanikal dan terma yang rendah. Dalam usaha untuk memanfaatkan kebaikan dari kedua-dua plastik, campuran kedua-dua polimer ini telah dicadangkan dalam kajian ini. PE telah dicampurkan dengan poli (3-hidrosibutirat-co-3-hidrosivalerat) (PHBV) yang terdiri dari 20 hingga 50% dari berat PHBV melalui kaedah pencairan adunan pada suhu 170^{o}C.

Campuran PE/PHBV kemudian diuji untuk sifat mekanikal, morfologi, terma dan kebolehtelapan (kadar transmisi oksigen, OTR dan kadar transmisi air, WVTR). Berdasarkan dari kajian ini, campuran polimer yang terdiri sehingga 30% kandungan PHBV mempunyai ciri mekanikal dan kebolehtelapan yang bagus. Nilai OTR daripada campuran polimer yang mengandungi 20 dan 30% PHBV telah berkurangan sebanyak 19-25% berbanding dengan nilai PE asli yang menunjukkan bahawa PHBV mampu berfungsi sebagai penghalang untuk ketelapan oksigen. Di samping itu, nilai WVTR bagi PE/PHBV (70/30) meningkat hampir 3 kali ganda berbanding dengan PE asli. Ciri-ciri kebolehtelapan ini adalah amat sesuai untuk diaplikasikan untuk pembungkusan makanan terutamanya bagi produk segar dan kering yang memerlukan nilai OTR yang rendah dan WVTR yang tinggi untuk mengekalkan jangka hayat produk. Perbandingan yang setara telah ditunjukkan bagi sifat mekanikal dan kebolehtelapan campuran PE/PHBV dengan plastik komersial.

Kaedah kitar semula PHA secara kimia juga telah diuji dalam kajian sebelum ini, bagaimanapun kitar semula kimia dalam bentuk campuran polimer belum pernah diuji.

Dalam kajian ini, pirolisis telah dilakukan pada suhu 310^{o}C dengan menggunakan ketuhar tiub kaca adalah untuk dua tujuan : i) untuk memisahkan PE/PHBV dengan mengeksploitasi perbezaan kestabilan terma mereka, dan ii) untuk mengitar semula PHA secara kimia. Perbezaan dalam kestabilan terma bagi PHA dan PE adalah satu kelebihan dalam kajian ini yang di mana PHA asli diurai pada suhu yang lebih rendah dan dengan itu ianya dapat diasingkan daripada PE. Hasil kajian telah menunjukkan bahawa, PE dan PHBV berjaya dipisahkan melalui kaedah pirolisis. Daripada analisis GC-MS dan ^{1}H-NMR ke atas pirolisat mengesahkan bahawa komponen PHBV dalam campuran polimer telah berjaya dipirolisiskan kepada monomer (asid krotonik, CA dan 2-pentenoik acid, 2-PA) dan oligomer, dan ini telah membuktikan bahawa PHBV mampu dikitar semula secara kimia

Keseluruhannya, campuran polimer pada kadar 20 dan 30% PHBV adalah boleh diterima untuk tujuan pembungkusan dengan kelebihan tambahan bagi ciri kebolehtelapan molekul oksigen dan air. Selain itu, PHBV boleh dipisahkan daripada gabungan polimer melalui pirolisis bagi menghasilkan produk yang bernilai sebagai contoh monomer dan oligomer. Pirolisat yang dikumpulkan boleh digunakan untuk membuat polimer lain atau boleh digunakan sebagai bahan kimia. PE yang tinggal boleh dikitar semula secara kimia atau mekanikal untuk penghasilan produk lain yang berguna. Secara keseluruhannya, ciri-ciri campuran PE/PHBV yang telah dikaji ini adalah selaras dengan prinsip-prinsip pembungkusan yang mampan dan penggunaan kitaran bahan polimer yang dicadangkan boleh menyumbang secara positif kepada ekonomi dan sosial.

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This list is far from exhaustive, I pray for forgiveness from those I did not mention by name and include then in my heart-felt gratitude.

I certify that a Thesis Examination Committee has met on 3 January 2014 to conduct the final examination of Mohd Nor Faiz b. Norrrahim on his Master of Science thesis entitled "Evaluation of properties and chemical recyclability of polyethylene/poly-(3-hydroxybutyrate-*co*-3-hydroxyvalerate) blend for sustainable packaging material" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The committee recommends that the student be awarded the Master of Science.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members for the Supervisory Committee were as follows:

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Date:

DECLARATION

Declaration by graduate student

I hereby confirm that:

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DECLARATION

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in Rule 41 Rules 2003 (Revision 2012-2013) were adhered to.

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Signature:	_____
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TABLE OF CONTENTS