



UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF FATTY ALCOHOL-BASED PHOSPHATE ESTERS
By

LEE CHING SHYA

FS 2008 15



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

January 2008



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment
of the requirement for the degree of Master of Science

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January 2008

Chair: Professor Nordin Hj. Lajis, PhD

Faculty: Science

Fatty chemicals based on edible and inedible tallow and a variety of vegetable oils have wide use in plastics industry. At present, there are some limitation and economic competition between plastics additives based on fats and oils and those from fossil fuels (crude oil and natural gas). The large growth of palm oil production in Malaysia and the rapid expansion of oleochemical production facilities in Malaysia imply strong growth for these chemicals in plastics application in the recent years. Oleochemicals has been reported being large used as emulsifiers and stabilizer in polymerization, as auxiliaries for processing and as structural materials in plastics industry. A preliminary study carried out has shown the compatibility between inorganic fillers (calcium carbonate, CaCO_3) and the polyvinylchloride resins (PVC) can be improved by adding oleochemical-based surfactant to the CaCO_3 , prior to its mixing with the plastic resins. A more homogeneous mixture was obtained, thus better PVC plastics was produced. This research was therefore undertaken to synthesize fatty alcohol-based phosphate ester using fatty alcohol as the starting material to be used as the coupling agent for the CaCO_3 and plastics resins.



In this study, the syntheses were carried out in three different routes and each route were divided into three steps. Fatty alcohol-based phosphate esters with diphosphate ester functional group were prepared by reacting a diol with phosphorus oxychloride (POCl_3) and then followed by addition of long-chained fatty alcohol.

In route one, C_{16} -fatty alcohol was used in the synthesis. The optimized reaction temperatures for each step of reaction in this route were 20 °C, 35 °C and 70 °C respectively. The reaction duration of each step was about 3 hours. Excess of phosphorus oxychloride (2.5 mole) was used and 0.1% (w/w) of catalyst tetrabutyl orthotitanate (based on the weight of fatty alcohol) was employed in the synthesis. The percentage yield of the final product obtained from the titration of acidic solution (HCl gas in distilled water) with NaOH solution was about 60 %. From the GC, GC-MS, LC and LC-MS analyses, monophosphate ester (dipropyl heptadecyl phosphate ester) with the percentage of about 4.8% was obtained. While, the major compounds obtained were 1,6-dichlorohexane and 1-chlorohexadecane with the total percentage ~ 70%.

In route two and three, the reactions were carried out under the reaction temperature of 20 °C, 90 °C and 90 °C for each step of the reaction respectively. The optimized reaction duration for each step was 2 hours, 2 hours and 1 hour respectively. In these syntheses, excess of phosphorus oxychloride (2.5 mole) was also used but no catalyst was applied in the reaction. The fatty alcohol used in route three was different with route one and two, whereby C_{18} -fatty alcohol was used. The percentage yield of the final product obtained under these conditions was about 10-40% (by titration method). From the GC-MS and LC-MS analyses, the major compounds obtained

from the synthesis were also 1,6-dichlorohexane and 1-chlorohexadecane which gave a total yield of ~74.06%. The phosphate ester obtained in this synthesis was a diphosphate ester (trihexadecyl hexyl diphosphate ester) with the percentage of about ~ 2.5%.

Finally the products obtained were applied in PVC compounding. Some basic formulations were prepared, which comprised the synthesized phosphate ester (PE/T10), PVC resin, plasticizer (DOP), stabilizer (TBLS) and calcium carbonate as filler (CaCO_3). The mixture of these polymers and additives was blended at 170 °C with a mixing speed of 70 r.p.m. The homogenized plasticized mixture was then compressed on a hot press at 170 °C for 10 min. Based on the tensile strength results, a slight decreased in the tensile properties was observed when the ester sample was added into the PVC compounding which could be due to the presence of chlorinated compound present as indicated by the analyses. The chlorinated compound may have reacted with the filler (CaCO_3) during the PVC compounding process and thus causing the decreased in tensile strength of the plastic sheets. However, in general, the physical appearance of the PVC sheet could be improved by the synthesized phosphate ester (PE/T10) after further dried with anhydrous calcium sulphate whereby a smooth surface was observed compared to the PVC sheet without added of phosphate ester (PE/T10).



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

SINTESIS FOSFAT ESTER BERASASKAN ALKOHOL LEMAK

Oleh

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Januari 2008

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Sebatian lemak yang diperolehi daripada haiwan samada boleh dimakan atau tidak, dan pelbagai jenis lemak daripada minyak sayuran mempunyai kegunaan luas dalam industri plastik. Walaubagaimanapun, wujud persaingan yang terhad dari segi plastik yang berasaskan minyak dan lemak haiwan atau tumbuhan dengan bahan api fosil (minyak mentah dan gas semulajadi). Sejak kebelakangan ini, pertumbuhan pesat industri penghasilan minyak sawit dan oleokimia di Malaysia membuktikan perkembangan penggunaan oleokimia untuk aplikasi dalam plastik. Sebatian oleokimia telah dilaporkan mempunyai penggunaan yang luas sebagai agen pengemulsian dan agen penstabilan dalam proses pempolimeran, bahan tambahan semasa pemprosesan termasuk sebagai bahan penstruktur dalam industri plastik. Satu kajian awal telah dibuat dan menyatakan bahawa untuk mempertingkatkan keserasian antara bahan tambahan inorganik dengan resin (PVC) dalam pnyelidikan plastik PVC, surfaktan berasaskan oleokimia boleh dijadikan sebagai bahan aditif dan perlu ditambah terlebih dahulu ke dalam mineral inorganik seperti kalsium karbonat (CaCO_3) sebelum dicampurkan dengan resin plastik. Suatu campuran yang lebih homogen diperolehi, maka plastik PVC yang lebih baik akan dihasilkan. Dalam

penyelidikan ini, ester fosfat berasaskan alkohol lemak yang disediakan daripada alkohol lemak akan diuji sebagai agen penyambung bagi CaCO_3 dengan resin plastik.

Dalam kajian ini, kerja sintesis telah dijalankan dalam tiga kaedah dan setiap kaedah melibatkan tiga langkah. Ester fosfat berasaskan alkohol lemak yang megandungi dua kumpulan berfungsi ester fosfat telah disediakan melalui tindak balas di antara diol dengan fosforus triklorida (POCl_3) dan alkohol lemak berantai panjang.

Dalam kaedah pertama, alkohol lemak yang digunakan adalah alkohol lemak C_{16} . Suhu tindak balas yang optimum bagi setiap langkah masing-masing dalam kaedah ini adalah $20\text{ }^\circ\text{C}$, $35\text{ }^\circ\text{C}$ and $70\text{ }^\circ\text{C}$. Masa tindak balas untuk setiap langkah adalah tiga jam. Fosforus triklorida yang berlebihan (2.5 mol) dengan mangkin tetrabutyl ototitanat (0.1 % w/w bergantung kepada berat alkohol lemak) telah digunakan dalam sintesis ini. Peratusan hasil yang diperolehi daripada cara penitratan antara asid dengan natrium hidroksida adalah lebih kurang 60%. Daripada keputusan yang analisis GC, GC-MS, LC, dan LC-MS, monofosfat ester (dipropil heptadesil fosfat ester) telah diperolehi dengan peratusan ~ 4.8%. Manakala, komponen yang utama dalam langkah ini adalah 1,6-diklorohexana dan 1-klorohexadekana dengan peratusan hasil ~ 70%.

Dalam kaedah kedua dan ketiga, suhu tindak balas bagi setiap langkah masing-masing adalah $20\text{ }^\circ\text{C}$, $90\text{ }^\circ\text{C}$ and $90\text{ }^\circ\text{C}$. Masa tindak balas yang optimum untuk setiap langkah masing-masing adalah 2 jam, 2 jam dan 1 jam. Dalam langkah ini, fosforus triklorida yang berlebihan (2.5 mol) juga telah digunakan dalam sintesis ini tetapi tiada mangkin digunakan dalam kaedah ini. Alkohol lemak yang digunakan dalam

kaedah ketiga adalah berbeza daripada kaedah pertama dan kedua, di mana alkohol lemak C_{18} telah digunakan dalam sintesis. Peratusan hasil yang diperolehi daripada cara penitratan antara asid dengan natrium hidroksida adalah lebih kurang 5-50%. Daripada keputusan analisis GC-MS dan LC-MS, komponen utama yang diperolehi dalam langkah ini adalah juga sama dengan langkah pertama, di mana 1,6-diklorohexana dan 1-klorohexadekana telah dihasilkan dalam tindak balas ini dengan peratusan hasil ~ 74.06%. Fosfat ester yang didapati dalam sintesis ini adalah sejenis difosfat ester (triheksadesil heksil difosfat ester) dengan peratusan ~ 2.5%.

Hasil tindak balas yang diperolehi kemudiannya digunakan sebagai bahan tambah dalam penyediaan plastik PVC. Beberapa formula yang asas telah dibuat dengan menggunakan fosfat ester (PE/T10) yang diperolehi daripada sintesis, resin PVC, bahan pemplastikan (DOP), agen penstabilan (TBLS) dan agen pemenuhan plastik ($CaCO_3$). Campuran plastik dan bahan tambahan ini digaul pada suhu $170\text{ }^{\circ}C$ dengan kelajuan 70 r.p.m. Akhirnya, campuran yang diperolehi dimampatkan di atas mesin pemampat yang panas selama 10 min pada suhu $170\text{ }^{\circ}C$. Bergantung kepada keputusan yang diperolehi daripada cara penegangan, penurunan dalam ciri-ciri tegangan telah diperhatikan apabila sampel ester telah ditambah kepada PVC. Ini adalah kemungkinan besar kehadiran komponen klorin dalam hasil tindak balas seperti yang telah dibuktikan dalam analisis. Komponen klorin ini mungkin telah bertindak balas dengan agen pemenuhan plastik ($CaCO_3$) semasa penyediaan plastik PVC dan seterusnya menyebabkan penurunan dalam ciri-ciri tegangan. Akan Tetapi, secara am, ciri fizikal kepingan plastik dapat dipertingkatkan dengan menggunakan fosfat ester (PE/T10) yang telah dikeringkan oleh kalsium sulfat anhidrida di mana

suatu permukaan yang lebih licin telah diperolehi bebanding dengan kepingan PVC yang tidak mengandungi fosfat ester (PE/T10).

ACKNOWLEDGEMENTS

I would like to express my sincere and deepest appreciation to Professor Dr. Nordin Hj. Lajis, the Chairman of my Supervisory Committee, for his intellectual advice, suggestions and guidance throughout the course of this project and reviewing this thesis with constructive criticisms. I am equally indebted to Associate Professor Dr. Mohd. Aspollah Hj Sukari who, as a member of my Supervisor Committee, gave invaluable supports guidance and comments. My sincere thanks and deepest gratitude must be extended to Dr. Hazimah Abu Hassan (a member of my Supervisory Committee), Director of Advanced Oleochemical Technology Division (AOTD), Malaysia Palm Oil Board (MPOB), for her kind, intellectual and direct supervision throughout my entire research work in her laboratory at AOTD, without which I would not be able to accomplish my MSc degree.

I am also heartily thankful to Dr. Ooi Tian Lye, Principal Research Officer and the Head of Oleochemical Products Development Unit of AOTD for his kind and intellectual guidance during my entire work in AOTD. I acknowledge with thanks for the financial support from MPOB Graduate Research Programme. I also would like to express my heartfelt thanks to staff of AOTD for their technical assistance throughout the entire course of my research, especially Puan Asma Don, Puan Sapiyah Hashim, Puan Sefiah Ariffin, Puan Selasih Abdullah, Puan Zamiah Hasham, Puan Rosmah Umam, Encik Halim Ariffin, Encik Roslan Ramli, Encik Mohammed Ahir Musa and many others. I would also like to thank Pn Azowa from Department of Chemistry, University of Putra and Dr. Chantara Theyv Ratnam from Malaysian



Institute for Nuclear Technology Research (MINT) for permission to conduct my project in their laboratory.

Last but not least, I am also greatly indebted to my parents, Lee Ah See and Loh Poh Chee; sister, Lee Ching Huey; and friends Aminah Nor Azizan, Chan Wai Theng, Cheong Mei Yee, Gladys Cho Hui peng, Lee Choy Sin, Lim Sheo Kun and Nur Musyahadah Mazlan; whose relentless encouragement and support have contributed towards the accomplishment of this project.



I certify that an Examination Committee met on 3rd January 2008 voce to conduct the final examination of Lee Ching Shya on her Master of Science thesis entitled “Synthesis of Fatty Alcohol-Based Phosphate Esters” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the Master of Science degree.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

LEE CHING SHYA

Date: 27 March 2008



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