24 JUL 2000

A STUDY OF LOW DENSITY POLYETHYLENE AND POLYSTYRENE BLENDS WITH REACTIVE COMPATIBILISERS

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR

THE DEGREE OF MASTER OF SCIENCE

(POLYMER SCIENCE)

FACULTY OF GRADUATE STUDIES

MAHIDOL UNIVERSITY

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2000

ISBN 974-664-330-4

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45022 ค.2

Thesis
entitled

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was submitted to the Faculty of Graduate Studies, Mahidol University
for the degree of Master of Science (Polymer Science)
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ACKNOWLEDGEMENT

I would like to express to the people who contribute a share in this thesis. The first one is my deepest appreciable advisor, Dr. Pranee Phinyocheep who has been giving the valuable guidance, encouragement, and helpful discussion throughout this research. The appreciation also goes to Dr. Kalyanee Premphet, Dr. Chakrit Sirisinha, Dr. Nuanphun Chantarasiri and Dr. Taweechai Amornsakchai for their helpful and constructive suggestions for the completion of this thesis.

Sincere thanks also go to the other lecturers in the Polymer Science and Technology program, Mahidol University, who gave very useful suggestions. Furthermore, I wish to thank the following people and organisation for various helps

Miss Peungpit Khomprapan, who operated the differential scanning calorimeter.

National Metal and Materials Technology Center (MTEC), who supported the use of capillary rheometer.

My grateful thanks go also to Mr. Wichai Sarakarnkosol, who is my appreciable brother for his useful advisableness, my good friends at Mahidol University, whose names are not mentioned here, for their help and kindness. Finally I wish to thank my family for their helpfulness and concern. And I would like to thank my mother who has not seen this thesis in this opportunity.

Wirote Sarakarnkosol

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4036460 SCPO/M: MAJOR : POLYMER SCIENCE; M.Sc. (POLYMER SCIENCE)
KEY WORDS : REACTIVE EXTRUSION, LOW DENSITY POLYETHYLENE, POLYSTYRENE, POLYPROPYLENE, MALEIC ANHYDRIDE, COMPATIBILISATION, FUNCTIONAL POLYMER

WIROTE SARAKARNKOSOL : A STUDY OF LOW DENSITY POLYETHYLENE AND POLYSTYRENE BLENDS WITH REACTIVE COMPATIBILISERS. THESIS ADVISERS: PRANEE PHINYOCHEEP, Doctorat de l'Université du Maine, KALYANEE PREMPHET, Ph.D.,CHAKRIT SIRISINHA, Ph.D., 174 p. ISBN 974-664-330-4

This study concerned blending of two polymers, low density polyethylene (LDPE) and polystyrene (PS). Compatibilsation of these two components was investigated by an addition of a reactive functional polymer or copolymer and by inducement of reactive compatibilisation.

Various compatibilisers including maleic anhydride grafted low density polyethylene (PE-*g*-MA), maleic anhydride grafted polystyrene (PS-*g*-MA), copolymers of PE and PS and various melt flow indices of copolymer of polypropylene and polystyrene (PP-*co*-PS) were prepared in a twin screw extruder. Chemical structure of the modified polymers and copolymers were analysed by Infrared spectroscopy. Determination of the MA grafting content was carried out by titration with tetramethylammoniumhydroxide using three different indicators, i.e. cresol red, bromphenolblue and phenolphthalein. It was found that cresol red gave the best and reliable result.

Blending of 75:25 LDPE/PS with 1, 3 and 5 phr of the prepared compatibilisers was carried in a twin screw extruder. The reactive functionalities of the PE-*g*-MA and PS-*g*-MA could slightly help in improvement of the mechanical properties of LDPE/PS blends. Copolymers of polyethylene and polystyrene prepared using Friedel Crafts alkylation (PE-*g*-PS), maleic anhydride linkage (PE-MA-PS) and hexamethylenediamine (PE-HMM-PS) resulted in improvement of mechanical properties of the blends particularly the impact strength. Higher loading of the copolymer resulted in higher impact strength. This may be due to the higher % grafting developped between the matrix and dispersed phase found during processing. Addition of PP-*co*-PS in LDPE/PS blend affected also mechanical properties of the blends. However the enhancement of impact strength of the LDPE/PS blend depended on the MFI value of the copolymers.

Scanning electron micrographs revealed that the blends containing compatibilisers have smaller particle size of the dispersed phase than the uncompatibilised blend. It was assumed that decreasing of the particle size of the PS dispersed phase is responsible for the enhancement of the blend compatibility. The copolymers could affect stabilising the PS dispersed phase and inhibit the coalescense, and hence providing better compatibility of the LDPE/PS interphase.

For reactive compatibilisation, blends containing PE-*g*-MA and PS-*g*-MA without diamine compound (EgSMA3), with hexamethylenediamine, HMD (EgSMA3H) and with 4,4′-diaminodiphenylsulphone, DAPS (EgSMA3D) were investigated. It was found that the compatibility of the blends was better than the blends containing functional polymers such as PE-*g*-MA or PS-*g*-MA. This may be due to the imide linkage developped during melt blending from the reaction between the anhydride appended polymers and amine functions. Consequently, the mechanical properties could be improved.

4036460 SCPO/M : สาขาวิชา: วิทยาศาสตร์พอลิเมอร์; วท.ม. (วิทยาศาสตร์พอลิเมอร์)

วิโรจน์ สารการโกศล : การศึกษาพอลิเมอร์ผสมของพอลิเอทธิลีนชนิดความหนาแน่นต่ำ-พอลิสไตรีนโดยการใช้สารช่วยผสมแบบเกิดปฏิกิริยา (A STUDY OF LOW DENSITY POLYETHYLENE AND POLYSTYRENE BLENDS WITH REACTIVE COMPATIBILISERS) คณะกรรมการควบคุมวิทยานิพนธ์ : ปราณี ภิญโญชีพ, Doctorat de l'Université du Maine, กัลยาณี เปรมเพ็ชร, Ph.D., ชาคริต สิริสิงห, Ph.D., 174 หน้า. ISBN 974-664-330-4

การศึกษาระบบพอลิเมอร์ผสมของพอลิเมอร์สองชนิดคือพอลิเอทธิลลีนชนิดความหนาแน่นต่ำ (LDPE) และพอลิสไตรีน (PS) โดยใช้สารช่วยผสมชนิดที่มีหมู่ว่องไวต่อปฏิกิริยาหรือโคพอลิเมอร์ และสารที่สามารถทำให้เกิดปฏิกิริยาขณะผสม

สารช่วยผสมหลายตัวเตรียมโดยใช้เครื่องอัดรีดชนิดตัวหนอนคู่ เช่น พอลิเอทธิลลีนชนิดความหนาแน่นต่ำที่ทำการกราฟท์ด้วยมาเลอิคแอนไฮไดรด์ (PE-g-MA), พอลิสไตรีนที่ทำการกราฟท์ด้วยมาเลอิคแอนไฮไดรด์ (PS-g-MA), โคพอลิเมอร์ของ LDPE และ PS และโคพอลิเมอร์ของพอลิพรอพิลลีนที่มีค่าดรรชนีการไหลต่างๆกันกับพอลิสไตรีน (PP-co-PS) โครงสร้างทางเคมีของพอลิเมอร์ที่ทำการดัดแปรและโคพอลิเมอร์วิเคราะห์ด้วยอินฟราเรดเสปกโตรสโคปี (IR) ส่วนปริมาณของมาเลอิคแอนไฮไดรด์นั้นสามารถหาได้โดยใช้เทคนิคการไตเตรตโดยใช้เตตระเมธิลแอมโมเนียมไฮดรอกไซด์ด้วยการใช้ตัวบ่งชี้ 3 ชนิด ได้แก่ cresol red, bromphenolblue และ phenolphthalein พบว่า cresol red ให้ผลการทดลองที่ดีและน่าเชื่อถือได้มากที่สุด

การผสมพอลิเมอร์อัตราส่วน 75/25 LDPE/PS กับสารช่วยผสมที่เตรียมได้ในปริมาณ 1, 3 และ 5 phr โดยใช้เครื่องอัดรีดชนิดเกลียวหนอนคู่นั้นพบว่า หมู่ที่ว่องไวของ PE-g-MA และ PS-g-MA นั้นปรับปรุงสมบัติเชิงกลของระบบ 75/25 LDPE/PS ได้เล็กน้อย ในขณะที่โคพอลิเมอร์ที่เตรียมได้จากปฏิกิริยาฟรีเดล-คราฟท์ (PE-g-PS), เชื่อมด้วยมาเลอิคแอนไฮไดรด์ (PE-MA-PS) และเชื่อมด้วยเฮกซะเมธิลลีนไดอะมีน (PE-HMM-PS) นั้นสามารถปรับปรุงสมบัติเชิงกลได้โดยเฉพาะการกันกระแทกโดยเพิ่มตามปริมาณของโคพอลิเมอร์ ทั้งนี้เนื่องจากเกิดการกราฟท์ขึ้นระหว่างเมตริกซ์กับเฟสกระจายขึ้นขณะผสม การเติม PP-co-PS นั้นมีผลต่อสมบัติเชิงกลของพอลิเมอร์ผสม แต่อย่างไรก็ตามการเพิ่มสมบัติการกันกระแทกนั้นขึ้นอยู่กับค่าดรรชนีการไหลของโคพอลิเมอร์ด้วย

ภาพจากกล้องจุลทรรศ์อิเล็กตรอนแบบส่องกราดบ่งว่าพอลิเมอร์ที่ทำการผสมด้วยสารช่วยผสมเหล่านี้มีขนาดของเฟสกระจายที่ลดลงซึ่งก็เป็นการยืนยันว่าเกิดการเข้ากันได้มากขึ้น โดยที่โคพอลิเมอร์นั้นทำให้เฟสกระจายของ PS นั้นมีความอยู่ตัวอีกทั้งยังป้องกันการรวมตัวได้ด้วย

สำหรับการเกิดปฏิกิริยาขณะผสมของพอลิเมอร์ผสมที่ใช้ PE-g-MA และ PS-g-MA โดยไม่ใช้สารประกอบไดอะมีน (EgSMA3) ใช้เฮกซะเมธิลลีนไดอะมีน (EgSMA3H) และใช้ 4,4'ไดอะมิโนไดฟีนิลซัลโฟน (EgSMA3D) พบว่าพอลิเมอร์ผสมที่ได้มีความเข้ากันได้มากกว่าใช้ PE-g-MA หรือ PS-g-MA เพียงอย่างใดอย่างหนึ่ง ทั้งนี้เนื่องจากเกิดอิไมด์ลิงค์เกจจากหมู่แอนไฮไดรด์และหมู่อะมิโนขณะผสมขึ้นได้ ทำให้มีสมบัติเชิงกลที่ดีขึ้น

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LIST OF ABBREVIATION

LDPE	=	Low density polyethylene
PS	=	Polystyrene
PP	=	Polypropylene
MA	=	Maleic anhydride
PE-*g*-MA	=	Maleic anhydride grafted low density polyethylene
PS-*g*-MA	=	Maleic anhydride grafted polystyrene
PE-*g*-PS	=	Graft copolymer of low density polyethylene and polystyrene
PE-MA-PS	=	Copolymer of low density polyethylene and polystyrene through maleic anhydride linkage
PE-HMM-PS	=	Copolymer of low density polyethylene and polystyrene through hexamethylene maleimide linkage
PP-*co*-PS	=	Copolymer of polypropylene and polystyrene
T_g	=	Glass transition temperature
T_m	=	Melting temperature

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CHAPTER I

INTRODUCTION

1.1 General introduction

Blending of two existing polymers has been the subject of intense investigation over the years for accomplishing new polymeric materials possessing wide range of desired final product properties. This technology has received growing attention because of its low cost effective for commercial application over the conventional polymerisation processes and the potential use of recycling polymeric wastes. Two polymers, low density polyethylene (LDPE) and polystyrene (PS) are accounted for high quantity usage general purpose thermoplastics. The use of these materials in packaging applications has caused problems in solid waste disposal.[1,2] It is costly to completely separate them before the recycling process, therefore, blending technology has become necessary. The benefit of combining the high modulus polystyrene with the ductility character of polyethylene through melt blending technology is not only to diversify the properties of the resulting materials but also to solve the problems of environmental point of view. However, simple melt blending of these two components generally results in product of poor mechanical properties arising from the inherent

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incompatibility between the components and thus poor interphase adhesion which results in weak or brittle mechanical behaviour.[3-7]

The key factor for compatibilisation of immiscible polymers which are to be melt blended is by the introduction of a suitable copolymer, known as *compatibiliser*, which will locate preferentially at the interface between the blended components and reduce the interfacial tension. This effectiveness aids to ultimate morphology control and the interfacial adhesion. Such copolymer can be synthesised and then used in the polymer blends. However, from an economic point of view, it is sometime more interesting to form the copolymer during the blending process by adding the constituent components, which afterward combines chemically in the blend. This method is known as *in-situ* compatibilisation, which has been developed in recent decades.[7-19]

Another popular approach is to present reactive groups onto one or both of the two polymers to be blended. These functionalised polymers may form the required compatibilisers during a subsequent reactive extrusion. Nevertheless, this approach sometimes requires complicated processes to produce the functionalised polymers. The use of peroxide initiated functionalisation of polyethylene and polystyrene has been reported. [5,7,20-24] The success of grafting the reactive groups is limited because of the difficulty in optimal condition achievement with the minimal level of accompanied reactions such as crosslinking in the case of PE or subsequent degradation reaction for PS. Moreover, an excellent melt processing reactor for reactive compounding is needed. It has been demonstrated that twin screw extruder is the most efficient and economically reliable reactor nowadays because the appliance is flexible in operation, with variable degree of shearing and temperature profiles, good mixing characteristics,

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satisfactory residence time distributions, effective devolatilisation, and uniform output rate.[5,6,25]

The objective of this work is to investigate the morphology and mechanical properties of PE-rich LDPE/PS blends compatibilised with several copolymers prepared through reactive extrusion.

1.2 Low density polyethylene

Low density polyethylene is the first commercial ethylene polymer. It was first produced in the laboratories of Imperial Chemical Industries, Ltd. (ICI), in a fortuitous experiment in which ethylene was subjected to 1400 atm of pressure at 170°C. Trace of oxygen caused polymerisation to take place.[26] After a period of relatively slow growth, the production of branched polyethylene has expanded rapidly and attained the first plastic with annual production exceeding 1 billion lb, in 1959.

Chemical structure and properties

Low density polyethylene (LDPE) is a partially (50-60%) crystalline solid melting at about 115°C, with density in the range of 0.91-0.94. It is soluble in many solvents at temperature above 100°C, but only a few solvent mixtures provide borderline solubility at or near room temperature. Infrared spectroscopy revealed that LDPE contains branches chains. These branches are generated from two distinct types. Branching caused by an intermolecular chain transfer, arising from reaction of the type shown in Scheme 1.1 leads to long branches, which are, on the average, as long as the

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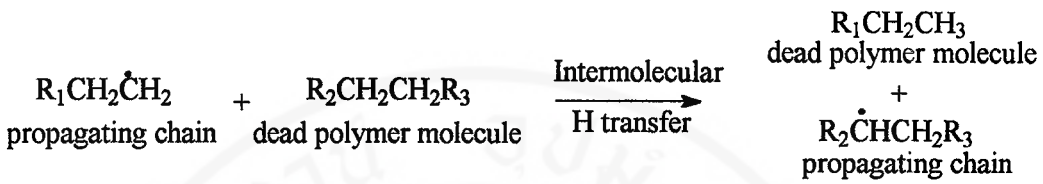
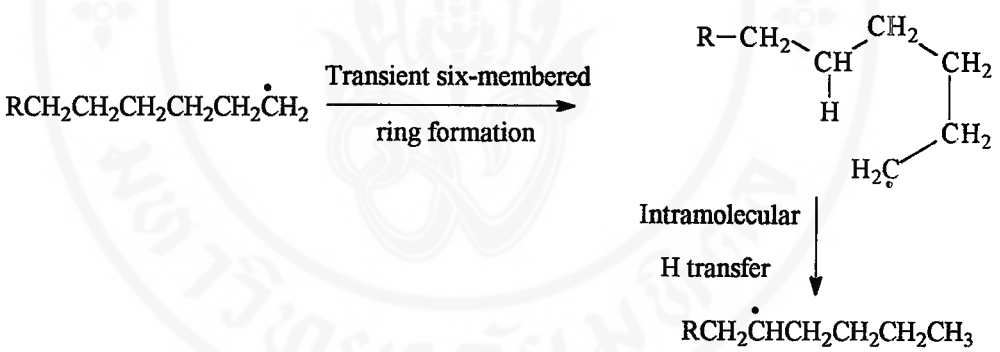
main polymer chains. This sort of branching has an observable effect on the solution viscosity of polymer and can be detected by comparing the viscosity of a branched polyethylene with that of a linear polymer of the same molecular weight.



Scheme 1.1 Intermolecular chain transfer of LDPE during polymerisation process

The second branching mechanism in polyethylene is postulated to produce short-chain branching by intramolecular chain transfer:



Scheme 1.2 Intramolecular chain transfer of LDPE during polymerisation process

The transient ring mechanism suggests four carbon atoms as the most probable length of the short branches. The studies of infrared absorption and degradation under high-energy radiation bombardment on polyethylene reveal the known branch structure of polyethylene, which are both ethyl and butyl branches.

A mechanism accounting for the ethyl branches assumes a transfer reaction of the type after an addition of one monomer unit to the radical resulting from a short-chain branching step by the previous mechanism.

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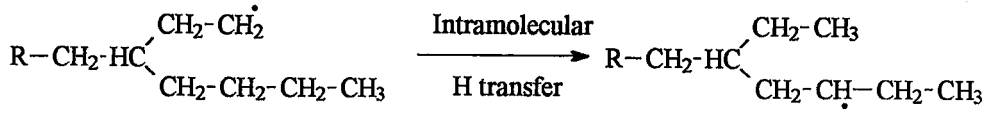

Scheme 1.3 Ethyl branch formation of LDPE

The degree of branching has a predominant effect on the physical properties of and hence on the density of polyethylene. The properties dependent on crystallinity such as stiffness, tear strength, hardness, chemical resistance and yield point, increase with increasing density or decreasing amount of short chain branching in the polymer, whereas permeability to liquids and gases, toughness and flex life are contradictory.

The effect of molecular weight is largely evidenced in properties of the melt and properties involving large deformations of the solid. The tensile strength, tear strength, low temperature toughness, softening temperature, impact strength and resistance to environmental stress cracking are increased [26], while melt fluidity, melt drawability and coefficient of friction are decreased when the molecular weight is increased. These properties are usually compared on the base of change in melt flow index, which varies inversely with molecular weight.

Polyethylene has good toughness and pliability over a wide temperature range. Its density falls off rapidly above room temperature, and some fabrication methods are difficult owing to the large dimensional changes. The relatively low T_m (about 115°C) limits the temperature range of good mechanical properties.

The electrical properties of polyethylene are outstandingly good. Its thick section is translucent because of its crystallinity, but high transparency is obtained in thin film.

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Polyethylene is very chemically inert. It does not dissolve in any solvent at room temperature, but is slightly swelled by liquids such as benzene and carbon tetrachloride, which become solvent at higher temperatures. It has good resistance to acid and alkalis. At 100°C it can stand for 24 hr in sulfuric or hydrochloric acid but chars in concentrated nitric acid. It is often used as containers for acid, including hydrofluoric.[26,27]

1.3 Polystyrene

Polystyrene (PS) is a thermoplastic with many desirable properties. It is clear, transparent, easily coloured and fabricated. Although PS has reasonably good mechanical and thermal properties. It is slightly brittle and become soft at the temperature below 100°C.

Chemical structure and properties

Polystyrene is a linear polymer, the atactic product being commercial and therefore amorphous. Isotactic polystyrene can be produced but offers little advantage in properties except between its glass transition (about 80°C) and crystalline melting point (about 240°C). Isotactic polystyrene is not of commercial interest because of the increased brittleness and more difficulty in processing than atactic product.

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Polystyrene is relatively inert chemically. It is quite resistant to alkalis, halide acids, oxidizing and reducing agents. It can be nitrated by fuming nitric acid, and sulfonated by concentrated sulfuric acid at 100°C to a water-soluble resin. Chlorine and

bromine are substituted on both the ring and the chain at elevated temperatures. The degradation of polystyrene produces the low molecular weight compounds that about 50 % are the styrene monomers. The characteristic odor of the monomer serves as identification for the polymer.

Polystyrene is outstandingly easy to process. It is an ideal polymer for injection molding technique because of its stability and flowability. Its optical properties such as colour and clarity are excellent, and its high refractive index (1.60) makes it useful for plastic optical components. Polystyrene is a good electrical insulator and has a low dielectric loss factor at moderate frequencies. Its tensile strength reaches about 1800 psi.

Polystyrene is easily attacked by large a variety of solvents. Its stability to weathering is poor, the yellowness and crazes on exposure are turned. Its major defects in mechanical properties are the brittleness and its relatively low heat-deflection temperature at 82-88°C, which means that polystyrene articles cannot be sterilised.

Many of these defects can be prevented by proper formulating, or by copolymerisation and blending. For example an addition of ultraviolet-light absorber improves the light stability of polystyrene enough to make it useful in lighting fixture such as fluorescence-light diffuses. Flame retardant polystyrene has also been developed through the use of additives.[26,27]

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1.4 Polymer blends miscibility

Polymer blends are mixtures of at least two macromolecular species, polymers and/or copolymers. The miscibility between polymers is recognised by the sign of free energy mixing(ΔG), which is written as:

$$\Delta G = \Delta H - T\Delta S$$

where H is enthalpy, S is entropy and T is temperature.

If polymers are miscible when ΔG is negative. The polymer/polymer miscibility has been found to limit in the range of independent variables, such as composition, molecular weight, temperature, pressure, etc.[28,29]

There are three aspects of compatibilisation to ensure high performance of immiscible blends.

- Reduction of the interfacial tension which facilitates dispersion
- Stabilisation of the morphology against changes during the subsequent processing steps
- Enhancement of adhesion between the phases, facilitating the stress transfer, and hence improving the mechanical properties of the product

To attain the above statements, two basic strategies of compatibilisation have been employed:

1. Addition of a compatibiliser such as block or graft copolymer
2. Inducement of reactive compatibilisation

With the first catagory, addition of block or graft copolymers are believed to be the most effective way for compatibilisation of blends. Usually, the copolymer is

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specifically designed to have one part miscible with one polymeric phase and the others with another. In other words, the block or graft copolymers containing segments chemically identical to the blend component polymers are obviously good choices as compatibilisers for giving blend miscibility. The compatibilisers normally locate preferentially at the blend interfaces to ascertain the adhesion between phases. Furthermore, the stabilisation of the generated morphology is assured when the central part of copolymer, which is a random copolymer, creates a thicker interface inhibiting the coalescence of the dispersed phase. The second type additive is generally a general purpose compatibiliser and impact modifier. It is often known as either a core-shell or multilayered copolymer containing reactive groups attached to either elastomeric or rigid part. The basic materials often used are acrylic and vinylic types. The utilisation of these materials in engineering polymer systems or specialty resins are not practical in turn of thermal stability. The inducement of reactive compatibilisation is comparatively a new method of producing compatible thermoplatic blends. It relies on the *in-situ* generation of linkage to form copolymer during melt blending. The interacting polymers may be occured between reactive groups of component polymers across the interphase or an interchange reaction in the backbone of the components during processing.

1.5 Compatibilisation by an addition of copolymers

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One of the most common methods for compatibilisation of immiscible blends involves an addition of a third component refering as a compatibiliser capable of

decreasing the interfacial energy, stabilizing the dispersion, and ascertaining the interfacial adhesion between the two different phases in the solid state.[28] Its important effects on the behaviours of polymer blends are presented as the followings.

1.5.1 Interfacial influences

The efficiency of compatibilisers is determined by their preferential location on the interface. At the point of thermodynamic equilibrium, an optimum amount of compatibiliser is attained to cover the interfaces and the compatibilisation is also accompanied by dissolution of the compatibilisers in both polymeric phases. Then the formation of micelles occurs at higher concentration resulting in subsequent formation of meso-phase. Compatibilisation is similar to the emulsification of classical colloids. The amount of emulsifier to saturate the interface depends on mixing time and equipment, the affinity of the emulsifier to the dispersed phase, the size of the dispersed phase, the orientation of the emulsifier at the interface and its ability to stabilise the interface against flocculation and coalescence.

In general consideration, the compatibilisation process is thermodynamic and kinetic. Its effectiveness depends on the diffusion rate. Accordingly, the compatibiliser should be designed by taking the thermodynamic and kinetic parameters into account. An effective compatibiliser of binary polymer blends should reduce the size of the dispersed particle and the interfacial tension coefficient. The block copolymer does not only reduce the interfacial tension coefficient, but it also alters the molecular structure of the interface. The block copolymer locates uniformly at the interphase. The

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penetration of block copolymer into the homopolymer phases and its location at the interphase has been observed. Consequently, the interfacial adhesion is improved, leading to an enhancement of mechanical behaviours.

1.5.2 Interfacial thickness

The interfacial thickness is another factor that plays a role for the compatibilisation of the blend system even though there has a few reports on its measurement.[28] It has been observed in the case of PE/PS blends that addition of 2-5 % wt of poly(hydrogenated butadiene-*b*-isoprene-*b*-styrene), P(hB-*b*-I-S), leads to an increase in the interfacial thickness to 10-12 nm for good performance blending. One can postulate the importance of thickness of the interface as a barrier against the thermal and flow coalescence. The migration of the compatibilisers to the polymers' surface is controlled by their structures (e.g. MW, composition, architecture, etc.) as well as by shear process. At the first stage of mixing, the dispersed phase is deformed, leading to an increase in the interfacial area and to a thin interphase. It then bring the adjacent dispersed entities into a close proximity for sufficiently long time for pinching the two interphases to form a single entity. Therefore, the thicker the interphase, the better the compatibilisation, and hence the finer the dispersion and the more rigidity of the interphase.

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1.5.3 Morphology

The morphology of polymer blends has been mostly characterised by scanning electron microscopy (SEM) or transmission electron microscopy (TEM). These techniques are used to investigate the changes of the sizes and the shape of the dispersed phase, including their distribution in the polymer matrix.

It is generally accepted that efficient compatibilisers, notably used in industries, do not have inherent structures. The charateristics of polymer blends obtained with their additions generate either drop type or extended morphology. [28,30] Many blends show co-continuous, elongated structures while some exhibits spheres, multilayer vesicles or lamellas morphologies. The high performance polymer blends generally exhibit fine and regular morphology with small dispersed particles.

1.5.4 Crystallisation behaviours

In the case of polymer blends comprising semi-crystalline polymers, an addition of compatibiliser may affect the crystallisation behaviour and the degree of crystallinity. Therefore, compatibilsation behaviour in immisible blends may not deal with the crystalline part of the polymer blend dued to the complexity of the crystallinity. Several variables play role as functions of crystallinity such as crystallisation conditions, processing parameters, compatibilisation methods, molecular structure and composition. Addition of a third component may either reduce or enhance these effects on the crystallinity. Different crystallisation mechanisms usually lead to different

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morphologies and compatibilisation characteristics. In most improved performance system, the copolymer added results in the reduction of spherulite size of the crystalline component and in an interphase adhesion improvement. An example is PA-6/EPR blends addition of EPR-*g*-SA. [31]

1.6 Compatibilisation by reactive blending

Development of compatibilisation in processing equipment is recently emerging for high performance immiscible blending systems. Principle for reactive compatibilisation, the interfacial agent is produced *in-situ* with segments from the two homopolymers. A copolymer can be formed during reactive blending through an inter-chain reaction within the five chemical processes as listed in Table 1.1.

Therefore, one should integrate polymer chemistry with polymer processing to define reactive processing as it combines chemical kinetics with flow and heat balance.

Reactive extrusion, involves the synthesis of materials by a melt phase reaction in an extruder. It is considered to be more interesting than batch type reactor. This technology can be used to develop profitable blends with new sets of properties when the following basic requirements are attainable for efficient reactive compatibilisation. [6]

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Table 1.1 Chemical processes for interchain copolymer formation in extruder reactor

Type of chemical reaction	Type of resulting copolymer
Chain cleavage and recombination resulting in either block or random copolymers	AAAAABBBBBB + AABBBBBAAA + AABBAAABBB, etc.
Reaction between end-groups	AAAAABBBBB
End-group of 1st polymer reacting with pendant functionality of 2nd polymer resulting in a graft copolymer	AAAAAAAAAAA B B B B B B
Reaction either between pendant groups or main chains of the two polymers	Graft copolymer or crosslinked network
Ionic bonding formation	Usually graft, frequently crosslinked system

-Sufficient mixing to achieve the desired dispersed morphology of one polymer in another

- Presence of reactive functionality for covalent or ionic bond formation

-Sufficient chemical activity to react across the phase boundary

-High reactivity to complete the reaction within the residence time of the extruder

- The formed bonds to remain stable in subsequent processing steps

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Compatibilising reactions in continuous processing equipment usually involve highly reactive functional groups that are stable under processing conditions. The reactions should be fast and irreversible. Because of the limitation of residence time in

the extruder, high conversion rate can be acheived by using a relatively high concentration of the reactive groups or efficient catalysts. The completed reaction in reactive extrusion has suggested to be within reasonable time, and be accompanied by low exotherms. The extruder should also be able to handle a variety of reactant feeds at various locations along the barrel and be equipped with vents for volatile removal. Knowledge of the reaction kinetics-particularly in a viscous molten polymeric medium are of paramount importance for the selection of extrusion conditions and geometry in order to vary residence times and optimise mixing.

In majority of cases, final product characteristics are often associated with compatibility attained through covalent or ionic bonds, rather than through weaker specific interactions; of course, in a given reacted polymer blend, secondary attractive forces such as hydrogen bonding, dipole interactions etc, are also operational. Figure 1.1 shows examples of some important compatibilising reactions that can take place easily across polymer phase boundaries. Functional groups such as epoxy, anhydride, isocyanate, oxazoline are highly reactive which meet the above requirements for interchain reactions to be conducted in continuous processing equipment. In addition, generation of free radicals during processing involves also in reactive compatibilisation through recombination reactions. The covalent bondings from these reactions are formed at the interface of the two polymers resulting in a reduced interfacial tension and in a the morphology stabilisation.

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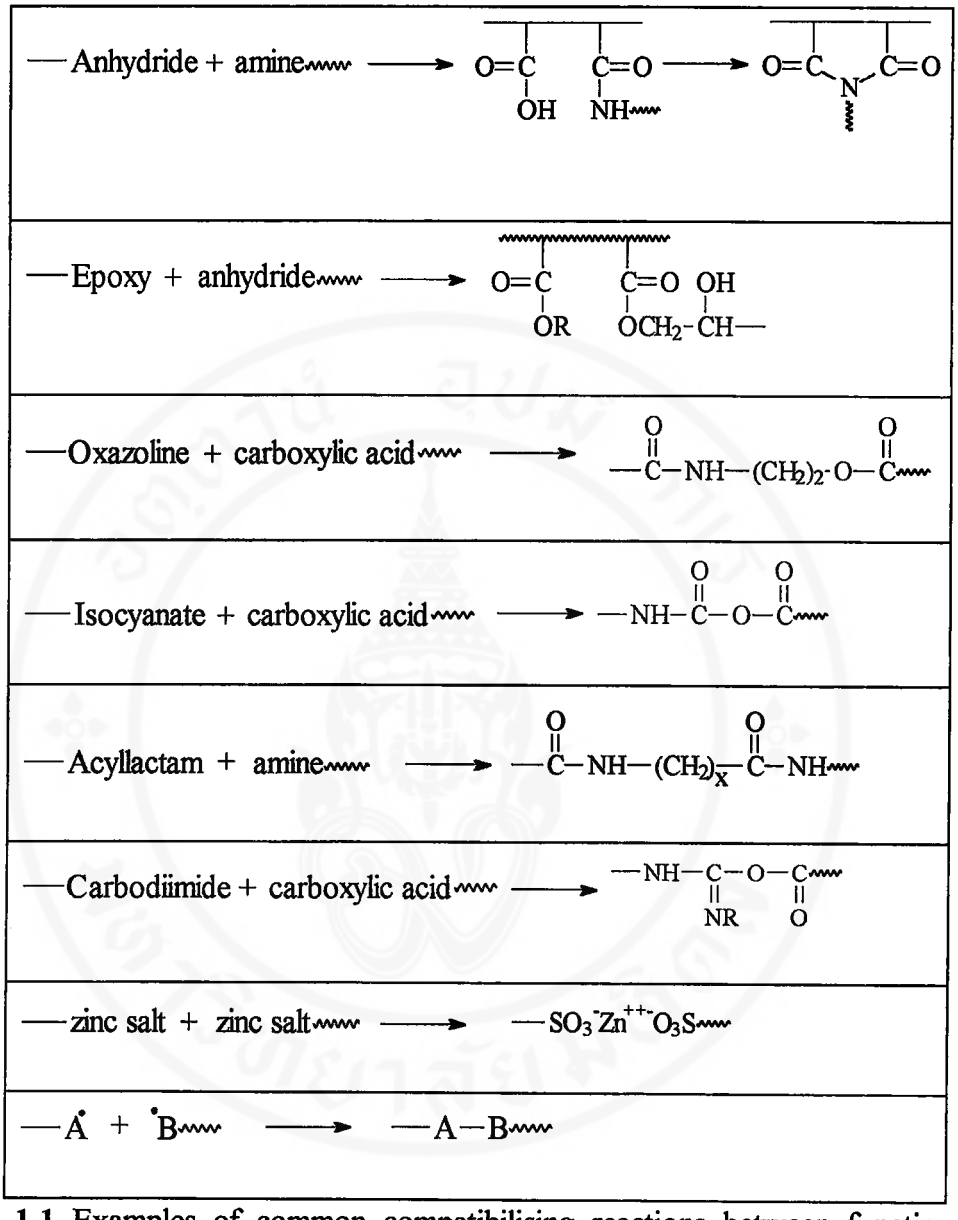

Figure 1.1 Examples of common compatibilising reactions between functionalised blend constituents.

It has also been reported that reactive compatibilisation enhances the mechanical properties of blends by the evidence of a reduction in size of the dispersed phase and a narrow size distribution.[6] This technology reveals that reactive blends show a thicker interphase than blends with or without added copolymer as shown in Table 1.2

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Table 1.2 Interphase thickness

Type of blend	Thickness (nm)
Immiscible	2
Block copolymer	4-6
Polymer/copolymer	30
Reactive compatibilisation	30-60
Radius of gyration	5-35

The advantages of reactive extrusion as opposed to alternative technologies include:

- Little or no use of solvents
- Simple product isolation
- Short reaction times
- Continuous process
- Relatively low infrastructure costs
- Possibility to synthesise graft copolymers

However, some disadvantages or difficulties associated with reactive extrusion include high reaction temperatures necessary to form a polymer melt, with accompanied by polymer degradation or crosslinking during processing.

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1.7 Radical-induced grafting of reactive monomers onto polyolefins by reactive extrusion

As mentioned earlier that the reactive extrusion is an effective tool for *in-situ* compatibilisation of immisible blends because of the fast reaction for occurring a copolymer formed by chemically combining the polymer component during blending process. However this technique cannot be successfully applied for blendings of polyolefins or polystyrene because neither of these polymers has any functional groups which can be used in the formation of a copolymer. Therefore, a functionalisation of these polymers is needed. Grafting of reactive monomer onto polyolefin backbone can be carried out by reactive extrusion through a radical-induced grafting principle.

The process generally involves combining the required polyolefins with a free radical initiator (such as peroxide compounds), a monomer or macromonomer. Several parameters concerning this technique are taken into account as the followings.

1.7.1 Radical initiators

Initiators needed for grafting experiments are the molecules that can generate radicals with high efficacy, short half life and high specificity towards the polyolefin substrates. But, if possible, the generated radicals should not react with the added monomers faster than the substrates.

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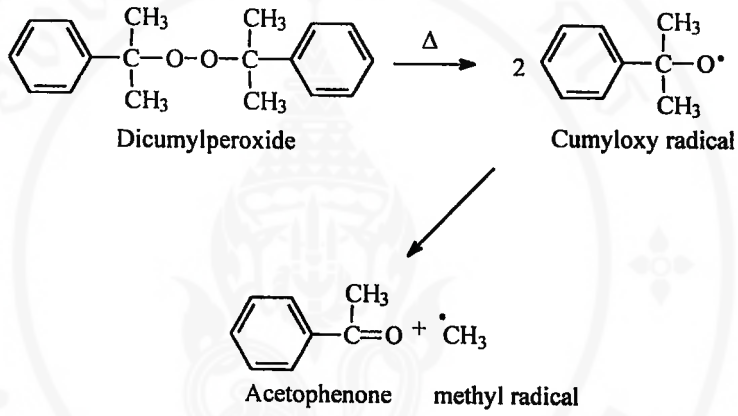
1.7.1.1 Mechanisms of radical generation

The most commonly used initiators in reactive processing are dialkyl peroxides. The decomposition mechanism of dialkyl peroxides is well established. It involves initial O-O bond homolytic cleavage to generate the corresponding alkoxy radicals. An example of dicumyl peroxide is shown in Scheme 1.4 [32,33].



Scheme 1.4 Decomposition of dicumylperoxide (DCP)

If the cumyloxy radical is not immediately trapped by the reaction with substrate, the initially formed alkoxy radicals undergo α-scission with preferential cleavage of the weakest C-C bond to form methyl radical and acetophenone. Carbon-carbon sp^3 are weaker than the sp or sp^2 types, and therefore the former tends to be broken rather than the sp or sp^2 carbons.

1.7.1.2 Initiator half-life

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The initiator half-life relates to the concentration of transient radical species generated with respect to the residence time of reactants in the reaction zone of the reactor. A number of factors need to be balanced.

It is desirable that the initiator is converted into radicals within the reaction zone of the extruder. An initiator with a half-life that is too long may not be completely utilised. This is unattractive from an economic vantage point. More important, however, is the negative impact that any residual initiator may have on ultimate product stability. Thus, ideally, the half-life of the initiator should be short compared with the residence time in the extruder. If the residence time corresponds to five half-lives, there will be >97% consumption of the peroxide.

A shorter half-life initiator will initially give a higher transient radical concentration for the same concentration of initiator. This may increase the likelihood of crosslinking by radical-radical combination. Another possible consequence is that grafting yields may become limited by the rate of monomer or macromonomer diffusion to the site of reaction particularly where the melt is heterogeneous.

It follows that, for short half-life initiators, the initiator concentration and the method of introducing the initiator will become more important and there may be difficulties in introducing such species into the polymer melt. In spite of these comments, some recent work suggests that the use of short half-life initiators may offer both higher grafting yields and a fewer side reactions.[1]

1.7.1.3 Other parameters

Other parameters to be considered when selecting an initiator include:

1. The solubility of the initiator in the polyolefin melt and its partition coefficient between the various phases in the case of multiphase melts

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2. The volatility of the initiator. It is a concern both in choosing the method of introduction and for safety considerations.

3. The physical form of the initiator

4. The method of introducing the initiator. In reactive extrusion, the initiator may be introduced with the polyolefin feedstock through the main hopper, with the monomer, or as a separate feed. It may be added directly, be adsorbed onto the polymer, or be added as a solution in the monomer or a solvent. It may be added all at once or by multipoint addition.

5. The extent of cage reaction and the formation of initiator derived by-products. The cage reaction depends on the nature of the initiator and increases in importance with the viscosity of the medium.

6. The susceptibility of the initiator to induce decomposition and other side reactions. Diacyl peroxides and hydroperoxides are particularly prone to induce decomposition.

1.7.2 Mechanism of grafting reaction

The grafting mechanism of monomer onto polymer backbone through radical reaction is rather well recognised. This method is known as chain transfer method. Free radical generated from the decomposition of radical initiator abstracts an atom such as hydrogen atom from a polymer chain to yield a radical site for the growth of branches. [25] The macroradicals then react with the added monomers as shown in Scheme 1.5.

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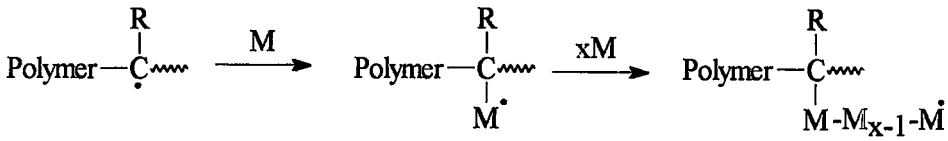

Scheme 1.5 Graft copolymer formation of macroradical with monomer

The success of chain transfer method in producing graft copolymers is dependent upon the structure of the monomer, the polymer and the catalyst or initiator. If a polymerisable monomer is used, a graft copolymer is produced. Methyl methacrylate, acrylic acid, glycidyl methacrylate are typical monomers being used for graft copolymerisation. [8,21,22,25] Therefore, utilisation of these monomers results in a long chain copolymer rather than a formation of functional group on the polyolefins. However grafting of polar functionality has been successfully carried out for polyethylene and polypropylene by using maleic anhydride monomer.[13,16,34] This monomer is not prone to homopolymerise but copolymerise. The anhydrides grafted on polyolefin are reactive functional groups for various nucleophilic sites such as amine, acid or alcohol functions. The success of a grafting experiment is usually measured in terms of the grafting yield, the fraction of the monomer that is either grafted onto the polymer or is consumed in side reactions such as homopolymerisation.

The nature of the origin polymer is important in that the active site generated on the backbone of the polymer will undergo and participate in a grafting reaction or not. The radical may be highly stabilised so that it has little tendency to react with a monomer from the reaction system. In addition, the radical site may bring to side reactions such as crosslinking or chain scission reactions.

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In reactive extrusion, melt temperatures are often difficult to measure or specify in an entirely satisfactory manner. The effects of shear heating are such that melt temperatures are seldom the same as, and can often be substantially different to, set barrel or reactor temperatures.

Under the applied shear in melt phase processing of polyolefins, polymer chain can be ruptured to produce free radicals at the ruptured end of the chain as well as along the polymer backbone. Therefore, in reactive processing, radicals are not only generated from the radical initiators added but also the degradation of the polymer backbone. Consequently, one can estimate the occurrence of grafting reaction often accompanied with side reactions which include

1. Radical-induced cross-linking of the polyolefin substrate
2. Radical-induced chain scission of the polyolefin substrate
3. Shear induced degradation of the polyolefin substrate
4. Homopolymerisation of the monomer

A major challenge in conducting monomer grafting experiments is to devise process conditions so as to minimise or control the aforementioned side reactions while at the same time maximising the grafting yield to achieve optimal product properties.

The extents of crosslinking and/or chain scission show a marked dependence on the particular substrate and the process conditions. Polyethylene is prone to branching or crosslinking caused by radical-radical recombination (Scheme 1.6). This process is characterised by the formation of gels or a partially insoluble product. Increases in torque during processing or changes in the melt viscosity are often quoted as an evidence of crosslinking. However, the grafting of active functionality is likely to give

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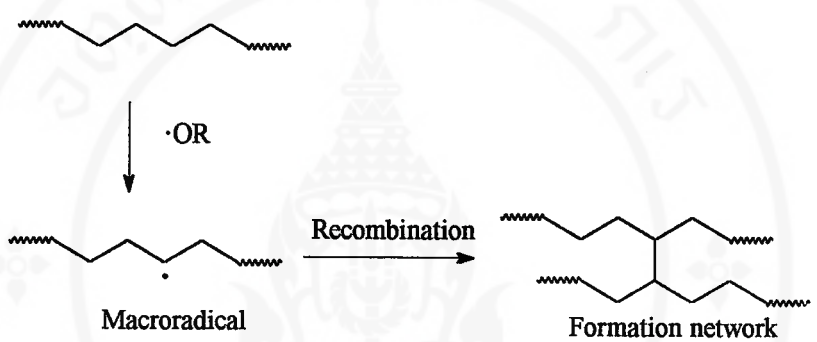
an increase in melt viscosity even if there is no crosslinking or molecular weight increase. Melt viscosity is expected to be higher for a modified polyolefin simply as a consequence of the specific interactions between the introduced functional groups. Various reports indicating the occurrence of crosslinking which are based wholly on torque or viscosity measurements should therefore be treated circumspectly. [1,4,5,7,20,21,23,35]



Scheme 1.6 Crosslinking of PE via radical recombination

Polypropylene (PP) and very low density ethylene/α-olefin copolymers may also undergo crosslinking in some circumstances. However, the most often cited side reaction is the degradation caused by the initially formed radical undergoing scission (Scheme 1.7). This process is well documented and is used in the synthesis of controlled rheology PP. This process should not always be regarded as a side reaction in polymer functionalisation. It has been proposed as an integral step in polypropylene block copolymer synthesis.

Thermal or shear-induced degradation of PP is also well documented and, in general, high shear processing conditions, as would cause substantial degradation by this mechanism, are to be avoided. However, one can note that `initiators' grafting processes based on the use of such mechanochemistry have been described , but the grafting yields are generally low. Shear induced degradation is also an essential step in

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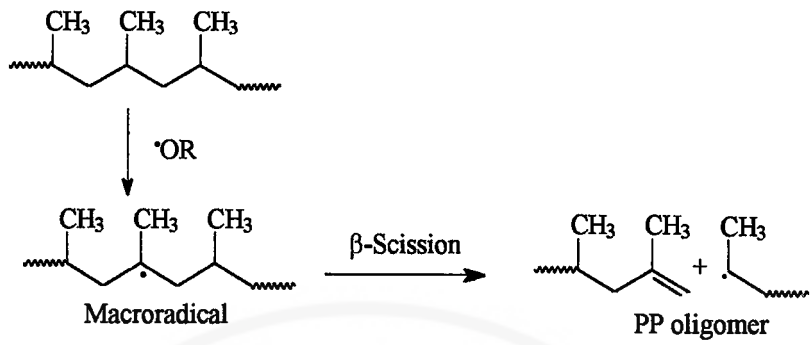

Scheme 1.7 Chain degradation of PP via β-scission

a new form of grafting which is based on the formation of crosslinked polymer as an intermediate.[20,35,37,38]

A high grafting yield and a low incidence of side reactions require that the radical sites on the backbone are efficiently transformed to graft sites. Noted that the trapping of a radical by monomer does not, in itself, prevent crosslinking due to radical-radical coupling. The outcome will depend on the properties of the radicals formed and, in particular, on the propensity for combination versus disproportionation.

1.7.3 Coagents

Various coagents have been described which improve grafting yields and reduce side reactions such as crosslinking, chain scission. In order to minimise side reactions, it is important that the radicals formed on the polyolefin backbone are trapped as rapidly as possible. Some monomers are more effective than others at trapping such radicals. This may arise from the relative high solubility of the monomers in the polyolefin melt or from the inherent reactivity of the monomers. One strategy for reducing side reactions and for increasing grafting yields takes advantage of this fact.

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This strategy involves choosing a monomer combination such that the coagent monomer is both effective in trapping the radicals formed on the polyolefin backbone and such that the propagating radical formed is highly reactive towards the desired monomer.

Various electron-rich comonomers, in particular styrene, have been shown to be effective as coagents for improving grafting yields and reducing side reactions of electron deficient monomers, in particular maleic anhydride (MA) and methacrylic (MMA) monomers onto both PP and LLDPE. In the case of the styrene-MA system, the improved grafting yields have also been attributed to the formation of a charge transfer complex between styrene and MA, and to the higher reactivity of this species versus MA or styrene.

The high grafting yields obtained with these coagents may be associated with:

1. Longer chain grafts. Rates of copolymerisation of electron donor-electron acceptor pairs (e.g. styrene/MA, styrene/glycidyl methacrylate (GMA)) are substantially greater than that for homopolymerisation (of MA or GMA).

2. More grafting sites. More efficient trapping of radical sites on the polymer backbone should lead to a greater number of grafts.

1.8 Determination of maleic anhydride content on the modified polymer by titration method

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Grafting of maleic anhydride onto polyolefins is one of the most interesting strategie for rendering reactive functional group onto the polymeric backbone. The

grafting ability can be determined by the simple analysis with Infrared spectroscopy. It is generally found that the modified polymers contain two characteristic absorption peaks of anhydride function at 1860 and 1780 cm^{-1}, accompanied by the presence of acid function at 1710 cm^{-1}, coming from the anhydride ring opening reaction. Consequently, the determination of the amount of maleic anhydride attached to the polymer chains by spectroscopic method cannot be a quantitative result due to the overlapping of the absorption peaks. The elemental analysis can also result in an error from determination of undefined amount of acid or anhydride functional groups. Titration is an alternative and successful method in determining the amount of the acid or anhydride groups on functionalised polymers. As most of the polymer samples are insoluble in water, it is therefore important to find the appropriate conditions such as indicator and titrant in non-aqueous system to well recognise the end point of the titration.

1.8.1 Choice of indicators

The method of end point detection in non-aqueous media and aqueous media with the mean of colour indicators is simplest and most convenient, particularly when occasional analyzes are required. In aqueous solutions, pH titration can easily be carried out accurately, even with very diluted solution. But in the case of non-aqueous solvents, the end point is much more difficult to discern. The best procedure was to titrate to a certain colour hue, but there are few indicators, which had been study in very dilute solutions to detect the end point. The sharpness of the colour changes might be quite adequate, and the only cases in which any difficulties are encountered.

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A wide range of indicators and the pH values at which their colour changes occur are known well for aqueous solutions, but only a few indicators are known for non-aqueous solvents particularly for solvent system of THF or alcohol. The considerations of the useful indicator in this case are:

1) The sharpness of colour changes near the end point was considerably less than in comparable titrations in aqueous media.

2) The indicator itself has a considerable influence on the sharpness of the colour change. Consequently, the concentration of the indicator should be kept as low as possible.

3) The pH of the end point is independent of concentration. The colour change of an indicator is affected by the concentration of the salt. However, this effect must relatively slight, and is largely eliminated by an incorporation into the normality factor of the standard solution if the solution is standardised with the indicator.

The dissociation constant of the compound can be one of the key for selecting the appropriate indicator for each system. Table 1.3 shows the dissociation constants of maleic acid and succinic acid. The latter is a derivative form of maleic anhydride attached to modified polymers. Table 1.4 shows the pK_I of several indicators ever used in non-aqueous titration.

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Table 1.3 Dissociation constants for acids [39]

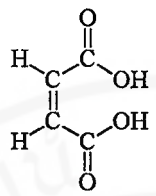
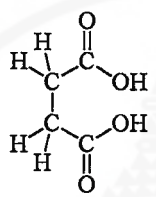
Acid	**Chemical structure**	**Dissociation constant in water, 25°C**	
		K_1 / pK_1	**K_2 / pK_2**
Maleic acid		1.20×10^{-2} 1.82	5.96×10^{-7} 6.59
Succinic acid		6.21×10^{-5} 4.18	2.32×10^{-6} 5.55

Table 1. 4 pK_I of various indicators.

Indicator		**Cresol Red**	**Bromphenolblue**	**Phenolphthalein**
pK_I of indicator	Water	7.0-8.8	3.0-4.6	8.2-9.8
	Methanol	No reference	8.5-9.2	Low colour intensity

The colour hue at the end point is not always exactly the same for different substances due to their different pK_a values. If the pK_1 and pK_2 of an acid match with the pK_I of indicator, the colour change of the indicator is observed near to equivalent point, and thus it can be used to determine the acid content.

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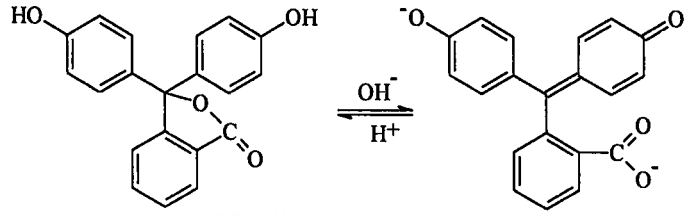
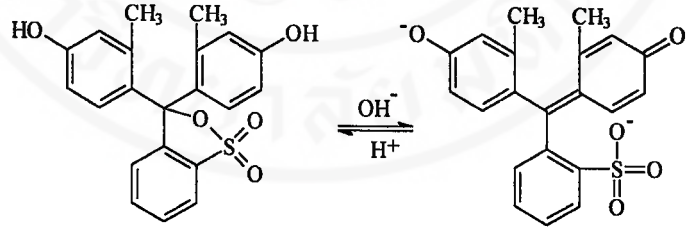
1.8.1.1 Phenolphthalein



Colourless Purple

Phenolphthalein is one of the most successful indicator for acid base titration in aqueous system. It had also been used in a determination of acid number of maleic anhydride grafted polystyrene.[19] But it has been reported that phenolphthalein is not the appropriated indicator in this case owing to the low colour intensity in alcoholic solvent.[39] However, whereas is found to work perfectly with the dimethylformamide, in which the colour change is extremely sharp and easy to observe.

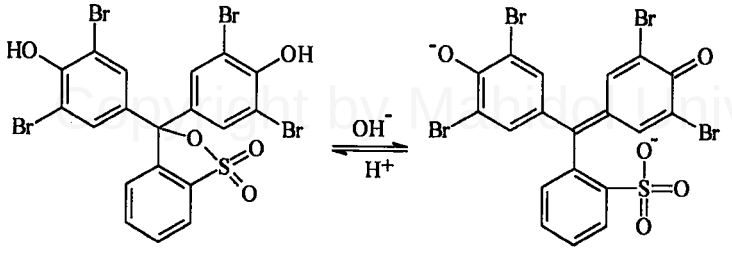
1.8.1.2 Cresol Red



Yellow Purple

In organic phase such as ether and alcohol, cresol red has certain advantages over phenolphthalein in acid number analysis eventhough no pK_I value is reported.

1.8.1.3 Bromphenolblue



Yellow Reddish blue

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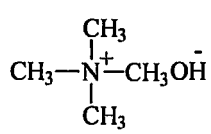
It was reported that bromphenolblue indicator has a colour change in the relative acidic range in aqueous media.[40,41] In methanol, the best condition for colour change is in rather basic condition which is similar to the phenolpthalein.

1.8.2 Choice of titrants

Generally in acid base titration, aqueous sodium hydroxide is considered to be successful titrant for determination of acid number. It has also been reported that the acid number of fully hydrolysed maleic anhydride grafted polystyrene was determined by titration with a standardised methanolic NaOH solution[19]. Tetramethyl-ammoniumhydroxide (TMAH) is another interesting titrant used in non-aqueous alkalimetry. It has numerous advantages such as a greater basic strength than alkali metal hydroxide, enable very weak acids to be titrated and also individual acids of different strengths in a mixture.[39,42] The majority of tetramethylammonium salts of weak acids are readily soluble. Nevertheless, its disadvantage is the low stability of the solution.



Tetramethylammoniumhydroxide (TMAH)

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1.9 Compatibilisation of polyethylene/polystyrene blends by an addition of copolymer

Blends of polyethylene (PE) and polystyrene (PS) have received appreciable attention, particularly with consideration to combine the inherent ductility of PE and the high modulus of PS. However, the immiscibility of PE/PS blends are obvious and responsible for the inferior mechanical properties of the resulting products. Attempts have been made to improve the blend performance by enhancement of the interfacial adhesion of the components through addition of a compatibiliser(block or graft copolymer) or by reactive compatibilisation.

Barentsen *et al.* .[29] studied blends of low density polyethylene (LDPE) and polystyrene (PS) using compatibilisation by an addition of a copolymer. They described the addition of graft copolymer of LDPE with PS (PS-*g*-LDPE) to LDPE/PS blends. The graft copolymers were prepared by Friedel-Crafts alkylation using melt mixing process at 195°C on laboratory mills. The graft copolymer was first melt blended with the polymer forming the dispersed phase before being added to the matrix polymer. Addition of 7.5% by weight of copolymer caused a substantial reduction in size of the dispersed phase, both PS rich and LDPE rich blends, which was evident from scanning electron micrographs as shown in Figure 1.2. The blends containing copolymer also possessed higher yield strength, elongation and breaking strength than the unmodified blends across the whole composition range, as well as possessed significantly increased impact strength.

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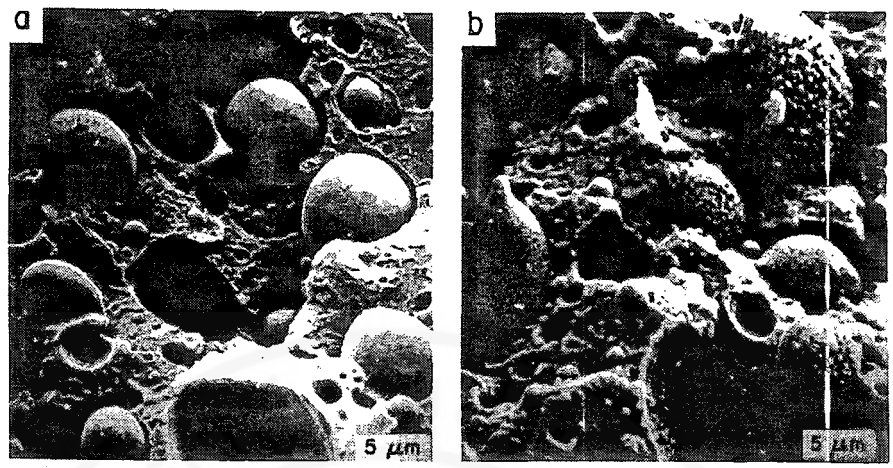

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Figure 1.2 Scanning electron micrographs of fracture surfaces of PS/LDPE blends with and without graft copolymer compatibiliser: (a) 75/25 PS/LDPE (b) 75/23.5/1.5 PS/LDPE/LDPE-*g*-PS

Locke and Paul also investigated LDPE/PS blends with the use of PS-*g*-LDPE graft copolymers as a compatibiliser for their systems.[29] This graft copolymer was formed differently by radiation grafting styrene monomer to LDPE backbone. LDPE pellets were swollen with styrene monomer then exposed to cobalt 60 γ-radiation. The copolymer produced with variation of the radiation doses was extracted and characterised. LDPE/PS (50/50) blends containing various levels of graft copolymer (up to 33% by weight) were produced by melt blending in a Barbender Plasticorder (10 min at 170°C). The most effective copolymer in terms of improving strength and elongation was that produced at a radiation dose of 0.5 megarads. The mechanism of blend properties improvement was believed to be due to the increased interfacial adhesion provided by the graft copolymer.

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Heiken *et al.* studied the effect of adding small amounts of both graft and block copolymer of PS and LDPE, with a wide range of structures, on the morphology and mechanical properties of PS rich LDPE/PS blends.[29] It was inferred that block

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copolymers had a tendency to form a third, low modulus, dispersed phase, in addition to being present at the LDPE/PS interface, effectively preventing some of the PS in the copolymer from contributing to modulus.

Fayt *et al.*[12] carried the melt blended of LDPE and PS in a two roll mill at 210°C in the presence of 9 % by weight hydrogenated diblock butadiene-styrene copolymers(hPB-*b*-PS) or tapered hPB-*b*-PS copolymers. The blends containing block copolymer showed improved dispersion of minor phase. The LDPE rich blends exhibit a finer dispersion of PS particles smaller than 1μm in LDPE matrix when modified with the tapered copolymer than with the pure copolymer. By contrast, PS rich blends show a fine, semicontinuous or continuous two phase structure. The strength and ductility of the blends were greatly improved by the addition of copolymers, particular for PS rich blends, and larger value of energy to break were reported. In particular, it was shown that the block copolymers produce better properties in the blends as shown in Table 1.5. [12,29]

The performance of the pure diblock copolymer was compared in the same composition and molecular weight with the tapered diblock copolymer. The authors found that the tapered diblock was a more effective compatibiliser than the pure diblock copolymer, in that it yields blends with finer morphology (for LDPE rich blends) and superior mechanical properties. Elongation at break values of the blends containing tapered diblock copolymer are twice those reported from the pure diblock blends at every composition.

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Table 1.5 Maximum improvement in ultimate tensile strength and elongation at break for LDPE/PS blends modified by graft or block copolymer

LDPE/PS composition (by weight)	Copolymer type	% Copolymer added (by weight)	Improvement in ultimate tensile strength (%)	Improvement in elongation at break (%)
70/30	Graft	9	100	*
	Block	9	70	900
	Block	9	90	3000
50/50	Graft	33	60	120
30/70	Graft	9	80	*
	Block	9	120	120
	Block	9	60	1300

Fayt *et al.* had also studied more systematically the effect of hydrogenated (PB-*b*-PS) on blends of PS with LDPE, LLDPE, HDPE and hydrogenated PB.[29] They concluded that in all cases phase size was significantly reduced and stabilised against coalescence in further processing, and interfacial adhesion was dramatically increased due to the added copolymers. Diblock copolymers with balanced composition were shown to be strikingly dependent on the molecular characteristics of the copolymers. The diblock was the most effective for this system to improve the elongation and tensile strength. The optimum condition was 10% weight loading of pure diblock and high molecular weight in 80:20 PS/LDPE blend system. It was possible to achieve toughening equivalent to that found in other commercial HIPS.

Ultracki and Sammut experimented on the LDPE/PS blends without or with 5 wt % of partially hydrogenated poly(styrene-*b*-isoprene) diblock copolymer (SEB).[43] Three compositions of blends were prepared containing LDPE:PS =1:2, 2:1 and 17:3 in a twin screw extruder. They found the dissymetry of the blend morphology in

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different blend compsitions. PS dispersed in spherical form in LDPE rich blends while at corresponding concentration LDPE formed fibril in PS matrix.

Hermes and Higgins[44] investigated melt mixed PS/PE blends in the presence of up to 16% of a semicrystalline PS-*b*-hPB diblock copolymers. They found that the diblock copolymers are capable of reinforcing the PS/PE interface depending on the molecular weight of the copolymers. As expected, the high molecular weight copolymers promote better adhesion between the phases than the low molecular weight copolymers. However, no corresponding trend is observed in the mechanical properties with copolymer molecular weight.

1.10 Compatibilisation of polyethylene/polystyrene blends by reactive processing

It is generally accepted in commercial application that *in-situ* compatibilisation of immisible blends is more interesting than by addition of a compatibiliser because of its cost effective. In reactive compatibilisation, it is necessary that each of the polymer to be blended possesses suitable reactive functionality. During melt blending, interchain block or graft copolymers may form through covalent or ionic bonding. The resulting copolymers which locate preferentially at the interface of the homopolymers lower the interfacial tension and also promote mechanical interlocking through entanglements, resulting in improved blend performance. [6] However, in some cases, coagents or functionalisers are added to better formation of interchain reaction between the components. Figure 1.3 shows general schematic of a sequential

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functionalisation/blending operation of functionalised polymers **A** and **B** in twin screw extrusion equipment.

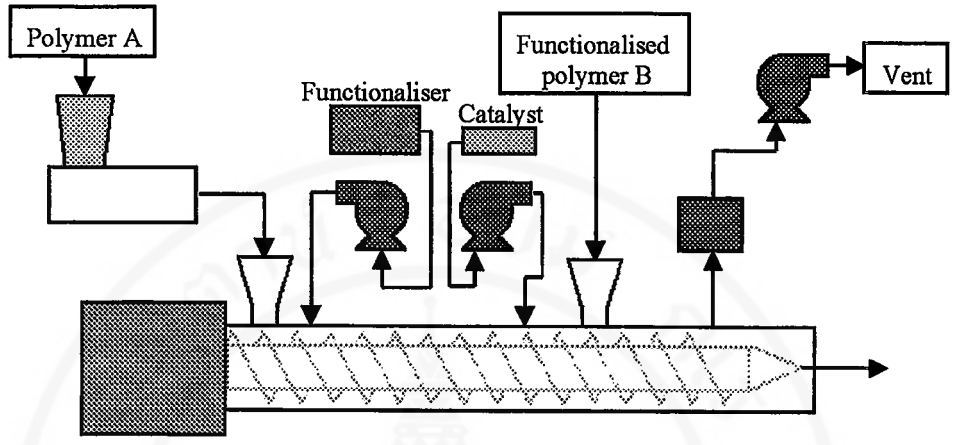

Figure 1.3 Schematic of a sequential functionalisation/blending operation in extrusion equipment.

Baker and Saleem investigated the influence of mixing conditions on mechanical, physical and morphology of reactive polystyrene with oxazoline functionality (OPS) and acid modified LDPE (CPE).[8] They found that the reactive blending of functional components gave materials with improved mechanical properties over unmodified PS/LDPE blends. The elongation at break was significantly higher for the reactive blend systems. This was attributed to the formation of an *in-situ* compatibiliser from the interchain reaction between the two blend components. The reaction mechanism is shown in Scheme 1.8.

If only one of the two polymers to be blended posscesses reactive functionality, *in-situ* compatibilisation may be occurred by an addition of radical initiators for providing free radicals in the graft reaction. It has been reported that polystyrene containing a minor amount of ortho-vinylbenzaldehyde is compatible with linear low density polyethylene (LLDPE) under the use of peroxide initiators and a

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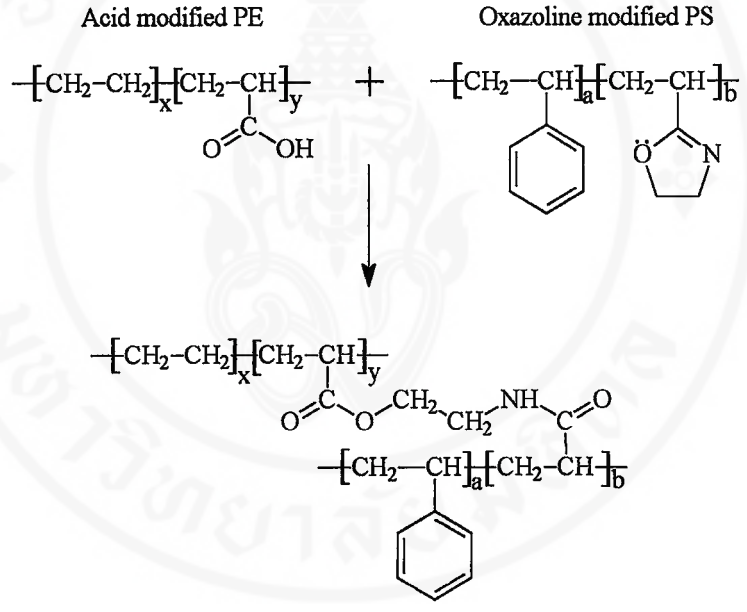
triallylisocyanurate (TAIC) as a coupling agent.[4]. It is apparent that a judicious loading of both peroxide and coupling agent gives positive effect on mechanical properties over the simple PS/PE blends. The presence of radical generators provide free radical on the polymeric backbone, followed by the establishment of effective coupling linkage occurs through the coupling agent. TAIC coagent displays significant role on enthalpy of fusion of blends and an improvement in adhesion between phases resulting from the grafting reaction, comparing to their additive-free counterparts.



Scheme 1.8 Proposed reaction between acid-modified PE and oxazoline-modified PS.

J.W. Teh and A. Rudin [5] described the addition of dicumyl peroxide (DCP) and triallyl isocyanurate (TAIC) coupling agent with 50/50 PS/PE blends. The Charpy impact strength of unnotched samples prepared from melt blending was found to be lower than that of the PS. Various processing conditions such as mixing rates of extrusion, screw speeds, and screw configurations did not affect the impact strength of the blends. It was found that the impact strength of reaction-extruded blends was initially reduced with a small addition of TAIC/DCP, but improved with further

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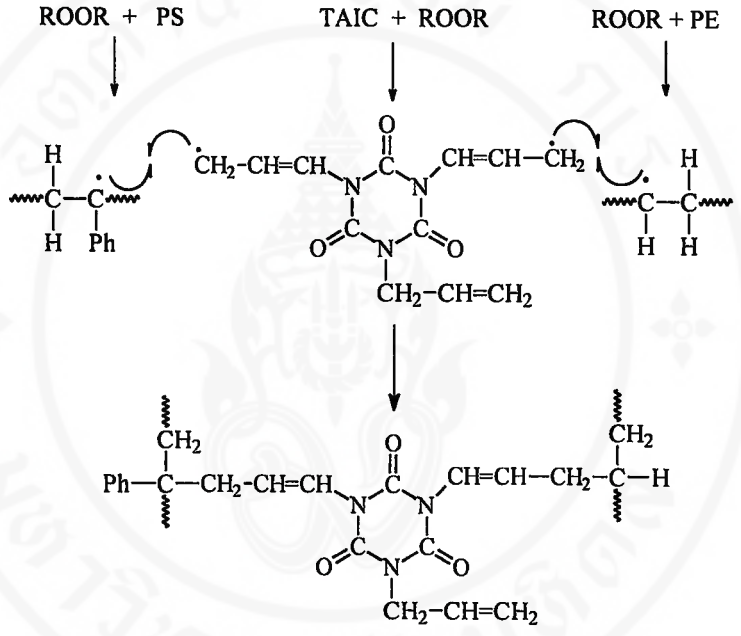
increase in the level of TAIC/DCP. However, with further increase in TAIC/DCP concentration, the impact strength decreased. The interfacial adhesion of the compatible PS/PE was postulated to be improved by the graft copolymers formed during reactive extrusion. A possible radical generation and coupling reaction in DCP/TAIC, PE and PS mixture is shown schematically in Scheme 1.9.



Scheme 1.9 Proposed radical generation of TAIC coupling coagent with DCP and coupling reactions between TAIC radical and PS and PE radicals

Examples of reactive compatibilisation of PE/PS blends involving copolymer formation through the catalytic reactions such as the use of Lewis acids in Friedel-Crafts reaction have been reported.[9,10] It is shown that PE-*g*-PS copolymer is established in PE and PS melt using a Lewis acid catalyst. The reaction mechanism is postulated through the mechanism of Friedel-Crafts benzene ring alkylation, as shown in Scheme 1.10.

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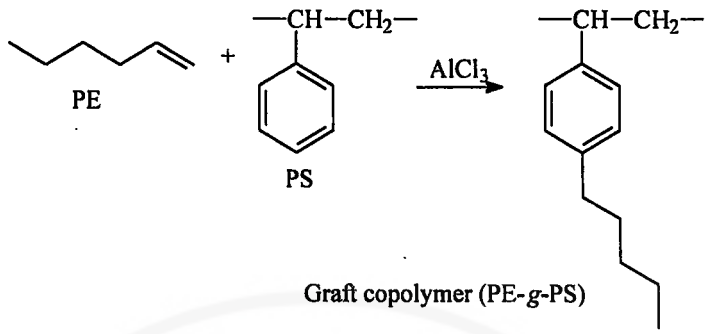

Scheme 1.10 Chemical reaction between PE and PS through Friedel-Crafts alkylation

The compatibilised blends had significantly improved mechanical properties, notably the elongation at break. The low catalyst concentrations and short resident time for extrusion led to a better compatibilised blend because of the lowering degradation of polymers. The crosslinking was not significantly observed as might be observed with peroxide compatibilisation of PE rich blend.

Zhang and Baker studied PE/PS blends using a new approach named a vector fluid system.[45] The concept is to convey a selected monomer or a vector fluid to a blend interface and induce *in-situ* copolymer formation. In their systems, styrene monomer and dimethyl phthalate (DMP) were chosen as the vector fluids for the polyethylene substrate. It was found that with the presence of radical generators, styrene can be grafted onto the PE surface without any crosslinking of PE. The PE-*g*-PS copolymer forms as a layer at the PE surface and therefore it has potential to compatibilise an immiscible PE/PS blends.

Zhi Wang *et al.* had developed the PE/PS blends with the first partially crosslinked the PE by a small amount of dicumyl peroxide (DCP) and subsequently melted blending with PS. [24] Finally, a styrene-butadiene-styrene block copolymer (SBS) was added to the melt and mixed. The residual free radicals in the PE reacted

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with SBS and induced crosslinking between the polymer chains. The crosslinking had a significant impact on the mechanical properties including the impact properties and the tensile properties. Scanning electron micrograph (SEM) results indicated the significant increase in the interfacial adhesion though the domain sizes had not much changed. Transmittion scanning micrograph (TEM) results revealed the encapsulation of the thin SBS layer on the PE particle.

1.11 Objective and scope of the present thesis

The aim of this thesis is to study the PE-rich LDPE/PS blend characteristics. Two approaches were planned; compatiblisation of the blend by addition of various types of compatibilisers prepared by reactive extrusion and *in-situ* compatibilisation. The influences of compatibiliser types and loadings on mechanical properties and rheological properties of the blends are also included.

The thesis including two parts;

Part 1: Preparation and characterisation of various types of compatibilisers using mainly a twin screw extrusion.

1. Functionalisation of low density polyethylene and polystyrene with maleic anhydride i.e. PE-*g*-MA and PS-*g*-MA
2. Copolymer of low density polyethylene and polystyrene
   2.1 LDPE grafted with PS by using maleic anhydride as a crosslinker (PE-MA-PS)

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2.2 LDPE grafted with PS by using amine compounds as a crosslinker (PE-HMM-PS)

2.3 LDPE grafted with PS by Friedel-Crafts alkylation (PE-*g*-PS)

3. Copolymer of polypropylene and polystyrene (PP-*co*-PS)

Part 2: Blending of 75:25 LDPE/PS blends.

1. Compatibilisation of LDPE/PS blends with 1,3 and 5 phr of various compatibilisers prepared in part 1.
2. *In-situ* compatibilisation of LDPE/PS blends by using reactive components such as PE-*g*-MA and PS-*g*-MA, with and without amine compounds.

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CHAPTER II

EXPERIMENTAL

2.1 Materials, chemicals and equipments

The materials, chemicals and equipments used in the present study were as follow:

2.1.1 Materials

Materials	Grade/Abbreviation	Suppliers
Commercial low density polyethylene	Polene MM 1018 (7.5 g/10 min) /LDPE	Thai Polene Industry
Commercial polystyrene	Styron 656D (8 g/10 min)/PS	Dow chemical
Commercial polypropylene	Profax 6331 (12 g/10 min)/PP12 El-pro P400S (3.5 g/ 10 min)/PP3.5	HMC Polymer Thai polyethylene
Degraded polypropylene	Prepared by degrading PP3.5 using 0.2 phr of DCP in a twin screw extruder/ PP55	-

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2.1.2 Chemical

Chemical	Grade/Abbreviation	Supplier
Dicumyl peroxide	Purum/DCP	Fluka chemical
Maleic anhydride	Purum/MA	Fluka chemical
Hexamethylenediamine	Purum/HMD	Fluka chemical
4,4′-Diaminodiphenylsulphone	Purum/DAPS	Fluka chemical
Anhydrous aluminiumtrichloride	Purum/$AlCl_3$	Fluka chemical
Tetrahydrofuran	Purum/THF	J.T. Baker
n-Heptane	Purum/C_7H_{16}	J.T. Baker
Toluene	Purum/C_7H_8	Fluka chemical
Decalin	Purum/$C_{10}H_{18}$	Fluka chemical
Benzoic acid	A.R.	Fluka chemical
Succinic acid	A.R.	Fluka chemical
Maleic acid	A.R.	Fluka chemical
Succinic anhydride	A.R.	Fluka chemical
Tetramethylammonium hydroxide	A.R./TMAH	Fluka chemical
Cresol Red	A.R.	Fluka chemical
Bromphenol Blue	A.R.	Fluka chemical
Phenolphthalein	A.R.	Fluka chemical
Molecular sieve	Type 4 Å, ⅛ " rod Pore diameter 4 Å	-

2.1.3 Equipments

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The equipments used in the present study are listed below.

1. Twin screw extruder (Prism TSE 16 TC, with a screw diameter of 16 mm)
2. Differential scanning calorimeter (Perkin Elmer DSC7)

3. Melt flow indexer (Kayaness D-7053)
4. Injection moulding machine (Dr. Boy 22S)
5. Tensile tester (Instron Model 4301)
6. Capillary rheometer (Rosand 2000)
7. Broching tool (Davenport serial no. 640/40)
8. Fourier transform infrared spectrometer (Perkin Elmer System 2000)
9. Scanning electron microscope (Hitachi S2500)
10. Impact tester (BS 2782)

2.2 Compatibiliser preparation

Six different types of compatibiliser were prepared as follows.

2.2.1 Reactive functional polymers

2.2.1.1 Maleic anhydride grafted low density polyethylene (PE-*g*-MA)

Maleic anhydride (MA) was grafted onto LDPE using dicumyl peroxide (DCP) as a radical initiator. The weight ratio of PE: MA: DCP is 100:5:0.2. The grafted reaction was carried out in a co-rotating twin screw extruder (Prism TSE 16TC) with a screw diameter of 16 mm and the temperature profile from feed zone to die was 190, 210, 220, 230 and 230°C, respectively. The screw speed was set at 50 rpm. The extrudate, obtained in the rod strand form, was cooled in water and then palletised into granule form.

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2.2.1.2 Maleic anhydride grafted polystyrene (PS-*g*-MA)

PS-*g*-MA was prepared by using weight ratio of PS: MA: DCP equal to 100:5:0.2. The processing conditions were the same as used in 2.2.1.1.

2.2.2 Copolymer of low density polyethylene and polystyrene

2.2.2.1 Low density polyethylene grafted polystyrene through maleic anhydride linkage (PE-MA-PS)

In this case MA was used to form a linkage between PE and PS. Dicumyl peroxide was used as a radical initiator. PE-MA-PS was prepared by using weight ratio of LDPE:PS:MA:DCP equal to 50:50:1:0.2. The processing conditions were the same as in 2.2.1.1.

2.2.2.2 Low density polyethylene grafted polystyrene through hexamethylenedimaleimide linkage (PE-HMM-PS)

Hexamethylenediamine (HMD) was used as a linkage between PE and PS. Weight ratio of 50:50:1:1:0.2 (LDPE:PS:MA:HMD:DCP) was used for preparation of the PE-HMM-PS. The processing conditions were the same as in 2.2.1.1.

2.2.2.3 Low density polyethylene grafted polystyrene through Friedel-Crafts alkylation (PE-*g*-PS)

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PE-*g*-PS was prepared by Friedel-Crafts alkylation, using $AlCl_3$ catalyst. Approximately 25 g of LDPE and PS, which were dried in vacuo for 4-5 hr before use, were placed in a 500 ml three necks round bottom flask. The reaction flask was

then equipped with a magnetic stirrer, a condenser connecting a two-ways, a septum and a stopper as shown in Figure 2.1. The system was evacuated and purged several times with dry N_2 before addition of 300 ml of dried decalin and 5 g of anhydrous $AlCl_3$ (dried in vacuo for 4-5 hr before use). The reaction was allowed to proceed with stirring for 12 hr at 130°C under dry N_2. The reaction mixture was cooled down and filtered to separate yellow solid or $AlCl_3$. Polymer product was obtained by precipitation in excess distilled methanol. The obtained product was finally dried in vacuo at 40°C at least 12 hr. It has to be noted that the decalin used in this study was kept in a conical flask containing 4Å molecular sieves at room temperature for at least 24 hr before utilisation.

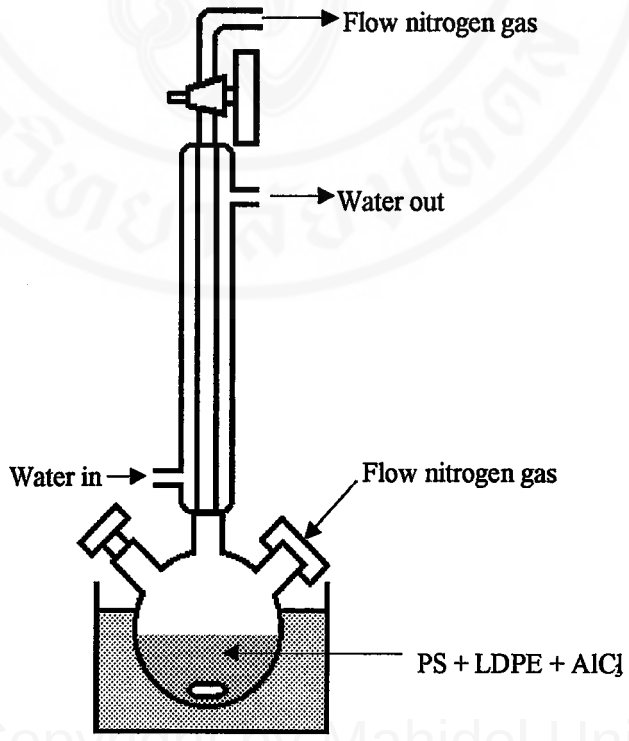

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Figure 2.1 Reaction apparatus for chemical modification of PS and LDPE by Friedel-Crafts alkylation

2.2.3 Copolymers of polypropylene and polystyrene (PP-*co*-PS)

The series of PP-*co*-PS were prepared through reactive extrusion. Composition of PP: PS was 50:50. Variation of MFI value of PP and DCP loading were carried out. The processing conditions were similar to that described in 2.2.1.1.

Table 2.1 Composition of materials for preparation of PP-*co*-PS series

Materials	2SP3.5	4SP3.5	2SP55	4SP12
PP3.5	50	50	-	-
PP12	-	-	-	50
PP55	-	-	50	-
PS	50	50	50	50
DCP (phr)	0.2	0.4	0.2	0.4

2.3 Determination of maleic anhydride content (MA content)

The amount of MA grafted on PS and LDPE was determined from acid titration with standardised tetramethylammoniumhydroxide (TMAH). The evaluation of the titration method was carried out by using maleic anhydride, maleic acid, succinic anhydride and succinic acid with three different indicators including bromphenolblue, cresol red and phenolphthalein were used for acheiving the best end point. In our system, the best indicator was cresol red.

For PS-*g*-MA, three different sample types were titrated with TMAH. The first one was crude PS-*g*-MA, the second was purified PS-*g*-MA obtained by dissolving the crude PS-*g*-MA in tetrahydrofuran (THF) and precipitated into methanol to remove the free maleic anhydride (MA). The precipitate was recovered and dried. The third type was hydrolysed PS-*g*-MA obtained from redissolving the purified PS-*g*-MA

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in THF and a little drops of distilled water was added. The solution was stirred overnight in order to fully hydrolyse the anhydride groups.

For PE-*g*-MA, three different sample types were also titrated with TMAH. The first one was crude PE-*g*-MA, the second was purified PE-*g*-MA obtained by dissolving the crude PS-*g*-MA in hot toluene (70°C) and precipitated into methanol to remove the free maleic anhydride (MA). The precipitate was recovered and dried. The third type was hydrolysed PE-*g*-MA obtained from redissolving the purified PS-*g*-MA in hot toluene and a half toluene volume of distilled water was added. The mixture was refluxed overnight in order to fully hydrolyse the anhydride groups.

The MA content was determined from Equation (2.1).

$$MA\,[wt\%] = \frac{98 \times V_t \times C_t}{n \times C_p} \qquad (2.1)$$

where V_t = Volume of TMAH solution (ml)

C_t = Concentration of TMAH solution (N)

C_p = Concentration of polymer solution (wt %)

n = Number of the substituted proton (H^+) with TMAH cation (1 or 2)

Note: 98 is the molecular weight of maleic anhydride

Standardisation of tetramethylammoniumhydroxide (TMAH) solution

0.2 ml of 2.2 N TMAH in methanol solution was placed in 500 ml volumetric flask. Making the volume with absolute methanol. Standard base solution was standardised against 0.001 N benzoic acid in THF solution (0.048 g in 500 ml).

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2.4 Polymer blending

2.4.1 Compatibilisation by an addition of copolymers

LDPE and PS of 75/25 were blended in a twin screw extruder with various compatibiliser loadings (1, 3 and 5 phr.). The screw speed was maintained at 125 rpm and percent torque at 30-50% while the temperature profile from feed zone to die was 190, 210, 220, 230 and 230°C, respectively. The extrudate was cooled in water before pelletising into granule form.

2.4.2 *In-situ* compatibilisation

In the case of *in-situ* compatibilisation of LDPE/PS blends, reactive functional polymers such as PE-*g*-MA and PS-*g*-MA and amine compounds such as hexamethylenediamine (HMD) and 4,4'-diaminodiphenylsulphone (DAPS) were employed. The compound formulation was shown in table 2.2 and the processing conditions were the same as in the section 2.4.1.

Table 2.2 Compound formulation of 75/25 PE/PS blends

Sample	LDPE	PS	PE-*g*-MA	PS-*g*-MA	HMD	DAPS
EgSMA3	75	25	3	3	0	0
EgSMA3H	75	25	3	3	1.5	0
EgSMA3D	75	25	3	3	0	3

2.5 Moulding

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The PE/PS compounds were moulded into tensile and impact test bars using an injection moulding machine (Dr. Boy 22S with a screw diameter 24 mm). The size

and shape of the tested specimens used as followed ASTM D-638-83 and ASTM D-256-93b, respectively. The first ten mouldings of each sample were discarded to ensure that the specimens with right composition were collected.

2.6 Mechanical property testing

2.6.1 Tensile testing

The tensile specimens were kept at room temperature for seven days before testing. The tensile tester (Instron Model 4310) was used to evaluate the tensile properties with a crosshead speed of 50 mm/min and load cell of 1 kN.

2.6.1.1 Yield stress

Tensile stress at yield and /or maximum tensile stress were calculated in relation to the original cross-sectional area of the test piece by the following equation.

$$\sigma = \frac{F}{A} \qquad (2.2)$$

where σ = The tensile stress (MPa)

F = The force (N)

A = The initial cross sectional area (mm^2)

2.6.1.2 Percent elongation at break

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The percent elongation at break was calculated in relation to the original gauge length by the following equation.

$$\text{Percent elongation} = \frac{(l - l_o)}{l_o} \times 100 \qquad (2.3)$$

where l = The distance in millimeters between the gauge marks at break

l_o = The original gauge length (115 mm)

2.6.1.3 Secant modulus

Secant modulus is the ratio of stress (nominal) to the corresponding strain at any specified point on the stress-strain curve. It is expressed in force per unit area, usually in MPa. In this experiment secant modulus at 1% strain was obtained with the following equation.

$$E_S = \frac{F}{(0.01 \times A)} \qquad (2.4)$$

where E_S = The secant modulus (MPa)

F = The force (N)

A = The initial cross sectional area (mm^2)

2.6.2 Impact testing

The impact specimens were kept at room temperature for seven days before notching with a broching tool (Davenport serial no. 640/40). The notch bars were tested in accordance with the Charpy test standard ASTM D256-93b, using a 2 J hammer. This arbitrary measurement of energy (J) can be converted into impact strength (kJ/mm^2) by dividing with the cross-sectional area of specimens.

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2.7 Rheological measurement

The rheological properties of the homopolymers and their blends were measured at 190°C using melt flow indexer and capillary rheometer .

2.7.1 Melt flow index (MFI)

A Kayaness melt indexer was employed in this study. The melt flow indices were determined at 190°C with 2.16 kg load as describe in the ASTM D1238 procedure. The extrudate was cut off and weighed every thirty seconds. These weights were used to calculate the flow rate in g/ 10 min.

2.7.2 Capillary rheometer

The experiments were carried out with LDPE/PS blends containing compatibilisers as mention in 2.2.6 using a Rosand 2000 capillary rheometer. The temperature was set at 190°C, die length was 16 mm and capillary diameter was 1 mm.

2.8 Compound characterisation

2.8.1 IR spectroscopy

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The chemical structure of polymer and copolymer samples was characterised using IR spectroscopy technique. Thin film of polymer sample was prepared and then

analysed on a Perkin Elmer System 2000 FTIR spectrometer with a number of scan of 16 and the wavelengths in the range of 4000-400 cm^{-1}.

2.8.2 Differential scanning calorimetry

Polymer sample of 0.01 g was put into an aluminum pan and sealed properly with an aluminum cover. Perkin Elmer DSC7 was used to determine the glass transition temperature (T_g) and melting temperature (T_m). The sample was heated from -150°C to 150°C with a scanning rate of 20°C/min.

2.8.3 Solvent extraction of compatibilisers and blends

2.8.3.1 PP-*co*-PS

PP-*co*-PS samples were put into Soxhlet apparatus. THF was used in the first step to extract PS homopolymer during 48 h. The insoluble part of THF extraction was further extracted with toluene for 48 h, to remove PP-*co*-PS and a little PP homopolymer. The residual was PP homopolymer.

2.8.3.2 LDPE/PS blends

Solvent extraction of various blends was carried out using Soxhlet apparatus. n-Heptane was used in the first step to extract LDPE homopolymer during 48 h. then the n-heptane insoluble compounds were extracted with THF for another reflux time of 24 h. The weight of the residue was recorded and calculated as % grafting using the equation 2.5.

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$$\% \text{ Grafting} = \frac{W}{W_o} \times 100 \qquad (2.5)$$

where W_o = Weight of sample before extraction

W = Weight of sample after extraction

2.9 Morphology investigation

The morphology of blends was analysed using scanning electron microscope (SEM). The cryogenic fracture of the notched impact bars were studied. The section containing the failured surface was cut from the test bar and the specimen was etched with THF and kept overnight to remove PS minor phase. The specimen was coated with Pd-Pt in Hitachi (E-102) ion sputter for 6 minutes before being examined with SEM (Hitachi S2500).

The average diameter measurement of the dispersed phase was carried out, using Image Pro Plus software. The average diameter of dispersed phase ($\overline{D}$) was calculated as equation 2.6

$$\overline{D} = \frac{\Sigma N_i D_i}{\Sigma N_i} \qquad (2.6)$$

where N_i is the number of particle with diameter D_i

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CHAPTER III

RESULTS AND DISCUSSION

Part 1 Preparation and characterisation of compatibilisers

3.1 Functionalisation of polyethylene and polystyrene with maleic anhydride

In many cases of polymer blending systems, chemical reaction occurring between the matrix and dispersed phase improves adhesion even though it is only one of the criteria for improving polymer properties. This is recognised as the basic of *in-situ* or reactive compatibilisation of immiscible blends. For polymers such as polyethylene and polystyrene, without reactive functional groups, they are hardly compatible as there are not the possibility of copolymer formation from these polymer components. Therefore, an introduction of functional groups onto these polymers backbone is required. It has been reported that a few percentage of functional groups presented in polymer chain is sufficient for reactive compatibilisation of immiscible polymer blends [8]. In our cases, 5% of maleic anhydride (MA) were employed for modification of polyethylene and polystyrene by using a twin screw extruder and dicumyl peroxide as an initiator. Under melt shearing as well as radical generators, macroradicals were formed on the polymer chains. These radicals then reacted with

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the monomers added. Since MA is a non-homopolymerised monomer, the active radical forming at the end of the double bond tends to abstract a labile hydrogen from another polymeric chain for termination. However, this active radical can also react with another macroradical to form interchain reaction. The general mechanism is known and presented in Figure 3.1.

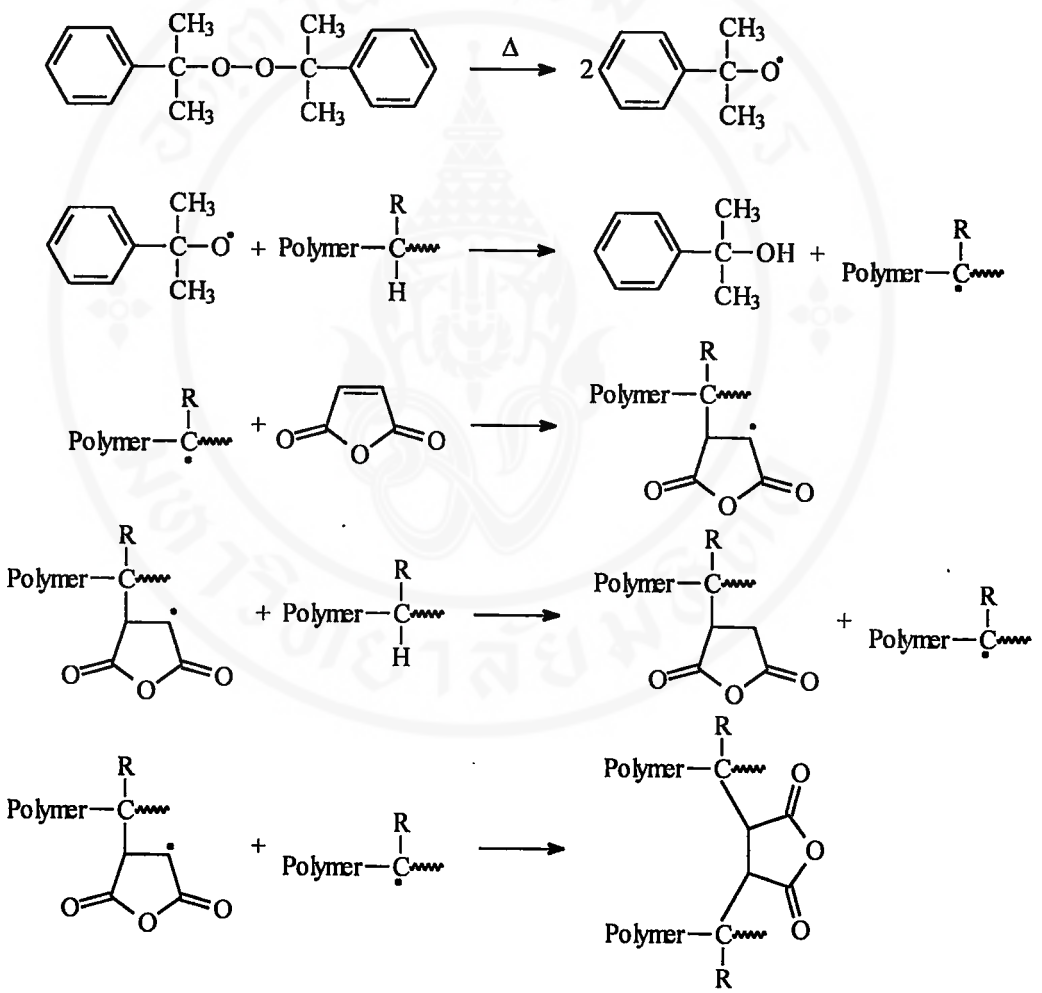

Figure 3.1 Proposed reaction between maleic anhydride with polymer in the presence of DCP [25,46]

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3.1.1 Chemical structure of modified polymers

In the case of low density polyethylene (LDPE) modified by MA, grafting of MA onto the PE backbone was generally expected. Macroradicals occured on the polyethylene (PE) chain by the attack of oxy radical reacted with MA monomer, resulting in maleic anhydride grafted low density polyethylene (PE-*g*-MA). The reaction mechanism is similar to Figure 3.1. However, it is not surprising that almost 50 % gel content were found which is due to PE macroradical recombination in competition with the reaction of MA. Additionally, the MA monomer can also act as a crosslinker between the polymer chains.[1] It has been published elsewhere that under the radical initiator, hydrogen atom on the polymeric backbone is easily abstracted, preferentially the tertiary hydrogen atom than secondary one. LDPE contains certain amounts of branch point, i.e. tertiary hydrogen, therefore facilitating the hydrogen abstraction for generation of macroradicals. The origin of gel formation may therefore come from two major reactions shown in Figure 3.2.

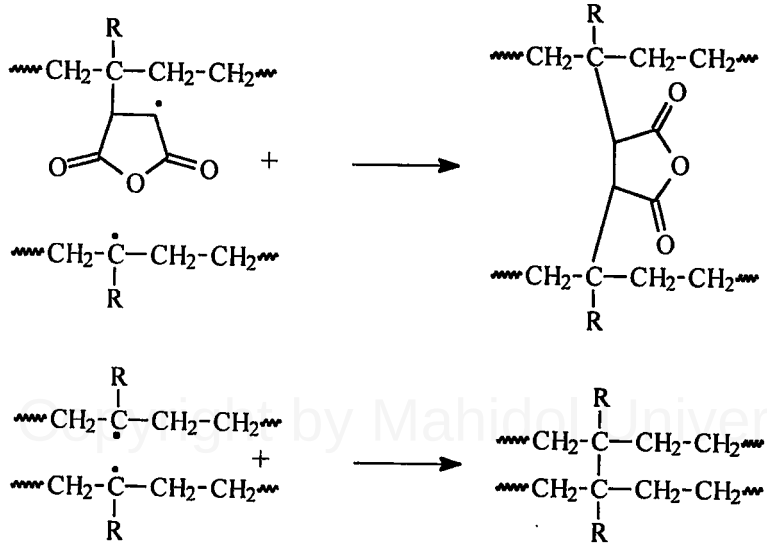

Figure 3.2 Proposed gel formation in LDPE during melt processing

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The modified LDPE was analysed by FTIR method. The FTIR spectrum of the starting material and the modified product are shown in Figures 3.4 to 3.9 as well as their band assignments are listed in Table 3.1. The chemical structure of PE-*g*-MA is composed of succinic anhydride ring attached to the polyethylene backbone. The extra absorption bands comparing to the virgin PE, appeared at 1860 and 1780 cm^{-1} corresponding to ν(C=O) of five membered ring of cyclic anhydride confirming the fixation of MA onto LDPE chains. The appearance of absorption band at 1235 cm^{-1} also indicated the stretching of C-O-C in cyclic compounds. However, the ring opening reaction of cyclic anhydride attached to the PE chain was detected, by the presence of an absorption band at 1710 cm^{-1} corresponding to ν(C=O) of carboxylic acid function. For commercial application, it is not interesting to purify the modified PE before utilisation therefore the crude product from the functionalisation of LDPE was also analysed by FTIR, similar characteristic absorption peaks were recognised as the purified product. It is therefore not possible to identify whether there is some residual MA presented in the modified products by simply characterisation by FTIR method. The comparison of the determination of MA content from unpurified and purified PE-*g*-MA in section 3.2.3 reveals that about 20 % of MA were decomposed during the melt processing and about 40% MA were attached to the PE backbone while about 40% MA were unreacted and stayed in the PE matrix. The residual MA might be able to further react with reactive radical in later utilisation.

When the PE-*g*-MA was hydrolysed, it was clear that the absorption peaks of cyclic carbonyl compound at 1860 and 1780 cm^{-1} were disappeared and the strong intensity of characteristic peak at 1710 cm^{-1} was occurred instead.

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For the fixation of MA onto polystyrene (PS), the reaction was carried out as in the case of PE-*g*-MA. The reaction occurring in melt blending of PS with MA is presented in Figure 3.3. The macroradicals generated from the attack of oxy radical (RO°) from peroxide were rather stable, due to delocalisation of the radicals into the benzene ring. Consequently, chain scission in β-position to the macroradical site of PS tends to take place. It was therefore found that the low molecular weight modified PS was obtained. However, fixation of MA onto PS was taken place in small quantity. There are not an evidence of crosslinked product detected. The absorption band at 1850 and 1780 cm^{-1} , in Figure 3.8 indicated the fixation of MA onto PS. These bands are corresponding to ν(C=O) of five membered ring of cyclic anhydride. The extra absorption band at 1235 cm^{-1} due to the stretching of C-O-C in cyclic compounds also confirms the existence of the MA on PS. The appearance of an absorption peak around 1710 cm^{-1} reveals the ring opening reaction of the cyclic anhydride similar to the case of PE-*g*-MA. This peak is characteristic of ν(C=O) of carboxylic acid, confirmed by the strong intensity of absorption peak when the modified PS is subjected to hydrolysis.

The characteristic absorption bands found for crude PS-*g*-MA are similar to those of the purified PS-*g*-MA. The results in section 3.2.3 reveal that small amounts of MA were fixed onto the PS backbone. About 30% of MA were decomposed and approximately 8% MA were fixed on the purified product. For the raw PS-*g*-MA, the percent modification was about 70%, therefore quite significant numbers of MA (over 60%) are not attacked by the macroradicals.

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The hydrolysed PS-*g*-MA was also investigated by FTIR technique. The 1850 and 1235 cm^{-1} absorption peaks were disappeared, but there was a small peak at 1780 cm^{-1} that may be attributed to ν(C=O) of carboxylic acid derivative. The comparison of IR spectra between purified and hydrolysed PS-*g*-MA is shown in Figure 3.9. The results indicate the conversion from anhydride ring to acid groups.

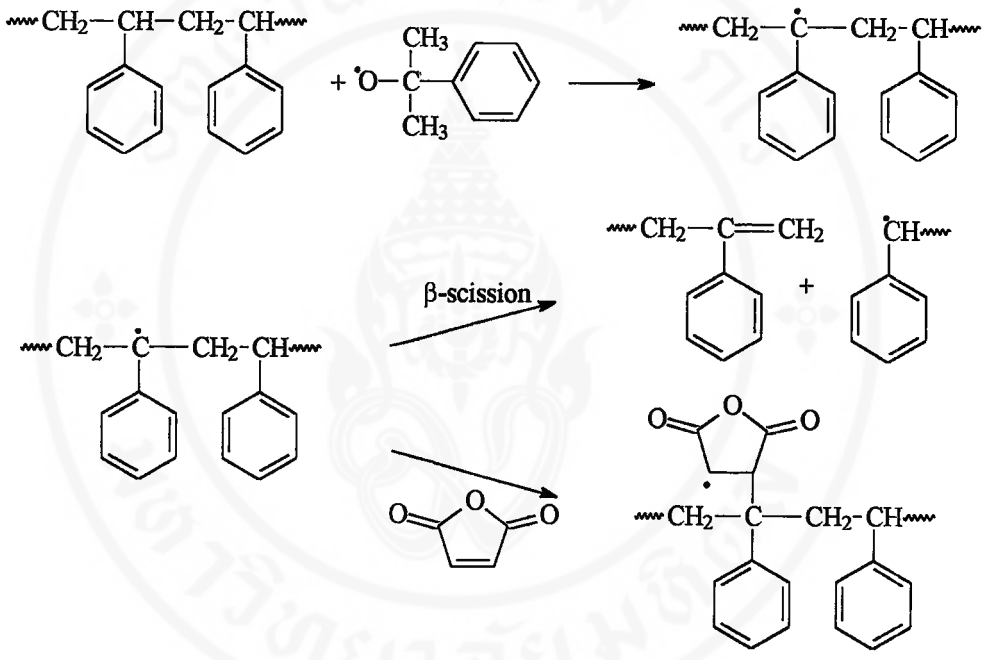

Figure 3.3 Proposed reaction between MA and PS in the presence of DCP

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Table 3.1 Assignment of IR absorption bands of polystyrene, low density polyethylene and their modified forms

Vibration	Wave number, ν (cm^{-1})									
	PS	**LDPE**	**PP**	**PE-*g*-PS**	**PE-*g*-MA**	**PS-*g*-MA**	**Hydrolyzed PS-*g*-MA**	**PE-MA-PS**	**PE-HMM-PS**	**PP-*co*-PS**
C-H stretching										
CH_2 (as)	2924	2923	2917	2924	2924	2923	2923	2923	2923	2915
CH_2 (s)	2850	2850	2829	2849	2850	2850	2850	2850	2850	2829
			2720							2720
C-H bending										
CH_3 (as), CH_2 (s)	1453	1463	1460	1463	1464	1452	1452	1452	1452	1460
CH_3 (s)	1374	1377	1376	1376	1377	1373	1372	1370	1370	1376
C-H rocking										
$-(CH_2)n-$ n = 2 or 4	-	730	-	-	730	-	-	730	730	-
$-(CH_2)n-$ n > 4		720			720			720	720	
C-H stretching (benzene ring)	3082,			3082		3082	3082	3082	3082	3082
	3060,	-	-	3062	-	3060	3060	3060	3060	3060
	3025			3025		3025	3025	3025	3025	3025
C=C stretching (benzene ring)	1601,			1601		1601	1601	1601	1601	1601
	1493,	-	-	1492	-	1493	1493	1493	1493	1493
	1452					1452	1452	1452	1452	1452
C-H bending summation bands	1943,					1943	1943	1943	1943	1943
(benzene ring)	1867,	-	-	-	-	1870	1870	1870	1870	1870
	1800,					1800	1800	1800	1800	1800
	1741					1748	1748	1748	1748	1748
C-H bending (out of plane)	757,	-	-	753	-	757	757	757	757	757
(benzene ring)	698			700		700	700	700	700	700
C=O stretching	-	-	-	-	1783	1780	1780	1780	-	-
(cyclic anhydride or acid)					1862	1850				
C=O stretching (conjugated)	-	-	-	-	1711	1711	-	1712	1711	-
C-O-C stretching (cyclic compound)	-	-	-	-	1226	1235	-	1227	-	-
C=O (imide ring)	-	-	-	-	-	-	-	-	1702	-
C-N or N-H stretching	-	-	-	-	-	-	-	-	1402	-

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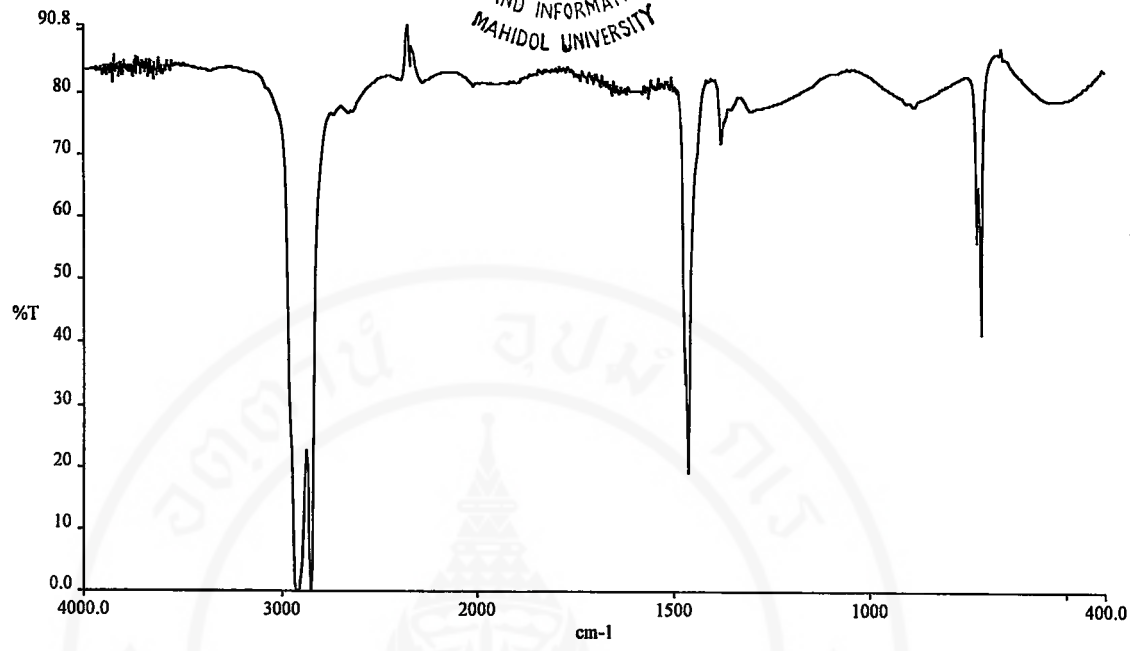

Figure 3.4 IR spectrum of LDPE (Polene)

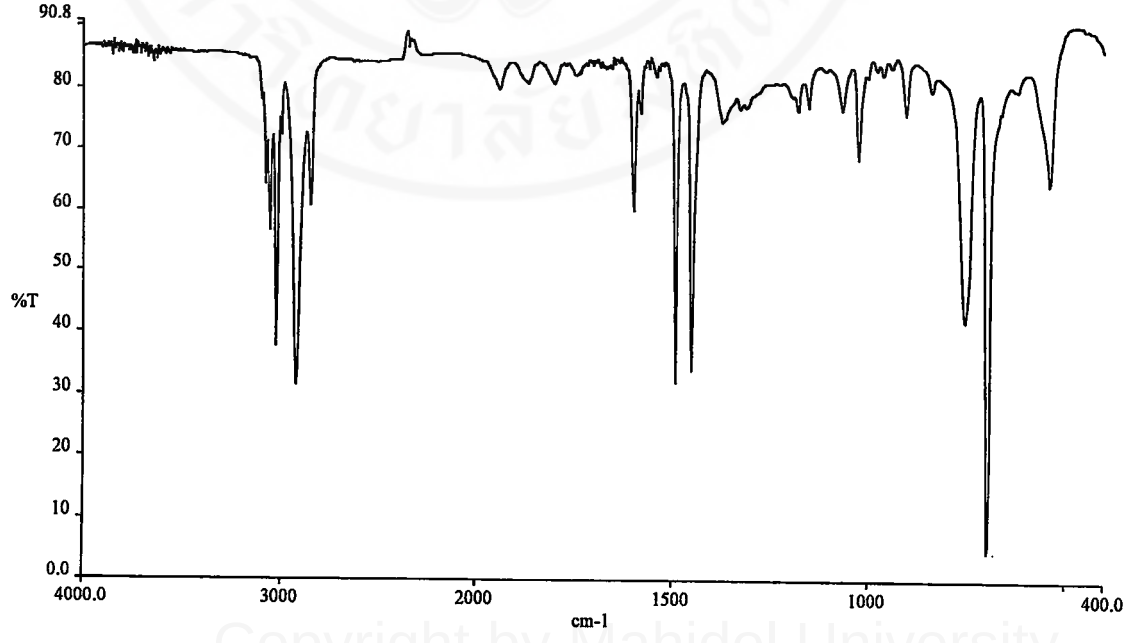

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Figure 3.5 IR spectrum of polystyrene (Styron)

45022

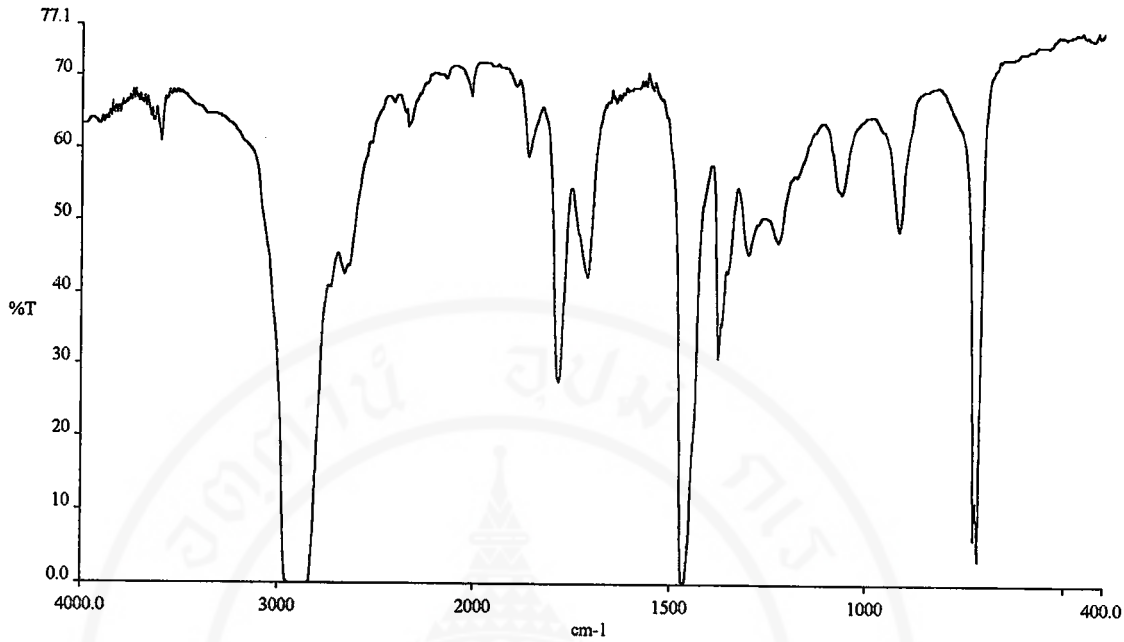

Figure 3.6 IR spectrum of crude PE-*g*-MA

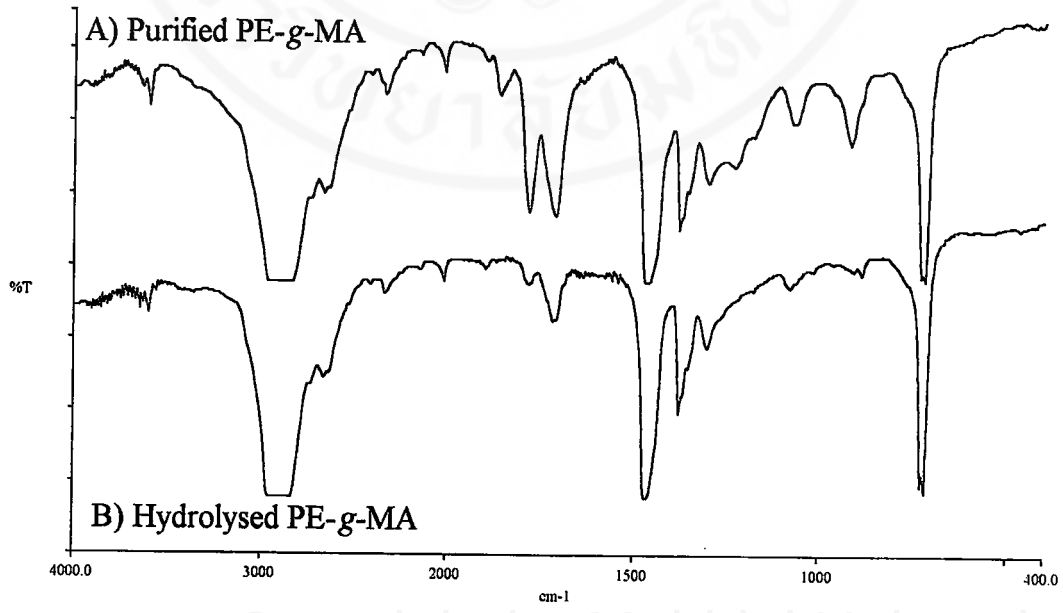

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Figure 3.7 Comparison of IR spectra of purified PE-*g*-MA and hydrolysed PE-*g*-MA

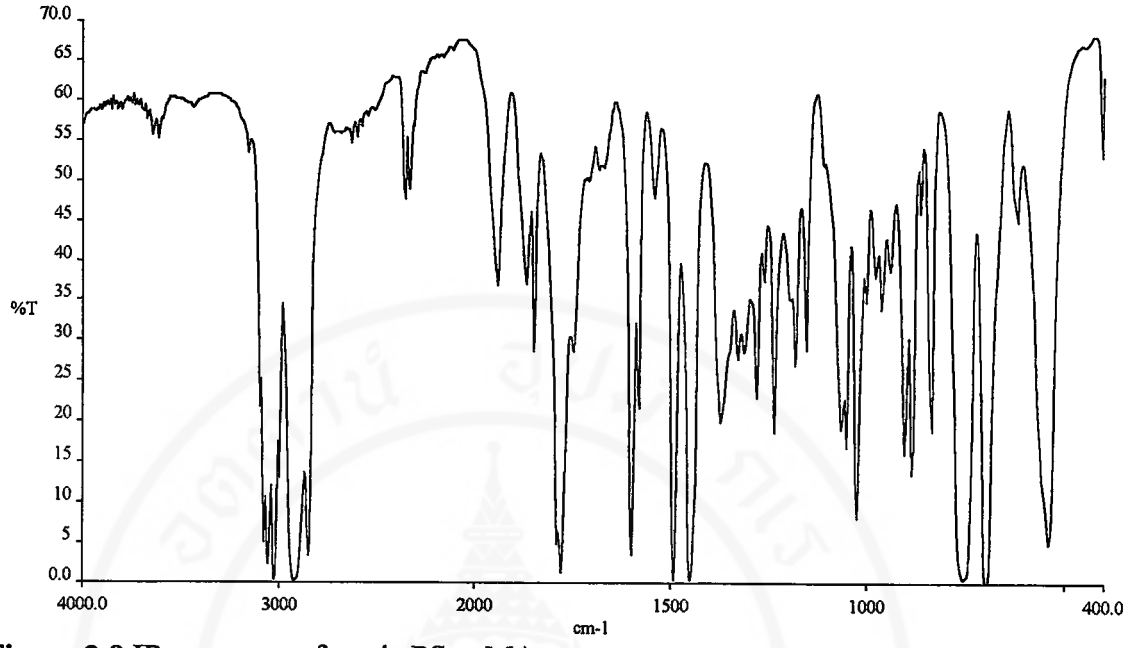

Figure 3.8 IR spectrum of crude PS-*g*-MA

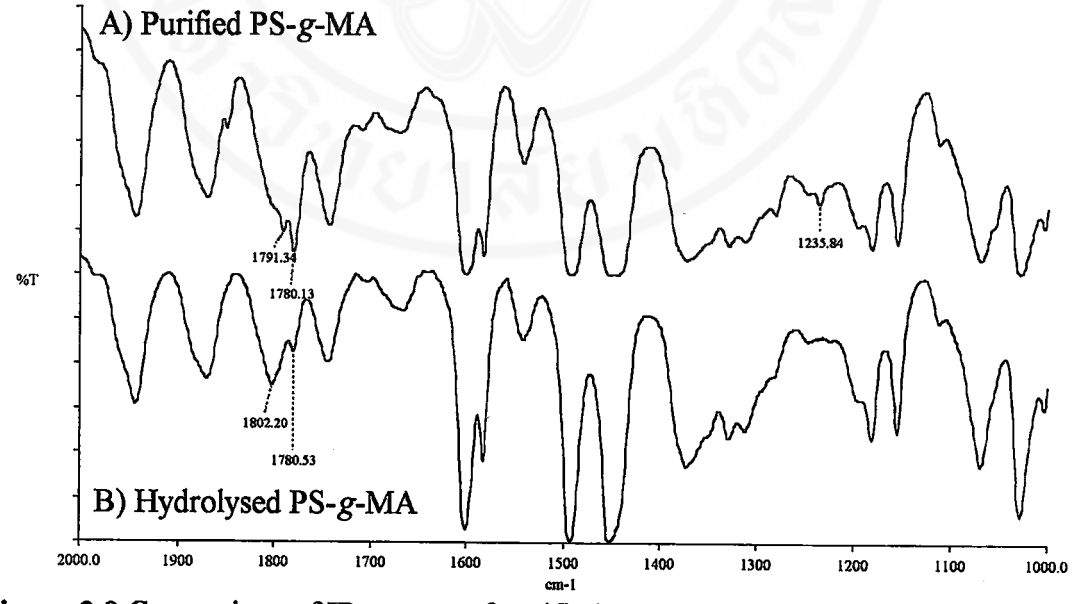

Figure 3.9 Comparison of IR spectra of purified PS-*g*-MA and hydrolysed PS-*g*-MA

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3.1.2 Determination of maleic anhydride content

The MA content of PE-*g*-MA and PS-*g*-MA can be quantified by various methods. Generally the extra oxygen atoms of MA attached to the polymeric backbone can be detected by elemental analysis technique. However, purified material is needed and defined molecular structure is important. For our system, the modified products contained both cyclic structure and ring opening moieties, therefore the elemental analysis of the amount of oxygen atom might not give a reliable result, due to an undefined amount of the ring opening of cyclic anhydride which caused excessive amount of oxygen atom. Titration of the MA grafted on the polymer chains is therefore a technique used in this investigation.

3.1.2.1 Titration of maleic and succinic derivatives as model compounds

It has been found that succinic anhydride and succinic acid can be easily quantified by titration with sufficiently strong base such as tetramethylammonium hydroxide (TMAH). [39,42] However, application of this technique for modified polymeric materials may cause some trouble because they are normally soluble in organic system, and therefore the titration of maleic anhydride, maleic acid, succinic anhydride and succinic acid in organic solution were initially clarified. In addition, the choice of a good indicator for the detection of the end point needs precious selection. In the case of non-aqueous solvents, the end point is much more difficult to discern, and the best procedure was to titrate to a certain colour hue. Among the few indicators being studied in very dilute solutions to detect the end point, phenolphthalein, cresol

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red and bromphenolblue give adequately the sharpness of the colour changes. Their characteristic equilibriums were already mentioned in section 1.8.

The use of three indicators in titration of maleic acid, succinic acid, maleic anhydride and succinic anhydride was compared. Three different known amounts of each model compound were titrated at the same condition. The reliability of each model compound is presented in Table 3.2 in terms of % experiment, which was calculated by the following equation:

$$\% \text{ Experiment} = \frac{\text{Amount of model compound obtained from titration x 100}}{\text{Amount of model compound used}}$$

Table 3.2 Reliability of the indicators in the term of % experiment

Reagent		% Experiment		
		Cresol Red	**Bromphenolblue**	**Phenolphthalein**
Maleic acid	Average	97.2	105.0	undetectable
	Variance	0.6	1.9	-
Succinic acid	Average	96.2	78.3	undetectable
	Variance	0.9	4.2	-
Maleic anhydride	Average	94.4	100.0	undetectable
	Variance	2.8	1.9	-
Succinic anhydride	Average	84.1	undetectable	undetectable
	Variance	5.2	-	-

It was found that the titration of maleic acid, maleic anhydride and succinic acid with the presence of cresol red, % experiment approached 100. For succinic anhydride, % experiment of 84.1 is obtained. This deviation may be due to the slower rate of hydrolysis of succinic anhydride than maleic anhydride. The colour change in this case was difficult to be visually observed hence less reliability. Furthermore, the double bond in maleic acid and its anhydride might bring in the effect of conjugated system and hence delocalisation of the pine electron, therefore these compounds were

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easier to be detected than the succinic components.[46] The pK_1 and pK_2 of succinic acid and its anhydride do not match with the pK_I of the indicator. It can be noted that phenolphthalein did not give clear colour change at the end point. The best results were obtained from the use of cresol red as an indicator. Bromphenolblue gave good results in the case of maleic acid and maleic anhydride. However, for the polymer modified by MA in later section, succinic derivative is to be considered. Therefore, bromphenolblue might not be a good indicator for such system.

3.1.2.2 Determination of maleic anhydride grafted on modified polymers

The amounts of maleic anhydride grafted on LDPE and PS were evaluated by using titration technique at the similar condition to the model compounds mentioned in section 3.1.2.1. Three different types of products were used for five repeating titrations. The first type was crude products which were the PE and PS modified by MA before purification. Second type was the purified products obtained from reprecipitation in methanol. Since the results of IR spectroscopy of both PE-*g*-MA and PS-*g*-MA mentioned in section 3.1.1 showed the characteristic peak of acid function, due to the ring opening reaction of anhydride moieties, fully-hydrolysed of the grafted products were the third type of our samples. The results of MA content detected by using three different indicators are shown in Table 3.3.

Considering first with the results using cresol red as an indicator. In the case of crude products, 4 % and 3.5 % weight of MA were found in PE-*g*-MA and PS-*g*-MA respectively. As 5 % weight of MA were added in both systems, about 20 to 30 % of MA were lost by decomposition. In these samples MA grafted on the polymer

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chains and residual or unreacted MA might be both involved and responsible for the results of MA content. The amount of MA grafted on the polymer which would be in the form of succinic anhydride derivative was quantified by titration. It is not surprising that the amount of MA contents formed was less than

Table 3.3 Titration results of maleic anhydride grafted on polyethylene and polystyrene using various indicators.

Modified polymers	MA content (% wt)	Cresol Red	Bromphenol blue	Phenolphthalein
Crude PE-*g*-MA	Average	4.1	3.3	undetectable
	Variance	0.2	0.1	-
Purified PE-*g*-MA	Average	1.8	0.9	undetectable
	Variance	0.1	0.0	-
Hydrolysed PE-*g*-MA	Average	1.8	0.8	undetectable
	Variance	0.2	0.1	-
Crude PS-*g*-MA	Average	3.5	2.8	undetectable
	Variance	0.2	0.0	-
Purified PS-*g*-MA	Average	0.4	0.2	undetectable
	Variance	0.0	0.0	-
Hydrolysed PS-*g*-MA	Average	0.4	0.2	undetectable
	Variance	0.0	0.0	-

the crude products i.e. 1.8 and 0.4 % weight for PE-*g*-MA and PS-*g*-MA respectively. It is noticed that MA could hardly graft onto PS chain. This is not unexpected, as in the presence of peroxide initiator, PS tends to degrade much more than generation of grafting reaction with monomers. For the fully hydrolysed products, acids function of the grafting sites were titrated. It was found that similar amount of MA attached to PE was found in the cases of purified PE-*g*-MA (1.81 %) and hydrolysed PE-*g*-MA (1.76 %). Similar the results were also obtained in purified PS-*g*-MA and hydrolysed PS-*g*-MA. These results not only reveal the grafting contents of MA on the polymer

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backbone but also assure the reliability of the technique used in this experiment. Similar trend of grafting results were obtained when bromphenolblue were used but at lower values. From the titration of model compounds, it can be concluded that the titration results from cresol red is more reliable than from bromphenolblue.

3.2 Copolymer of low density polyethylene and polystyrene

It has been reported that in LDPE/PS blend system with an addition of compatibiliser, the performance of the blends depends in positive direction of the amounts of copolymer i.e. PE-*g*-PS found in the blend components.[9,10,29] Therefore, it is optimisticly interesting to prepare such components for further utilisation in LDPE/PS blends. Three types of copolymers were planned; PE grafted with PS by using MA as a crosslinker, PE grafted with PS in the presence of MA and amine compound (hexamethylene bismaleimide, (HMM) and hexamethylene bissuccinimide, (HSM)) and PE grafted with PS by Friedel-Crafts alkylation.

3.2.1 PE grafted with PS by using MA as a crosslinker (PE-MA-PS)

It was reported earlier that in melt shearing of PE and PS in the presence of radical generator, macroradicals were generated on the backbone of PE and PS. In this section, both PE and PS were melt-blended with MA in the presence of DCP similar reaction might occur. It might be postulated that the macroradicals generated in both PE and PS chains reacted with MA generating PE-*g*-MA and PS-*g*-MA. The competition with interchain reaction between PE and PS macroradical with the grafted MA chain, resulting in formation of PE-MA-PS products, crosslinked PE and PS chain scissioned. The proposed structure of PE grafted with PS through MA

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crosslinker is shown in Figure 3.10. The FTIR studies of the purified PE-MA-PS demonstrated the absorption bands at 1780 and 1870 cm^{-1} corresponding to ν(C=O) of conjugated cyclic anhydride unit. The other characteristic peaks were 1712 and 1227 cm^{-1} corresponding to ν(C=O) of carboxylic group and ν(C-O-C) of cyclic ether, respectively. Significant peak at 1601 cm^{-1}, characterisic of aromatic component of PS was also detected. IR spectra and assignment of absorption bands in Fig. 3.12 and Table 3.1,respectively.

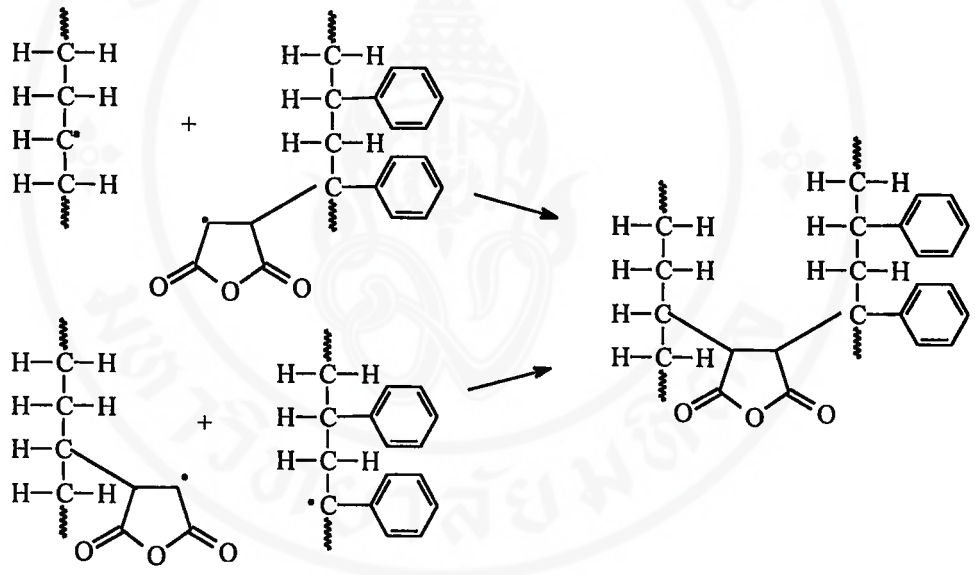

Figure 3.10 Proposed reaction between PS and LDPE through MA linkage

3.2.2 PE grafted with PS by using amine compound as a crosslinker (PE-HMM-PS)

According to the section 3.2.1, if the MA grafted with PE or PS without instantaneous attack to the macroradical of PS or PE respectively, only PE-*g*-MA or PS-*g*-MA would be the major products. Additional compound is needed and amine compound is generally known as a good nucleophile for tranformation of cyclic anhydride into cyclic imide. Therefore, hexamethylene bismaleimide (HMM), and

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hexamethylene bissuccinimide (HSM), were selected for promoting the interchain reaction between PE and PS through imide linkage, and therefore copolymers of PE-HMM-PS and PE-HSM-PS could be occurred respectively. The proposed imidisation reaction occurring between PE and PS is shown in Figure 3.11.

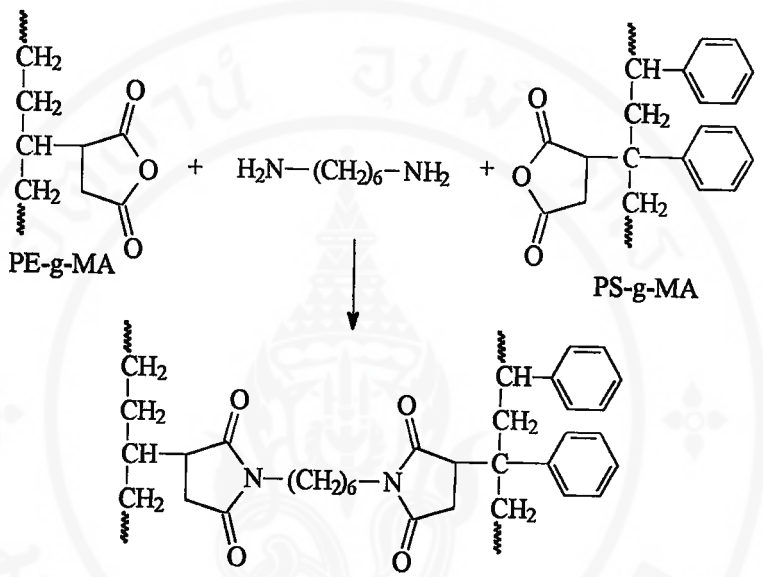

Figure 3.11 Proposed imidisation reaction between diamine compound and MA grafted on polymer

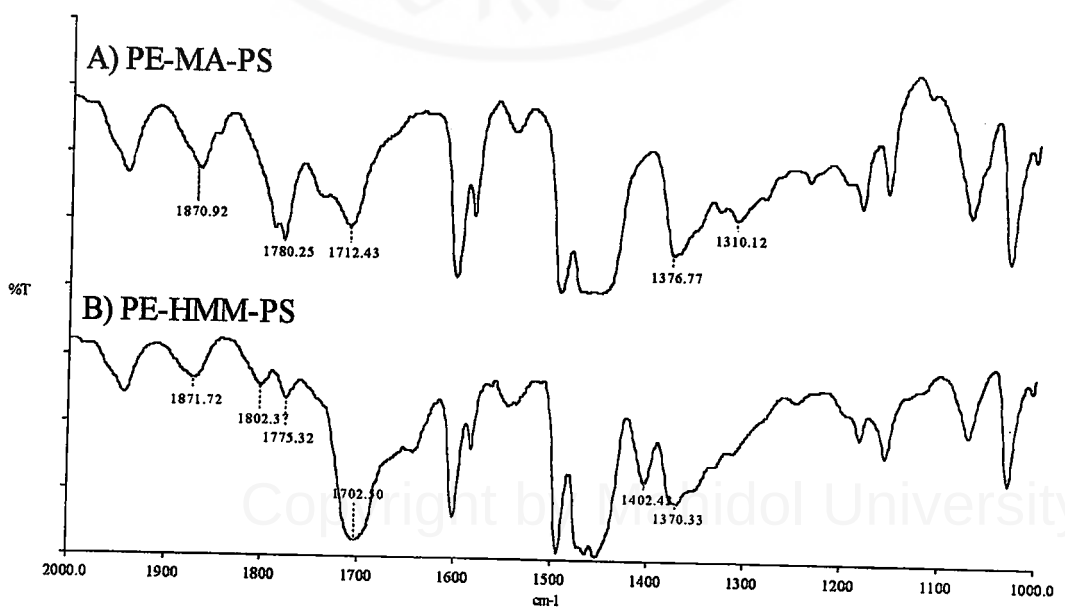

Figure 3.12 Comparison of IR spectra of PE-MA-PS and PE-HMM-PS

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IR spectrum of the PE-HMM-PS shows the extra absorption bands at 1702 cm^{-1} corresponding to ν(C=O) of cyclic imide compound. The other characteristic peak is found at 1402 cm^{-1} corresponding to ν(C-N) or ν(N-H) of primary amine compound. [30,27] The IR spectra and data were compared with the PE-MA-PS to distinguish the functional group taking place that was shown in Figure 3.12 and Table 3.1 respectively. Similar characteristics in IR absorption spectra were also noticed in the case of PE-HSM-PS copolymer.

3.2.3 PE grafted with PS by Friedel-Crafts alkylation (PE-*g*-PS)

In the case of PE grafted with PS (PE-*g*-PS) by using Lewis acid catalyst such as $AlCl_3$, the reaction is believed to occur through the Friedel-Crafts alkylation principle as reported previously. [9,10] The generation of electrophilic sites on the PE chain can be occurred from the reaction of catalyst with impurities such as water to form a complex, which then reacts further with unsaturated compounds, that is presented from the disproportionation reaction of the PE preparation. The PE carbocation reacts with the benzene ring of PS, forming PE-*g*-PS. The reaction steps of Friedel-Crafts alkylation were presented in Figure 3.13. The resulting PE-*g*-PS has the structure as the branched polyethylene grafted on the benzene ring on the PS, generally at the *para* position owing to its steric hindrance effect. IR spectrum in Figure 3.14 shows the main characteristic absorption peaks of LDPE in conjunction with the appearance of the absorption bands at 1601, 1492 and 700 cm^{-1}, implying the presence of PS in this copolymer.

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The PE-*g*-PS copolymer prepared by Friedel-Crafts reaction was purified by solvent extraction. LDPE was extracted by n-heptane and PS was extracted by THF.

The residual product was believed to be the copolymer PE-*g*-PS. The graftability of PS on the backbone of LDPE was evaluated by construction a calibration curve of %PS in PE/PS blends. The peak height ratio between 720 and 700 cm^{-1}absorption bands of LDPE and PS respectively was used for the calibration curve as shown in Figure 3.15 and Table 3.4. However, it is clearly shown that the straight line is not obtained, and therefore it might not be able to get a good result from this calibration

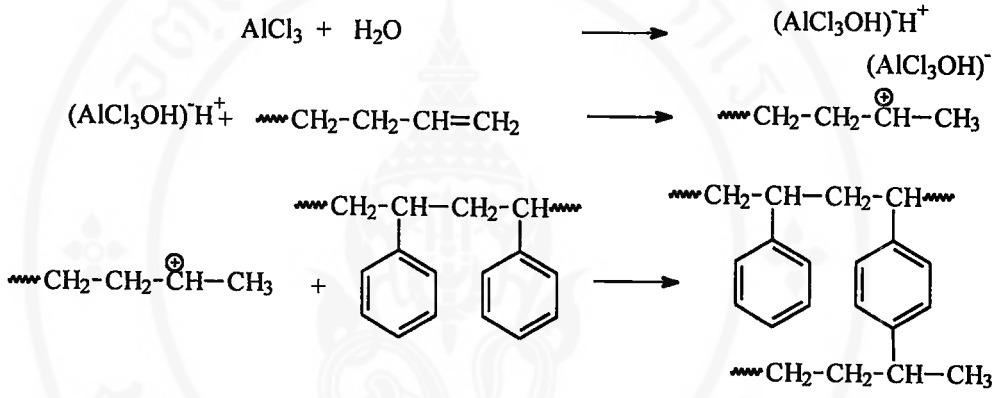

Figure 3.13 Proposed mechanism of Friedel-Crafts alkylation between PS and LDPE with the presence of $AlCl_3$ catalyst

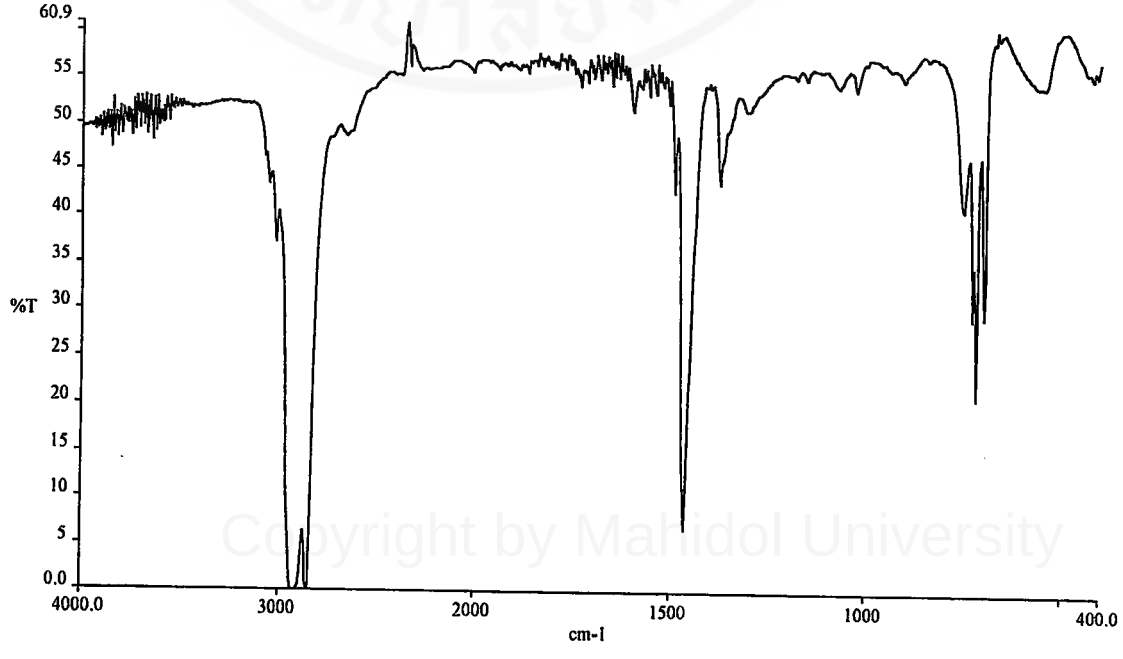

Figure 3.14 IR spectrum of PE-*g*-PS

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curve. It was found that the peak area ratio of PE and PS found from PE-*g*-PS is beyond the curve, resulting in an undetermined amount of the PS in PE-*g*-PS, it can be assumed that very small quantity (less than 10 %) of PS attached to the LDPE.

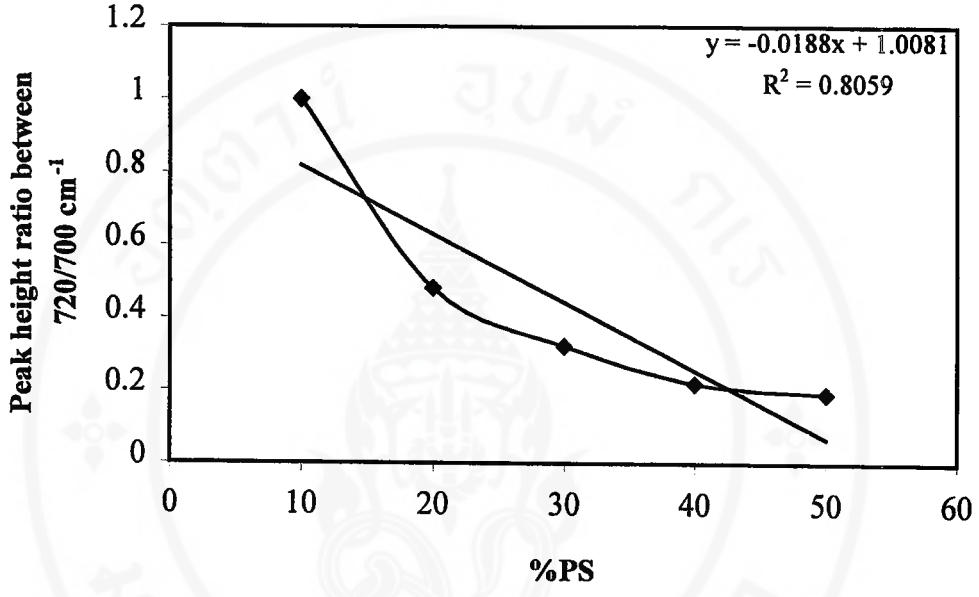

Figure 3.15 Calibration curve of %PS versus peak height ratio between 720 and 700 cm^{-1} in LDPE/PS blends

Table 3.4 PS content of PE-*g*-PS

Spectrum peak	PE-g-PS
720 cm^{-1}	2.1
700 cm^{-1}	0.9
Peak height ratio	2.33
% PS in the copolymer	Not available

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3.3 Copolymer of polypropylene and polystyrene (PP-*co*-PS)

Polypropylene (PP) has a comparative nature to PE in terms of chemical structure but it behaves at a similar manner as PS in melt shearing in the presence of a radical initiator, i.e. tendency to degradation reaction via chain scission. Therefore, melt blended PP and PS in the presence of DCP, tentative forming of copolymer between PP and PS is optimisticly expected. In this section, various molecular weights PP defined in terms of melt flow index (MFI) of 3.5, 12 and 55 were used to react with PS. The reaction between PP and PS was carried out in a twin screw extruder with different amounts of dicumyl peroxide initiator (0.2 and 0.4 phr). Both PP and PS macroradicals are generated from the attack of oxy radical undergo β-chain scission as shown in Figure 3.16, resulting in possibly terminal active end radicals. Cross-chain recombinations of these radicals lead to termination, forming copolymer of PP and PS, optimistically a block type. Terminated products can also be homopolypropylene and homopolystyrene. In addition, graft copolymer of polystyrene and polypropylene could be formed during mixing. Over all reaction mechanisms were proposed in Figure 3.17.

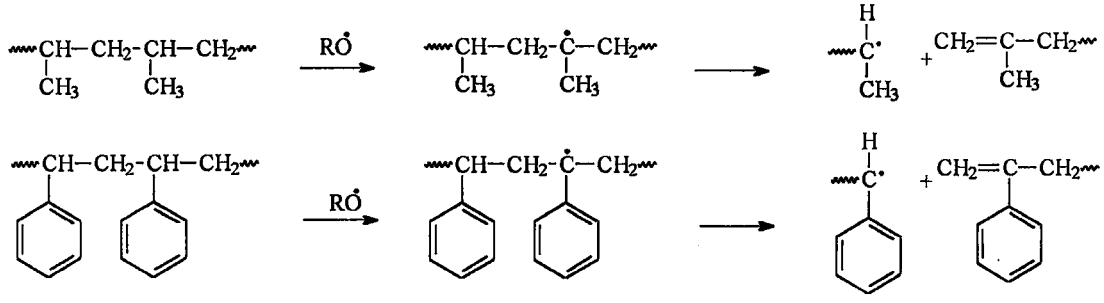

Figure 3.16 Degradation of PP and PS via β-scission

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The homopolystyrene was separated from the PP and the PP-*co*-PS by extraction in THF for 48 h in Soxhlet apparatus. Then, toluene was used for the

second extraction of the copolymer. PP which is crystalline polymer remained unattack by toluene and THF. Percentages by weight of each homo- and copolymer for different PP samples were compared as shown in Table 3.5. It was found that relatively low amount of the copolymer was formed. This is in accordance with the nature of PP and PS which favour degradation reaction rather than grafting reaction.

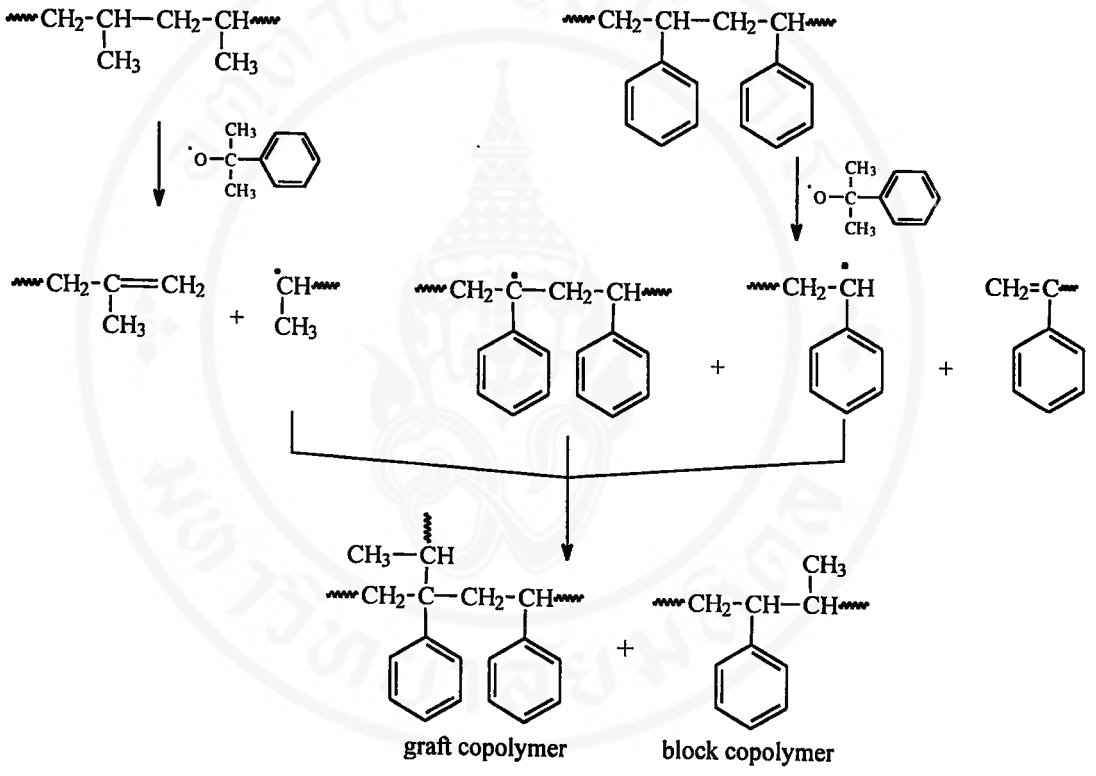

Figure 3.17 Reaction of PP and PS during melt processing via macroradical

Table 3.5 % Weight of homopolystyrene, copolymer and polypropylene from reaction between PP and PS through reactive extrusion

Weight (%)	2SP3.5	2SP55	4SP3.5	4SP12
Homopolystyrene (THF extracted part)	48.28	49.13	43.77	43.74
PP-*co*-PS (toluene extracted part)	2.47	2.14	11.96	13.67
Homopolypropylene (residue)	49.25	48.73	44.27	42.59

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The PP spectra of various MFIs are shown in Figure 3.18. It was found that there is no significant difference in characteristic absorption band detected. The PP-*co*-PS extracted product was analysed by FTIR. The IR spectra in Figure 3.19 show the occurrence of significant absorption peaks of PP at 1376 cm^{-1} and PS at 1600 and 1493 cm^{-1}, confirming the formation of PP and PS copolymers. The 1376 cm^{-1} peak of PP was used for calculation of grafting ability with the peak of 700 cm^{-1} of PS.

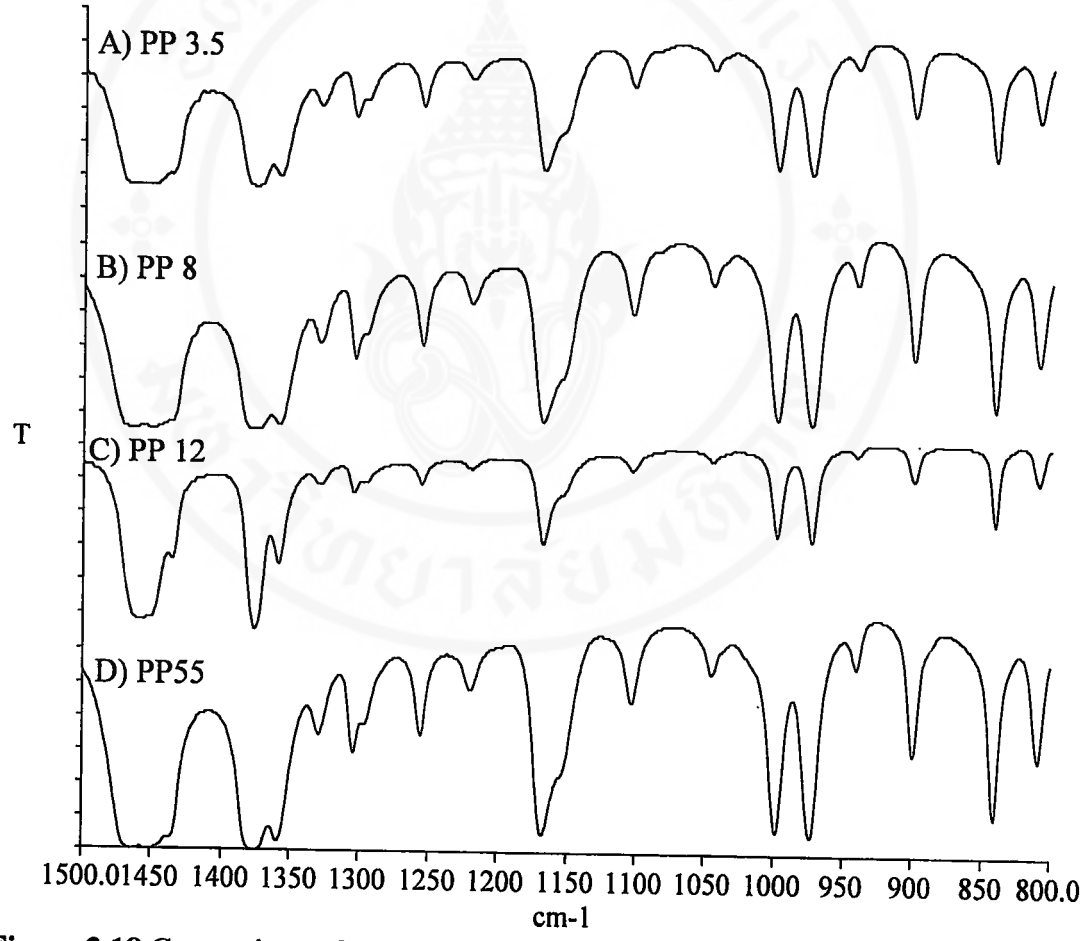

Figure 3.18 Comparison of IR spectra of PP with different MFI

The residual PP reveals the presence of ketone or aldehyde group at about 1720-1730 cm^{-1} in IR spectrum (Figure 3.20), coming from degradation and oxidation reaction at the elevated temperature.[50] The reaction mechanism was proposed in Figure 3.21.

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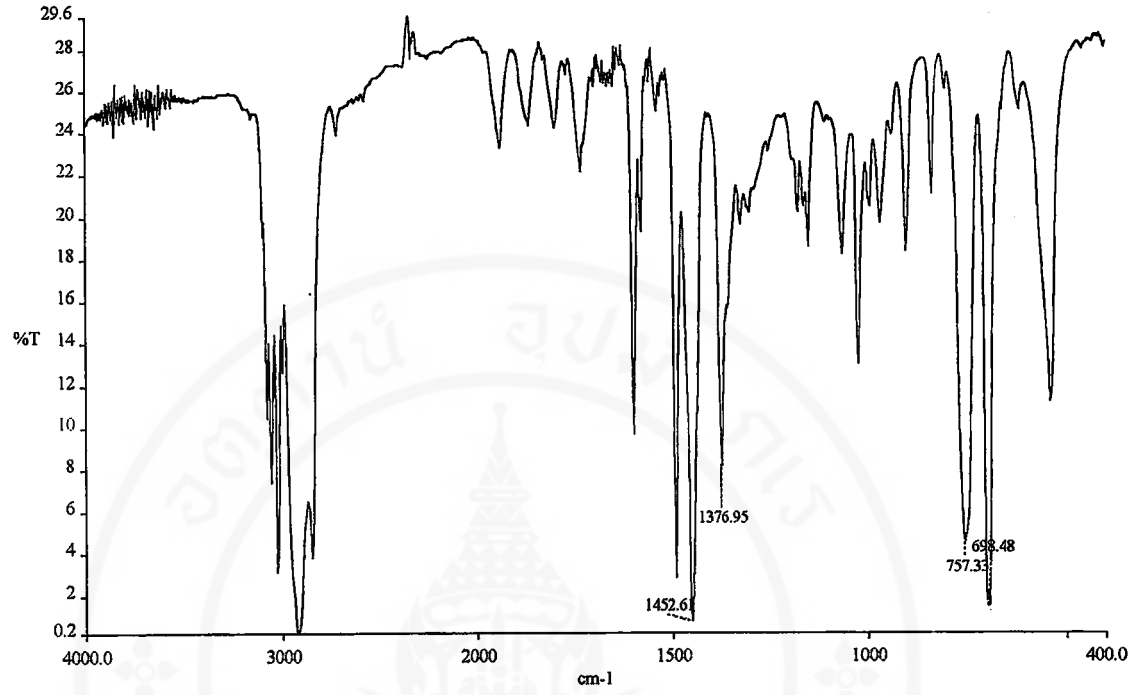

Figure 3.19 IR spectrum of PP-*co*-PS (4SP12)

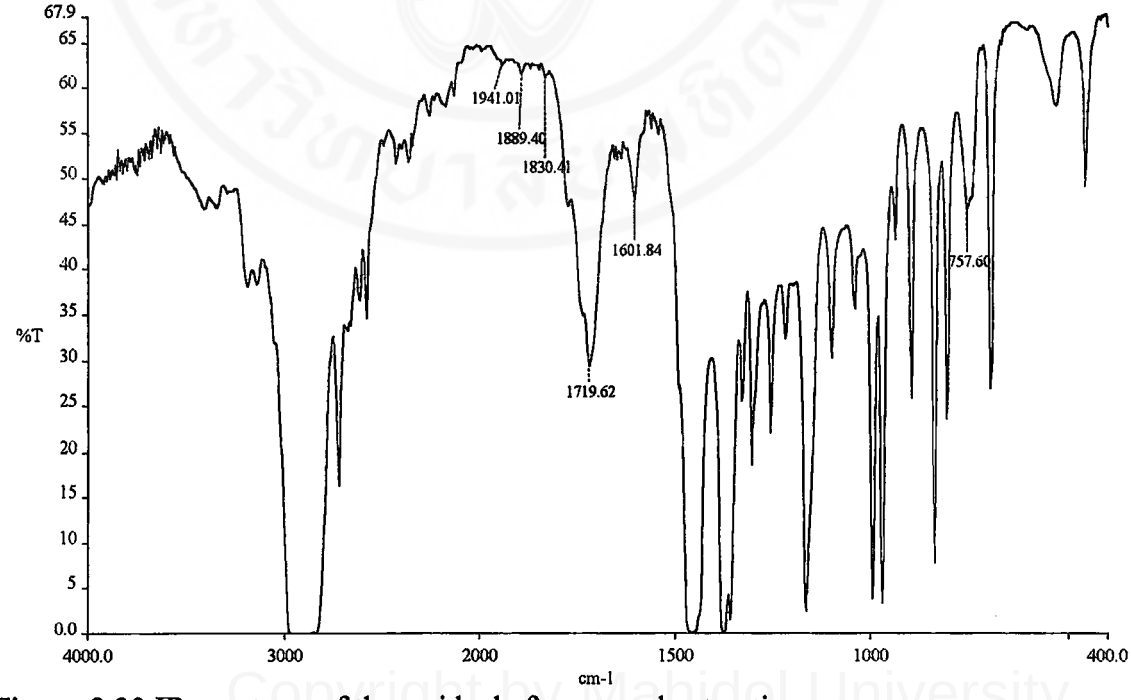

Figure 3.20 IR spectrum of the residual after second extraction

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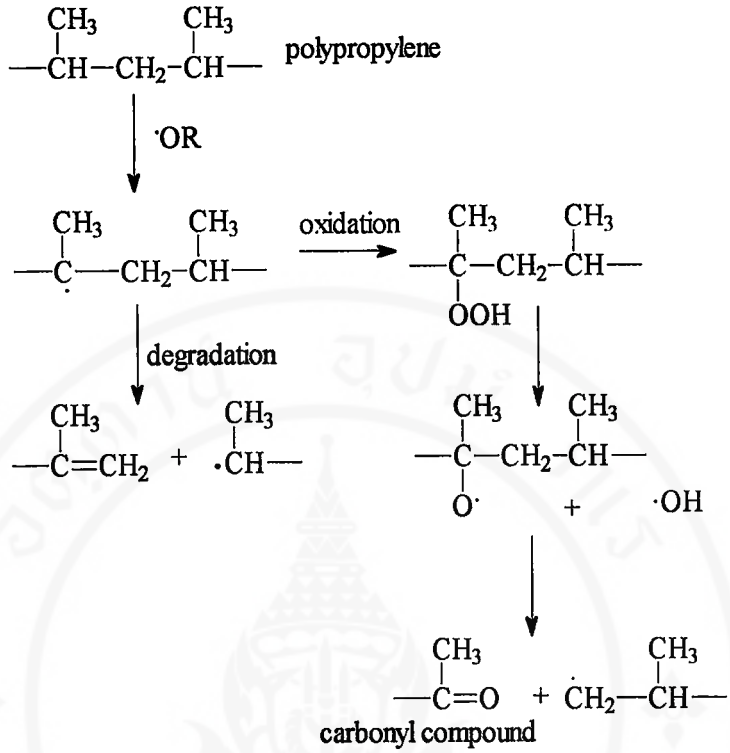

Figure 3.21 Formation of carbonyl compounds during high-temperature processing of polypropylene

For the PP-*co*-PS, the amount of PS presented in the copolymer can be determined by preparing a calibration curve of % PS in the blend of PP and PS, using the peak height ratio of PP and PS at 1376 and 700 cm^{-1} respectively. Figure 3.22 shows typical calibration curve of % PS prepared in this study. The amounts of PS in two copolymers, 4SP3.5 and 4SP12 were investigated. Table 3.6 shows that the percentage of PS in the PP-*co*-PS was found. It was obvious that about 50% and 45% of PS grafted on PP were obtained in the case of 4SP3.5 and 4SP12, respectively. It is noted that the use of higher molecular weight PP (4SP3.5) resulted in higher percentage of PS in the copolymer. In the cases of 2SP55 and 2SP3.5, the amounts of the copolymer obtained were quite small (about 2 %), and therefore % PS in the copolymers was not investigated.

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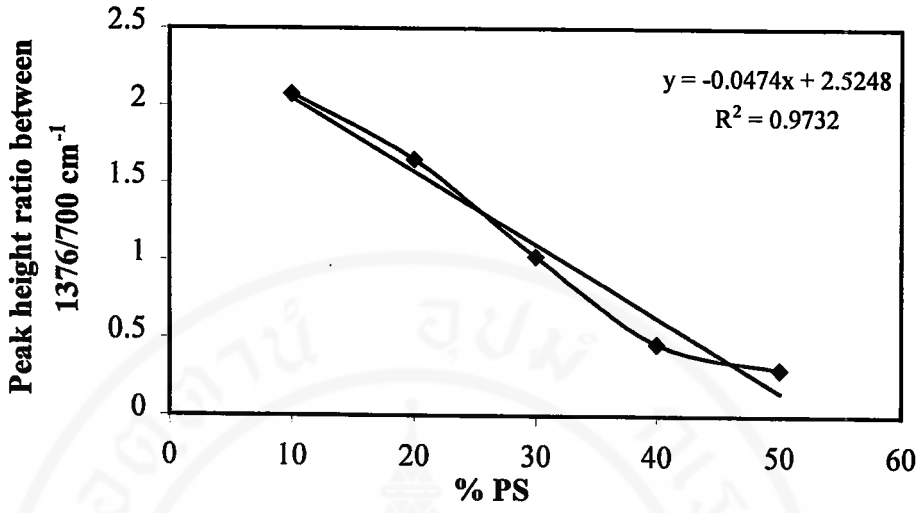

Figure 3.22 Calibration curve of %PS versus peak height ratio between 1376 and 700 cm^{-1} of PP/PS blends.

Table 3.6 PS content of PP-*co*-PS

Spectrum Peak	4SP3.5	4SP12
1376 cm^{-1}	1.6	3.8
700 cm^{-1}	15.6	10.3
Peak height ratio	0.102	0.36
% PS in the copolymer	50.52 %	45.67 %

3.4 Thermal characterisation of compatibilisers

The Differential Scanning Calorimeter (DSC) was used to investigate the thermal behaviour of all compatibilisers. The transition temperature of the compatibilisers was expressed in terms of melt transition temperature (T_m) in the case of semicrystalline polymer, such as PP and LDPE, and of glass transition temperature (T_g) in the case of the amorphous PS polymer and amorphous part of LDPE.

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3.4.1 PS-*g*-MA

In general, the T_g is strongly influenced by the chemical structure of the repeating unit and will be increased when the flexibility of the polymer main chain is decreased. The presence of aromatic units or rigid groups in the main chain or an incorporation of bulky substituent groups or non-rotational groups in the main chain affect the movement of the polymer chains and lead to a reduction in chain flexibility. The amorphous regions in the semicrystalline polymers are also assumed a glassy state, i.e. T_g being independent of % crystallinity to the first approximation. The magnitude of the phenomena associated with T_g however decreases with the amorphous content. As a result, T_g is sometimes difficult to detect in highly crystalline polymer.

Table 3.7 Glass transition temperature of PS and PS-*g*-MA

Polymer	T_g (°C)
PS	98
PS-*g*-MA	86

The T_g of PS at about 100°C is comparing to the T_g of PS-*g*-MA shown in Table 3.7. It was found that T_g of PS-*g*-MA is lower than the original PS owing to the lower molecular weight resulting from degradation reaction during melt processing. This proposed explanation was confirmed by measurement of MFI values as shown in table 3.11. The lower molecular weight is reasonable to assume that each chain end, at any temperature, moves more rapidly than the middle portion, because a chain end has only one chain attached to it, whereas the middle part has two. Despite the fact

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that MA attached to the backbone is able to promote the intermolecular force from its polar groups in the polymer chain, the effect of molecular weight is the key responsible for the glass transition temperature in PS-*g*-MA.

3.4.2 Copolymer of PE and PS

In the case of LDPE and their derivatives, it was shown in Table 3.8 that the T_g of LDPE and PE-*g*-PS copolymers could not be detected. The T_g of LDPE part from the reactive extrusion samples (PE-MA-PS and PE-HMM-PS) is higher than its physical blending with PS due to the formation of copolymer and possibly crosslinked product during melt processing that restricted the mobility of the polymer chains.

Table 3.8 Glass transition temperature of LDPE part in various constituents

Sample	T_g of LDPE part (^oC)
LDPE	undetectable
LDPE/PS 50:50	-80
PE-*g*-PS	undetectable
PE-MA-PS	-67
PE-HMM-PS	-76

PE-MA-PS copolymer has the highest T_g among the samples in this series, because of the highest restriction of the chain or mobility. In PE/PS blend, there is no chemical bonding between the chains while PE-MA-PS and PE-HMM-PS, chemical linkages between PE and PS restrict the movement of the PE chain. The distance between the chains in PE-MA-PS is shorter than PE-HMM-PS copolymer leading to a

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higher T_g for PE-MA-PS. Changes in T_g are evidence of linkage occurring in the copolymers prepared.

3.4.3 Copolymer of PP and PS

In the cases of PP-*co*-PS series, the % crystallinity and T_m values shown in Tables 3.9 and 3.10 indicated that T_m is not related to the % crystallinity of the PP.

Melting temperature, T_m of PP and LDPE is usually taken to be independent of molecular weight in the polymer range, but it is strongly dependent with chain flexibility, steric-factors such as type of the side chain. [47] Furthermore, T_m is a property of a well-ordered crystalline material while T_g is a property of the amorphous material. It may, therefore be imagined that the prediction of T_m should be easier than the prediction of T_g. In fact, just the reverse is true. While two key factors determining T_g (i.e. chain stiffness and interchain cohesive forces) are also important in determining T_m, the chain packing are an additional importance key determining T_m.

Table 3.9 % Crystallinity of PP and LDPE from heat of fusion and T_m

Polymer	LDPE (MFI 7.5)	PP (MFI 2.1)	PP (MFI 3.5)	PP (MFI 8)	PP (MFI 12)	dPP (MFI 55)
ΔH_o (J/g)	140.6	209				
ΔH (J/g)	52.76	92.65	101.33	103.89	100.17	96.18
T_m (°C)	111	167	167	167	169	163
% crystallinity	37.5	44.1	48.5	49.7	47.9	46.0

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Table 3.10 % Crystallinity of PP and T_m of the prepared PP-*co*-PS compounds

Sample	PP/PS (50:50)	2SP3.5	4SP3.5	4SP12	2SP55
% crystallinity	65	42.49	36.5	45.83	39.94
T_m (°C)	157	168	169	167	166

3.5 Melt flow index measurement

Melt flow index (MFI) is a mass flow rate is expressed in g/10 minutes and it is used to indicate viscosity as well as relative molecular weight of the polymer. The MFI is also an indication of chain scission occurring in the polymer processing. Higher value of MFI implies lower molecular weight. From Table 3.11, it was found that MFI of PE-*g*-MA, PE-MA-PS and PE-HMM-PS cannot be evaluated. This may be due to the possibilty of interchain reaction or interpenetrating network developed during processing. Blending of PE and PS gave lower MFI (4.6) than the LDPE (7.3). This is not a suprising result as the blend contains high-MFI LDPE and low-MFI PS. The higher MFI of PS-*g*- MA comparing to the virgin PS confirms the chain scission of PS during processing. [50,51]

For PP-*co*-PS series, a comparison of MFI of PP/PS blend with different amounts of initiator and PP types is shown in Table 3.12. It was found that 2SP3.5 has lower MFI value than the 4SP3.5, due to the different loading of initiator in the preparation process. Therefore, the amount of the radical initiator is responsible for the degradation of the PP and PS.

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Table 3.11 MFI of blends and compatibilisers of LDPE and PS

Sample	MFI (g/10min)	Standard deviation
LDPE	7.3	0.3
PE-*g*-MA	0	0
PS	1.3	0.1
PS-*g*-MA	6.9	1.3
LDPE/PS 50:50	4.6	0.2
PE-MA-PS	0	0
PE-HMM-PS	0	0

Table 3.12 MFI of blends and PP-*co*-PS

Sample	Average	Standard deviation
PP/PS 50:50	3.0	0.0
2SP3.5	24.5	0.9
4SP3.5	38.9	2.6
4SP12	59.3	5.1
2SP55	47.3	4.2

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Part 2 Investigation of LDPE/PS blends in the presence of various compatibilisers

Generally, melt mixing of two different polymers results in rarely compatible blend which is also the cases of LDPE and PS blends. However, these two polymers are quite demanding as the success in achieving high performance PE/PS blends results in new polymeric material combining the inherent ductility of PE and high modulus of PS. It has been reported that the performance of the immiscible blends may be improved by the introduction of a third component acting as a surface active modifier or by promoting interchain reaction to form a copolymer during melt mixing. The modifier can be a block or graft copolymer or the better a reagent capable of *in-situ* producing grafted copolymer during melt processing. In this study, various compatibilisers prepared were used in LDPE/PS (75:25wt%) blends, in order to compare their effect on mechanical properties and morphology of the blends.

3.6 Tensile and impact properties

3.6.1 Low density polyethylene (LDPE)/ polystyrene (PS) (75:25wt%) blend.

LDPE and PS were blended in a twin screw extruder. Then the mechanical properties of the extrudates were evaluated from the injection moulded specimens. The tensile properties of the PE-rich LDPE/PS blend comparing to the pure PE and PS homopolymers are shown in Table 3.13 and Figure 3.23.

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Table 3.13 Tensile properties of LDPE, PS and 75:25 LDPE/PS blend

Sample	Yield stress (MPa)		Secant modulus at 1% strain (MPa)		% Elongation at break	
	Average	Variance	Average	Variance	Average	Variance
LDPE	11.07	0.12	161.10	8.44	92.11	3.93
PS	44.69	1.00	2536.66	85.48	2.26	0.19
75:25 LDPE/PS	12.58	0.12	609.4	16.61	35.03	2.76

The yield stress and secant modulus at 1% strain of PS is very high inversely to its % elongation at break, due to its brittle failure behaviour. The contradictory properties of LDPE to the PS is obviously seen. The blend of 75:25 LDPE/PS presented moderate tensile properties with the tendency towards those of LDPE. This is due to the majority of the PE components. The stress-strain behaviour of each sample is shown in Figure 3.24. It can be seen that the blend can resist to moderate load even though the % extension is not satisfactory.

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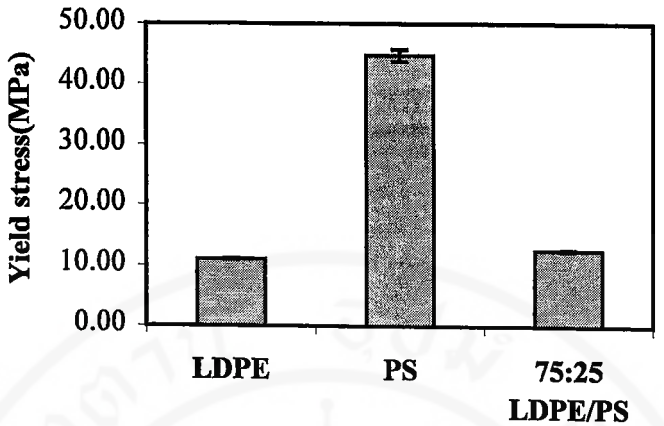

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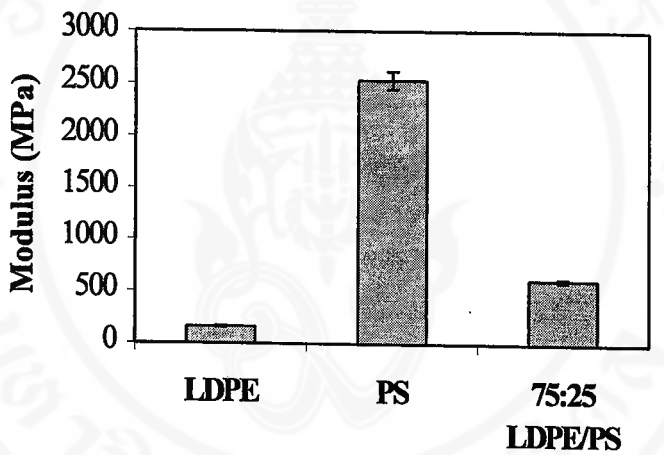

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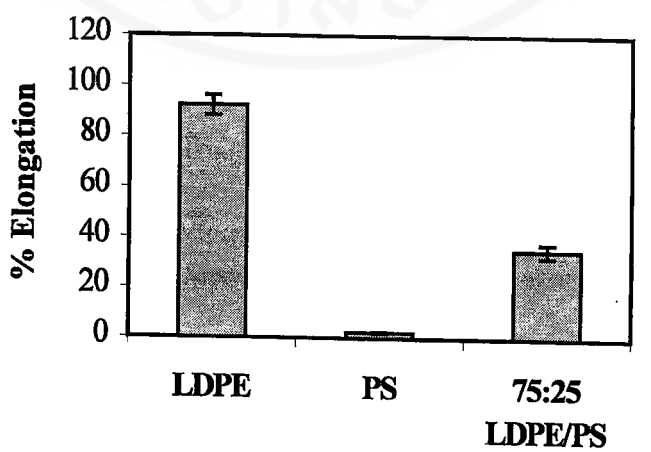

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Figure 3.23 Tensile properties LDPE, PS and their blend; A) Yield stress; B) Secant modulus at 1 % strain; C) % Elongation at break

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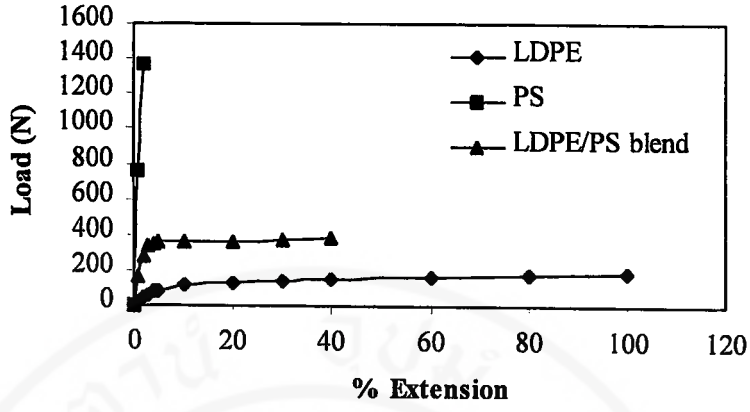

Figure 3.24 Stress-strain behaviour of LDPE, PS and 75:25 LDPE/PS

The impact properties of the pure LDPE, PS and their blend are shown in Table 3.14. The rigid PS has low impact property and is usually toughened by incorporation of a dispersed rubbery phase. In this case, the presence of the PS as a minor component in PE deteriorate the inherent toughness of the PE, resulting in low impact strength of the PE-rich blend. Furthermore, analyses of graft copolymerisation of PE and PS component by solvent extraction found to be 0.2 % reveal that there is no interchain reaction developed during processing.

Table 3.14 Impact strength of LDPE, PS and 75:25 LDPE/PS blend

Sample	Impact strength (kJ/mm^2)	
	Average	Variance
LDPE	44.51	2.39
PS	0.77	0.09
75/25 LDPE/PS	6.66	0.22

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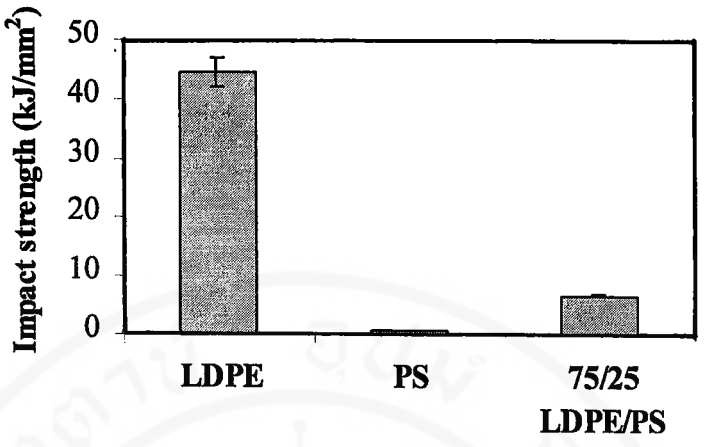

Figure 3.25 Impact strength of LDPE, PS and 75:25 LDPE/PS

3.6.2 Compatibilised LDPE/PS blends by addition of compatibilisers

3.6.2.1 PE-*g*-MA and PS-*g*-MA

Generally, functionalised polymers have been used as a modifier in polar and non-polar blending system.[6,16,19,28,48] Polyamide and polyurethane are two examples of polar polymers having been used to blend with LDPE and PS. Modification of these non-polar polymers with maleic anhydride resulting in the functionalised polymers be able to react with free amino and amide linkage of polyamide or isocyanate of polyurethane. The performances of these blends were improved by formation of grafted copolymers in the systems. It is therefore postulated that if both PE and PS contain reactive functional groups, blending of the two polymers might render compatibilising through the formation of linkage between the reactive moieties. Functionalisation of PE and PS with maleic anhydride has been shown in previous section the polymers bearing the anhydride function. It was also found that the melt mixing of maleic anhydride with PE and PS in the presence of

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peroxide initiator resulted in PE-*g*-MA and PS-*g*-MA containing unreacted MA. These functionalised polymers were brought to use as compatibilisers for LDPE/PS blends. It is expected that addition of the PE-*g*-MA or PS-*g*-MA prepared in the PE/PS blend might render interchain reaction from the reactive anhydrides bearing on the polymer chains and the residual unreacted MA with the blend components, that might improve the mechanical properties of the blends. The tensile properties of the blends containing 1, 3 and 5 phr of the PE-*g*-MA and PS-*g*-MA compatibilsers are shown in the Figure 3.26.

It was found that PE-*g*-MA did not effect on the yield stress of the blends but gave slight effect on the secant modulus. However, addition of PE-*g*-MA increased the % elongation at break of the blends and higher amount of the PE-*g*-MA, better improvement of the blends were found. This may be due to the presence of the higher percentage of the inherent ductility of PE component. It may be also optimisticly thought that there are some improvement of interfacial adhesion between the PE and PS phases due to the interaction between the PE and PS as slight improvement of impact properties were also obtained.

Addition of PS-*g*-MA into the PE/PS blends effected mostly on the improvement of the yield stress and modulus of the blends. The obvious reason might be due to the inherent rigidity of extra amount of the PS component. With increasing the amount of PS-*g*-MA, lower % elongation at break was obtained. However, at 1 and 5 phr loading of PS-*g*-MA and PE-*g*-MA, respectively, an improvement of % elongation of the blend was found (Figure 3.26).

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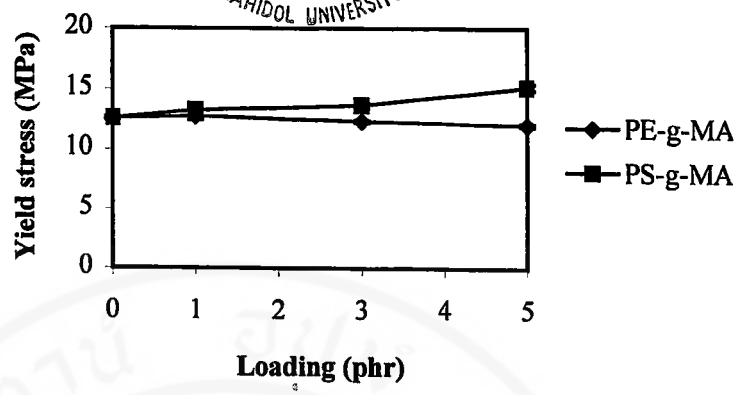

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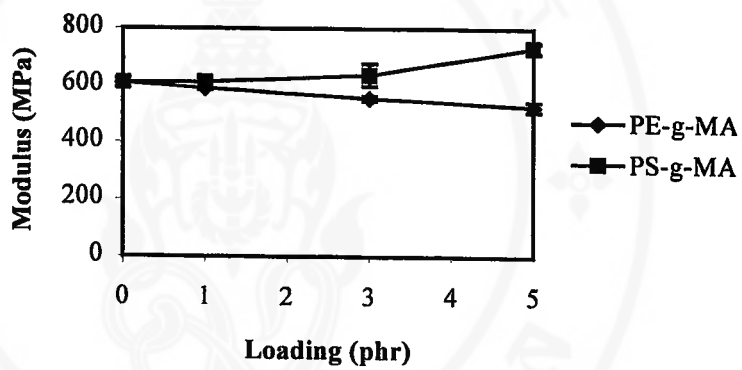

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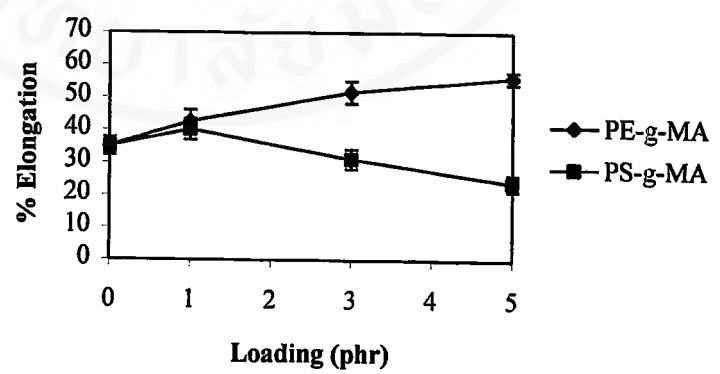

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Figure 3.26 Tensile properties of LDPE/PS blends containing various amounts of PE-*g*-MA and PS-*g*-MA compatibilisers; A) Yield stress; B) Secant modulus at 1% strain; C) % Elongation at break

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The impact properties shown in Figure 3.27 indicate that PE-*g*-MA gave slight improvement in impact properties at various loadings while PS-*g*-MA rather maintained this property except at 5 phr loading.

It can be concluded that the hypothesis of formation of graft copolymer between PE and PS during processing in the presence of PE-*g*-MA or PS-*g*-MA in PE-rich LDPE/PS blends might be occured in small quantity, the crosslinked structure of polyethylene (see section 3.5) may be taken place instead resulted in slight improvement in mechanical properties of the compatibilised blends. However, the amounts of the grafted copolymers were not investigated.

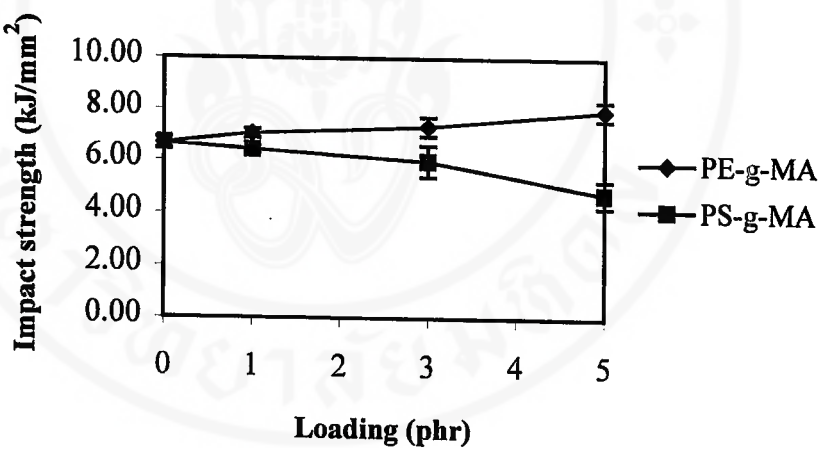

Figure 3.27 Impact strength of LDPE/PS blends containing various amounts of PE-*g*-MA and PS-*g*-MA compatibilisers.

3.6.2.2 PE-*g*-PS, PE-MA-PS and PE-HMM-PS

As the addition of functionalised polymers, i.e. PE-*g*-MA or PS-*g*-MA, in LDPE/PS blends cannot enhance significantly the performance of the blends, and therefore prior grafted copolymers were considered. Three types of copolymers used were PE-*g*-PS, PE-MA-PS and PE-HMM-PS. The main difference among these three

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copolymers is the distance between the polymer chains. In PE-HMM-PS, the PE is linked to PS by imide linkage of HMM, and hence longest distance. However, it has to be noted that the crosslinked structure in PE-MA-PS and PE-HMM-PS may occur during preparation. The tensile properties of the blends compatibilised with these copolymers are shown in Figure 3.28.

It has been reported that PE-*g*-PS occurred during blending of PE and PS is responsible for the performance of PE/PS blends.[9,10,29] In our case, previously prepared grafted copolymers played small effect on the tensile properties of the LDPE/PS blends. The addition of PE-*g*-PS, PE-MA-PS and PE-HMM-PS improve neither the yield stress of the blends but rather maintaining this property, nor the modulus. However, % elongation at break increased with increasing the amount of PE-*g*-PS. Additions of PE-MA-PS and PE-HMM-PS to the LDPE/PS blend, however, gave lower % elongation at break than the uncompatibilised LDPE/PS blend. This may be due to the fact that PE-MA-PS and PE-HMM-PS containing crosslinked structure that restricts the movement of the matrix. The crosslinked structure of PE-MA-PS and PE-HMM-PS affected also the rheological property of the blends, i.e. undetermined MFI values due to the high viscosity (section 3.5). But the crosslinked product of the compatibilisers may act as fillers, hence slight increase of the modulus and yield stress of the blends.

The PE-*g*-PS is the graft copolymer synthesised by Friedel-Crafts alkylation, and thus principlely crosslinked product does not occur. The % elongation at break is improved by this compatibiliser while the yield stress and modulus are vastly decreased owing to its low polystyrene content found in the copolymer (see section 3.2.3).

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The impact properties of these blends are shown in Figure 3.29. It was found that additions of PE-*g*-PS, PE-MA-PS and PE-HMM-PS gave a slight improvement in impact strengths of the blends which were superior to the use of PE-*g*-MA or PS-*g*-MA. It may be postulated that these compatibilsers stabilised the PS dispersed phase giving smaller particle comparing to the uncompatibilised LDPE/PS blend (see section 3.7). The particle size distribution is also responsible of the best impact strength of the blend containing 1 phr of PE-MA-PS and 5 phr of PE-HMM-PS. Furthermore a significant amount of % graft copolymer developed during processing in each blend may be responsible for the improvement of the compatibility of the blend, and hence the improved impact strength.

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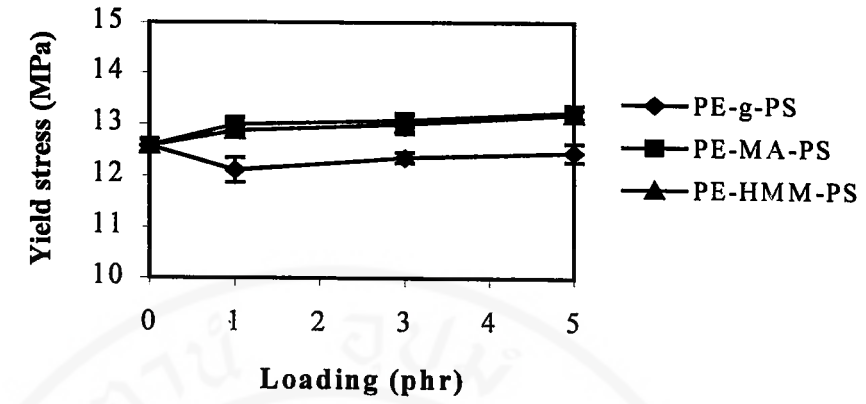

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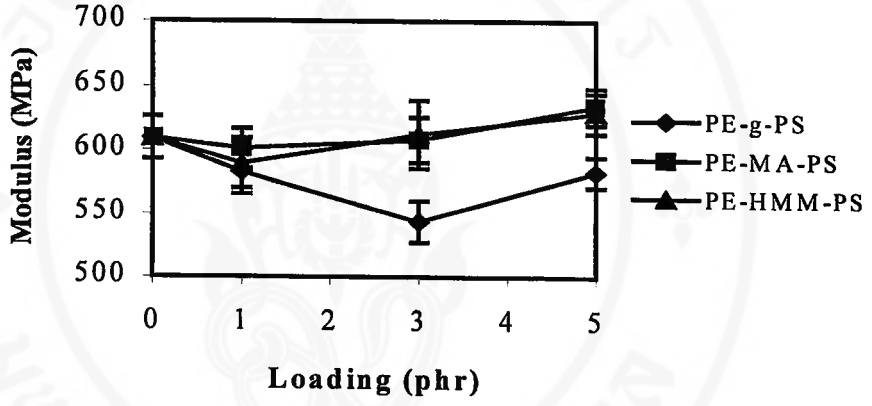

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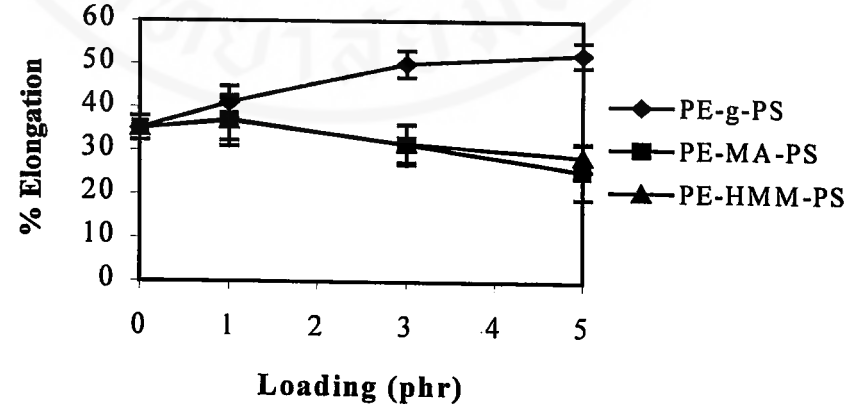

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Figure 3.28 Tensile properties of blends containing various amounts of PE-*g*-PS, PE-MA-PS and PE-HMM-PS compatibilisers; A) Yield stress; B) Secant modulus at 1% strain; C) %Elongation at break

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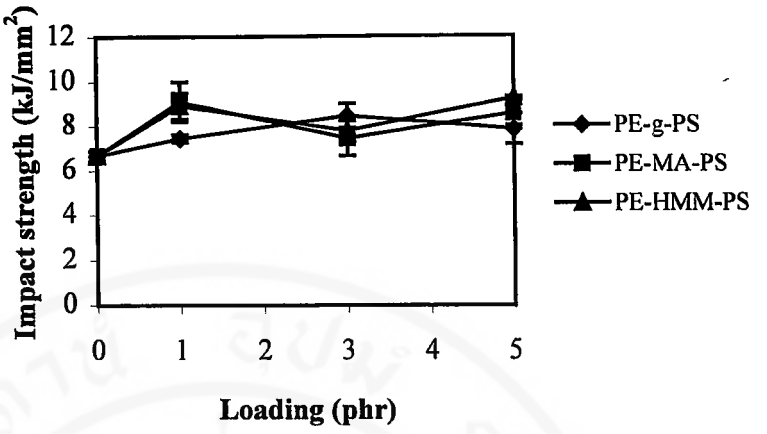

Figure 3.29 Impact strength of blends containing various amounts of PE-*g*-PS, PE-MA-PS and PE-HMM-PS compatibilisers

3.6.2.3 PP-*co*-PS

As mentioned earlier in section 3.3 that PP was chosen to graft with PS as it has the same behaviour as PS under melt. Both PS and PP tend to degrade in the presence of oxy radical rather than formation of crosslinking. Therefore, copolymer of PP and PS could be obtained. Various melt flow indices of PP-*co*-PS were added to LDPE/PS blends. The tensile properties of this series are shown in Figure 3.30. The yield stress of blends containing 2SP3.5 and 4SP12 are increased with increasing the compatibiliser loadings. The blends containing the 4SP12 gave stronger effect than those of containing 2SP3.5. An addition of 2SP55 into LDPE/PS blends also gave slight improvement of yield stress to the blend except at 1 phr loading. In the case of the blend containing 1 phr of 4SP3.5 copolymer, improvement of yield stress is interesting but, at higher loading, the blends show similar properties as the original components. It can be postulated that molecular weight or melt flow index of the copolymers prepared play a role on the miscibility of the blends. It seems likely that

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4SP12 has suitable molecular weight in compatibilising the LDPE/PS blends, and hence improved yield stress particularly at 3 phr loading. It was found that addition of 5 phr of 4SP12 cause reduction of the yield stress due to the excess compatibiliser acted as a filler in the LDPE/PS blend system. Result in Figure 3.30 reveals that the blends containing 4SP12 did not increase the modulus as much as the 2SP3.5 did. This may be due to the low molecular weight of the 4SP12 (highest MFI). The addition of four copolymers gives decrease in % elongation at break.

From Figure 3.31, it is obvious that all compatibilisers in this series effect in improved impact strengths of the blends. Particulary at 1 phr loading of each compatibiliser. The highest efficient compatibiliser is 4SP12 and followed by 2SP55, 2SP3.5 and 4SP3.5, respectively. This may be because the suitable chain length of the copolymer at the low amount can stabilise the interphase but at the higher amount the phase separation occurs leading to reduction in the impact strength.

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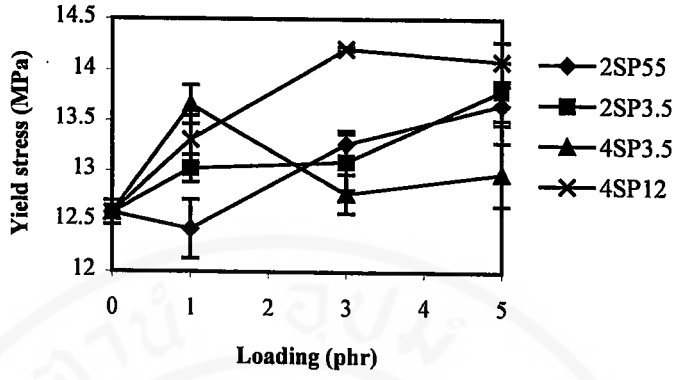

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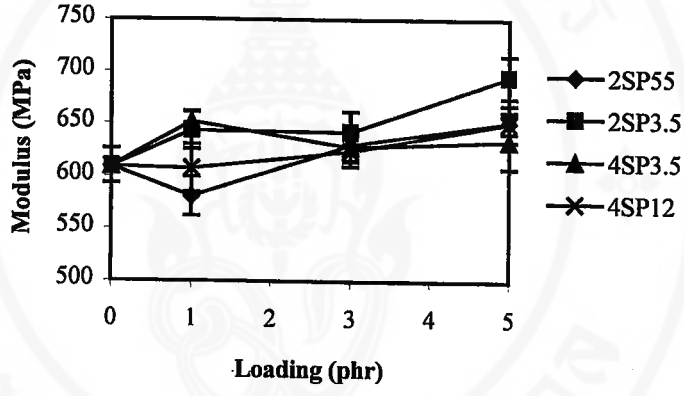

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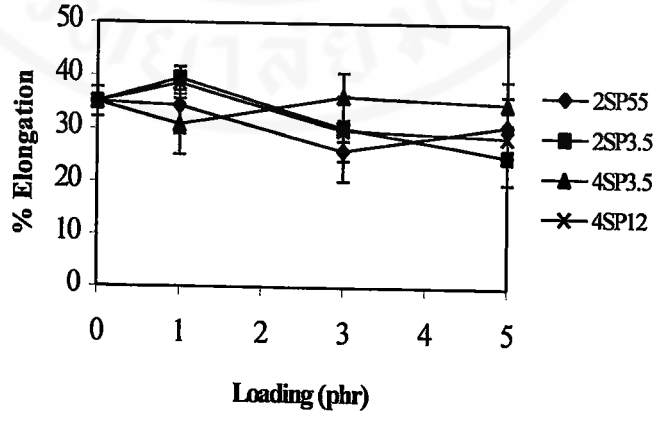

C)

Figure 3.30 Tensile properties of blends containing various types of PP-*co*-PS; A) Yield stress; B) Secant modulus at 1% strain; C) %Elongation at break

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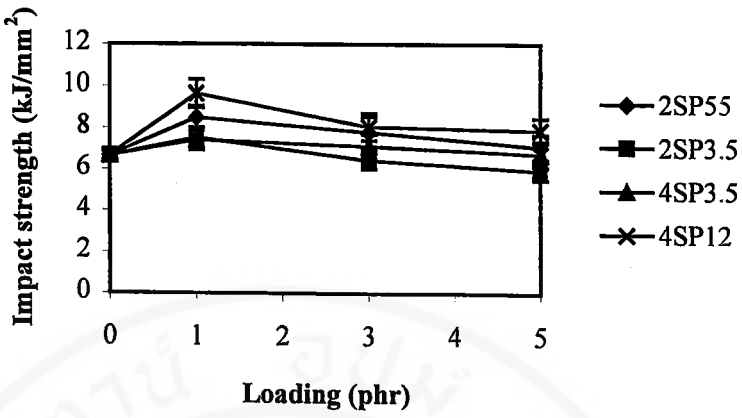

Figure 3.31 Impact strengths of blends containing various types of PP-*co*-PS

3.6.3 *In-situ* compatibilised LDPE/PS blends

In this section, additions of both PE-*g*-MA and PS-*g*-MA in LDPE/PS blends with and without amine crosslinking agents (hexamethylene diamine, HMD and 4,4′-diaminodiphenylsulphone,DAPS) were investigated. In this approach, three samples were prepared: 3 phr of PE-*g*-MA and PS-*g*-MA in LDPE/PS blend (EgSMA3), 3 phr of PE-*g*-MA and PS-*g*-MA and 1.5 phr HMM in LDPE/PS blend (EgSMA3H), 3 phr of PE-*g*-MA and PS-*g*-MA and 3 phr DAPS in LDPE/PS blend (EgSMA3D). In the case of EgSMA3, it was expected that the MA appended polymer in both LDPE and PS might resulted in the *in-situ* formation of the reactive functional groups. The FTIR spectrum of ESgMA3 in Figure 3.32 shows strong absorption band at 1795 cm^{-1} corresponding to acyclic anhydride that might be occurred from the reaction between the MA from different polymeric chains during melt processing. (see Figure 3.33). This characteristic peak is found in neither PE-*g*-MA nor PS-*g*-MA compatibilisers. Therefore, interchain reaction is believed to occur in the blends.

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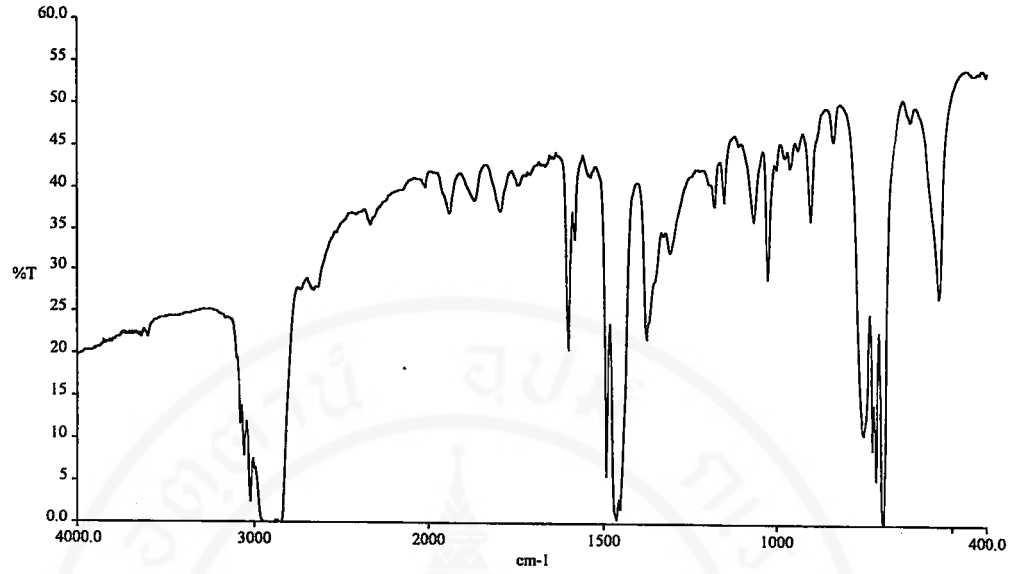

Figure 3.32 IR spectrum of the ESgMA3

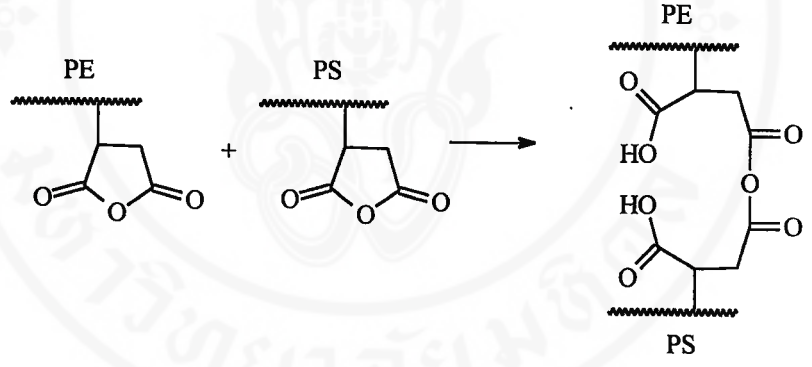

Figure 3. 33 Formation of acyclic anhydride in melt processing

For the EgSMA3H and EgSMA3D, the hypothesis is the *in-situ* reaction between the MA appended polymer with the diamine compound forming an imide linkage as previously shown in Figure 3.11. This link is considered fast and irreversible. Thus this linkage may be stable for post processing. The tensile properties of the *in-situ* compatibilised blends are presented in Figure 3.34. It was found that these reactive components gave insignificant improvement in modulus and % elongation at break of the resulting blends. The *in-situ* compatibilised blends show decrease in impact properties as shown in Figure 3.35. The lowest impact strength

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was found in EgSMA3H due to the highest reactivity of HMD that links among anhydride groups. The linkage is dense more than the critical crosslinked density needed, and therefore no improvement in mechanical properties of the blends. This observation is also found in EgSMA3D but it is lower reactivity. DAPS is less reactive than HMD owing to the stabilised effect on aromatic ring in DAPS, and therefore less effect on crosslink possibility.

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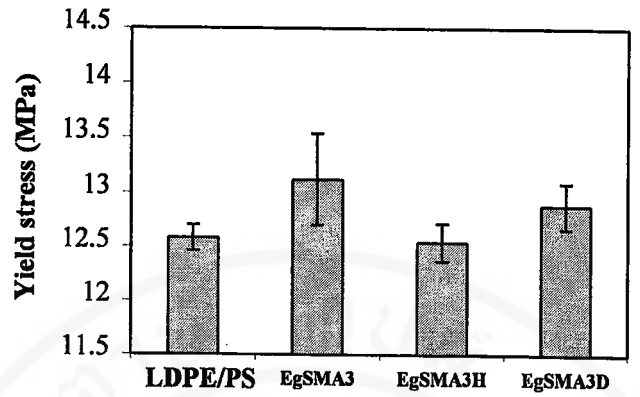

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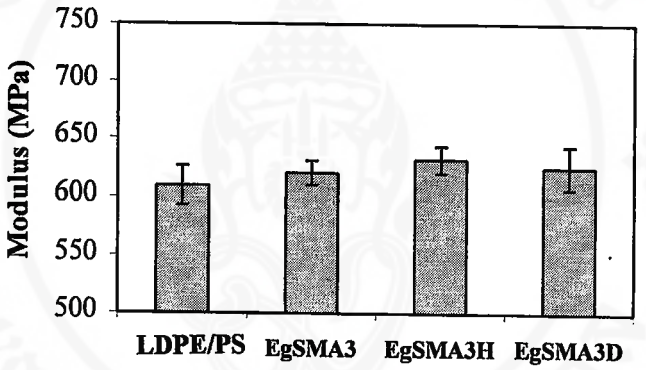

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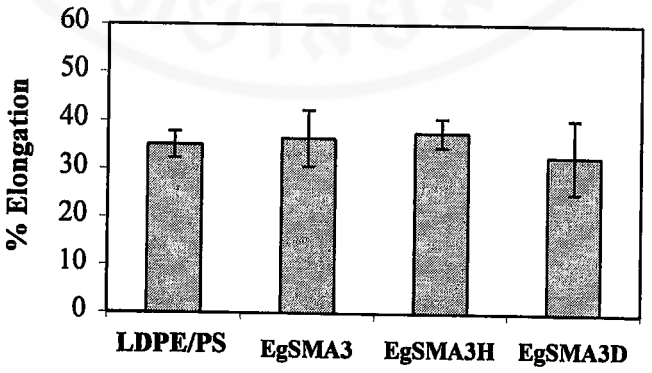

C)

Figure 3.34 Tensile properties of blends containing both of PE-*g*-MA and PS-*g*-MA with and without diamine compounds; A) Yield stress; B) Secant modulus at 1% strain; C) %Elongation at break

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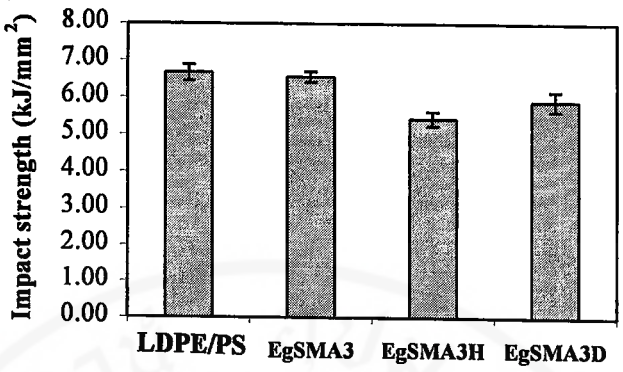

Figure 3.35 Impact strengths of blends containing both of PE-*g*-MA and PS-*g*-MA with and without diamine compounds

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3.7 Particle size and size distribution of PS dispersed phase

Generally, in immiscible polymer blend, the minor component, is dispersed in a matrix of a majority component as droplet. The mechanical properties of the blends are affected by the orientation of the dispersed phase. [30,47] Usually, the spherical domain is formed in the system where the phase separation occurs during melting. An addition of the third component, usually a block or graft copolymer is to improve the adhesion properties of the interface between the matrix and dispersed phase. The size and the shape of the dispersed phase in the blend have been found to influence the mechanical properties of the final blends. In the present work, the morphology of 75:25 LDPE/PS blend and the compatibilised blends were investigated by using scanning electron microscopy (SEM), particularly in size and the size distribution of the dispersed phase.

3.7.1 Low density polyethylene (LDPE) / polystyrene (PS) (75:25 wt%) blend.

In PE-rich LDPE/PS blend, it is naturally expected the PS droplets dispersing in PE matrix. Figure 3.36 shows scanning electron micrographs (SEM) of fractured surfaces for 75:25 LDPE/PS blend. The average diameter of dispersed phase size is obtained by dividing the diameter of all particles with a number of particles. It can be seen a discrete interphase between two phases which suggests poor interfacial adhesion. The average particle size of the dispersed phase observed is about 1.8 μm (Table 3.15) and the size distribution is broad which can be seen in Figure 3.37.

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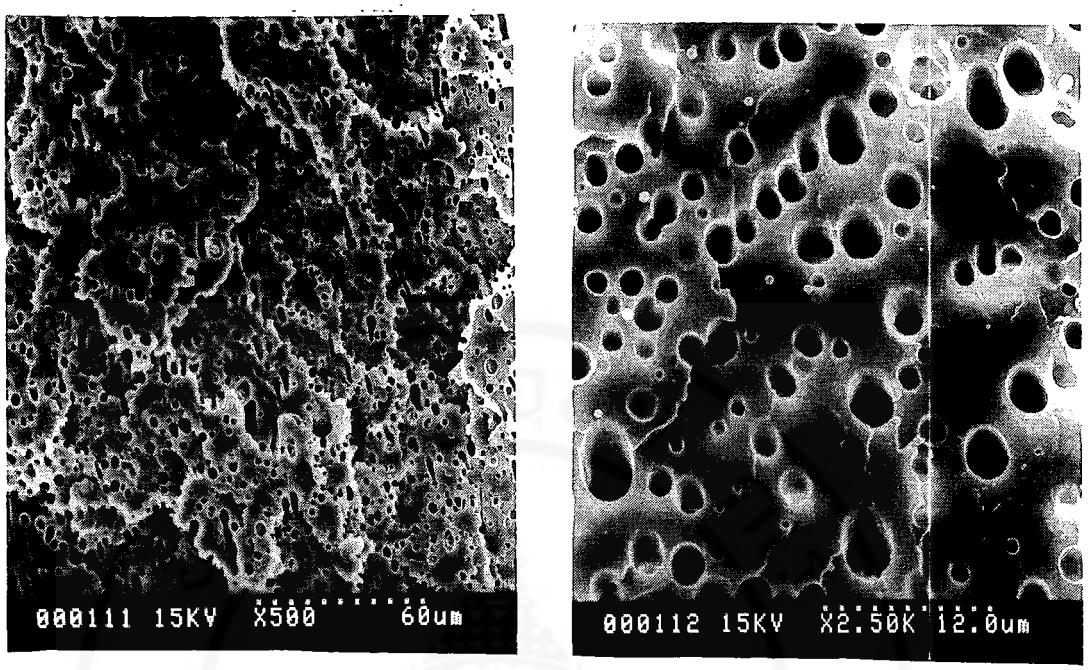

Figure 3.36 SEM micrograph of 75:25 LDPE/PS blend: A) x 500; B) x 2500

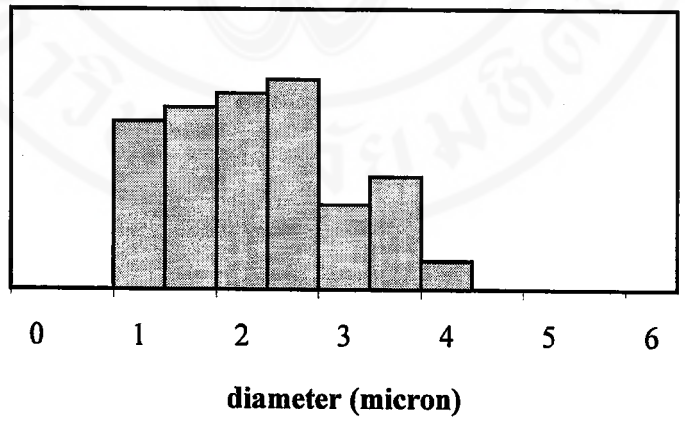

Figure 3.37 Particle size distribution of 75:25 LDPE/PS blend

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Table 3.15 Average diameter of dispersed phase in LDPE/PS containing various copolymers

Copolymer	Loading (phr)	Average diameter (micron)
Control	0	1.88
PE-*g*-PS	1	1.16
	3	1.08
	5	0.86
PE-MA-PS	1	1.16
	3	1.16
	5	1.80
PE-HMM-PS	1	1.40
	3	1.24
	5	1.38

3.7.2 LDPE/PS blends containing various copolymers

3.7.2.1 PE-*g*-PS, PE-MA-PS and PE-HMM-PS

It was found in Table 3.15 and Appendices D1-D3 that addition of PE-*g*-PS copolymer into the LDPE/PS blend results in decreasing the particle size and particles size distribution of the dispersed phase. Addition of 1 phr into the LDPE/PS blend PE-*g*-PS resulted in decreasing the particle size of the disperse phase from 1.9 μm in uncompatibilised blend to about 1.1 μm for the compatibilised blend. Increasing loading of PE-*g*-PS upto 5 phr, particle size of the disperse phase decreased to about 0.8 μm (less than a half of the uncompatibilised blend). The result is responsible from

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the increases in %elongation at break and impact strengths of the compatibilised blends mention earlier.

The particle size distribution of the LDPE/PS blends is found to decrease with various loadings of PE-*g*-PS as shown in Appendix C1. The spherical forms of dispersed phase in each blend were observed. The regular shape and the narrow particle size distribution suggest the formation of uncrosslinked product resulting in an appropriate unchange in melt flow index. The reduction in particle size caused lower interfacial tension among them. Therefore increasing the surface area was achieved by the small dispersed phase. It can be concluded that PE-*g*-PS prepared plays as an effective compatibiliser between LDPE and PS components.

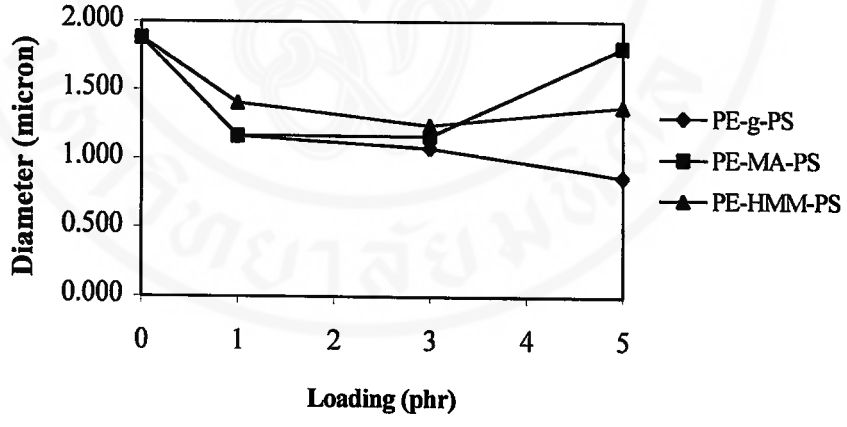

Figure 3.38 Average particle size of the 75:25 LDPE/PS blends with PE-*g*-PS, PE-MA-PS and PE-HMM-PS

For the blends compatibilised with PE-MA-PS and PE-HMM-PS, the results in Table 3.15 show that the particle sizes of the dispersed phase of all blends are higher than 1 μm but still smaller than the uncompatibilised blend. This may be due to the higher molecular weight of the copolymers and the possibility of the presence of

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some crosslinked structure that can not be broken down during the melt processing, and hence less efficiency in compatibilising effect on the dispersed phase.

It was also found that both the blends containing PE-MA-PS and PE-HMM-PS gave non-spherical shapes with rather broader distribution than in the case of the blends containing PE-*g*-PS (see Appendices D4-D9). However, at 5 phr loading of PE-MA-PS and PE-HMM-PS gave the best tensile yield stress and impact strength. Therefore, it is not always true that an increase in interfacial strength between the immiscible blend components by decreasing the particle size of the dispersed phase will result in improvement of mechanical properties.

3.7.2.2 PP-*co*-PS

It was found in Table 3.16 and Figure 3.39 that all of copolymers in PP-*co*-PS series give smaller particle size of the dispersed phase compared to the LDPE/PS blend.

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Table 3.16 Average diameter of dispersed phase of 75:25 LDPE/PS with PP-*co*-PS

Copolymer	Loading (phr)	Average diameter (micron)
Control	0	1.88
2SP55	1	1.39
	3	0.87
	5	1.05
2SP3.5	1	1.57
	3	1.46
	5	1.37
4SP3.5	1	1.23
	3	1.01
	5	1.51
4SP12	1	0.61
	3	1.16
	5	0.93

It was found that the addition of 4SP12 in LDPE/PS blend results in the smallest particle size of the dispersed phase, compared to other copolymers particular at 1 phr loading. However, at 3 phr loading of 2SP55, 4SP3.5 and 4SP12, similar effectiveness of copolymers on the reduction in dispersed phase were obtained. In the case of 2SP3.5 copolymer, it gives relative large particle size of PS-dispersed phase (1.4-1.6 μm). Due probably to the high molecular weight copolymer.

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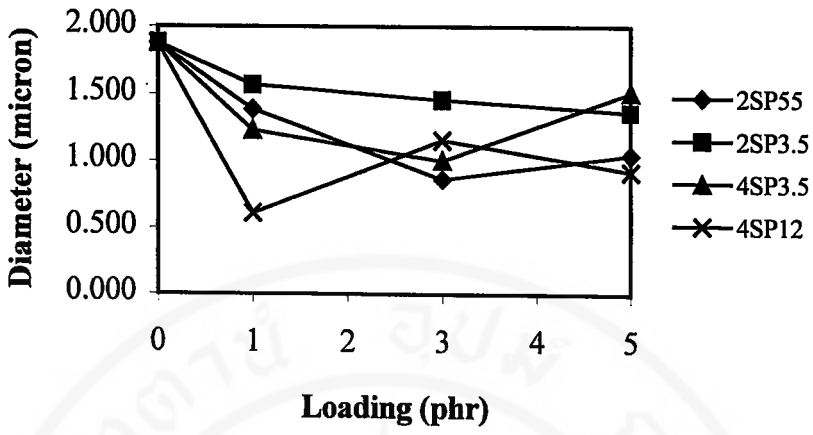

Figure 3.39 Average particle size of blends containing PP-*co*-PS

Appendices D13-D24 show the SEM micrographs of the LDPE/PS blend containing series of the PP-*co*-PS. The particle size distributions of the dispersed phase are shown in Appendices C7-C10. The dispersed phase shapes of PS in all blends are in the spherical form. This may suggest the absence of the crosslinked products. However, the % grafting of the blends found in Table 3.20 may come from the insoluble PP.

All of the series of PP-*co*-PS provide the similar trend of narrow distribution of the PS-dispersed phase at low PP-*co*-PS content but at higher content of the compatibiliser, broader distribution was obtained. The broader distribution suggests the separation of compatibiliser phase which result in poor mechanical properties. From the earlier discussion in the average diameter of the dispersed phase size, the most efficient copolymer is the 4SP12, followed by 4SP3.5, 2SP55 and 2SP3.5, respectively. These results are corresponding to impact properties of the blends.

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3.7.3 *In-situ* compatibilised LDPE/PS blends

In this section, LDPE/PS blend containing reactive functional polymers such as PE-*g*-MA, PS-*g*-MA and diamine compounds are considered. Table 3.17 shows the results of particle size distribution of PS-dispersed phase in LDPE/PS blends. It was found that EgSMA3D gave the particle size of the dispersed phase of 0.7 μm that is 40 % reduction comparing to the uncompatibilised blend. This evidence is correlated to the small change in mechanical properties of the blend which may be due to the rigidity of the component coming from the imide linkage of the 4,4′-diaminodiphenyl-sulphone. The aromaticity of this compound makes the component more rigid than in the case of HMD, and thus the size of the interface is thicker.[6] Therefore, the coalescence of the dispersed phase in the blend compatibilised with EgSMA3D is more difficult to occur than the blends compatibilsed with EgSMA3H and EgSMA3, resulting in a smaller size of the dispersed phase. The rigidity can stabilise the dispersion of the dispersed phase, but it also reduces the energy dissipation that mean the concentration of the stress at the interphase occurs.

Table 3.17 Average diameter of dispersed phase of *in-situ* compatibilised LDPE/PS blends

Sample	Average diameter (micron)
Control	1.88
EgSMA3	1.13
EgSMA3H	0.97
EgSMA3D	0.73

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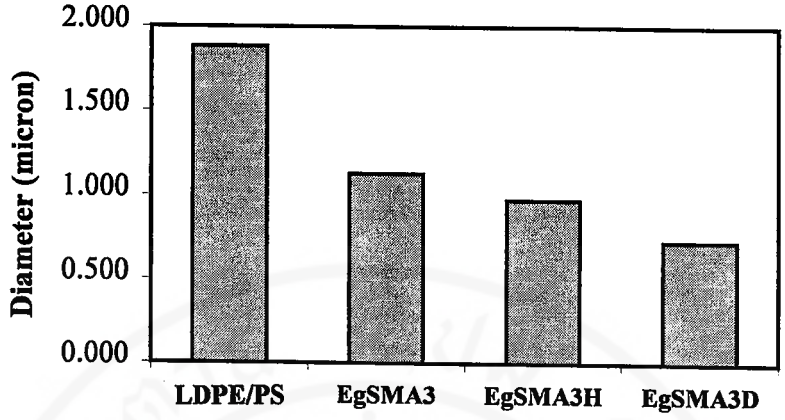

Figure 3.40 Average particle size of the blends containing both PE-*g*-MA, PS-*g*-MA with and without diamine compounds

The particle size distribution of this series are shown in Appendices C4-C6 while their SEM micrographs are shown in Appendices D10-D12.The EgSMA3D gave the most narrow distribution, followed by EgSMA3H and EgSMA3, respectively. It can be seen that approximately particle sizes of the dispersed phase could be obtained despite the presence of the crosslinked product from the compatibilisers.

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3.8 Rheological properties

Rheological characteristic of polymers is a key factor in melt blending of two different components. This can mostly be expressed in terms of either torque developing during processing or melt rheological curve of shear stress against shear rate. The immiscibility of immiscible blends can also be predicted by the rheological properties of the final blends. Melt flow index (MFI) is the simplest indicator of the rheological properties, which can be used to express melt viscosity, as well as relative molecular weight, and to predict the crosslinked structure. [47] The torque rheometry is used to investigate the rheological properties of PP-*co*-PS blend compounds in the present study.

3.8.1 Rheological properties of LDPE, PS and 75:25 LDPE/PS blend

Melt viscosity behaviour of polymer blends is known to be complex, depending on blend compositions. In some cases, an addition of about 10% of a more viscous second component causes the melt viscosity of the blend to become lower than that of the homopolymers while other blend compositions give melt viscosity curves between those of the homopolymers.[5] From Table 3.18, it is found that the addition of 25 % of high viscosity PS exhibits the MFI of the PE-rich blend between the two homopolymers near the homopolyethylene-rich matrix, which is due to the dilution effect.

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Table 3.18 MFI of LDPE, PS and 75:25 LDPE/PS blend at 190°C

Polymer	MFI (g/10 min)	
	Average	Variance
LDPE	7.3	0.3
PS	1.3	0.1
75:25 LDPE/PS	6.5	0.3

3.8.2 Effects of PE-*g*-MA and PS-*g*-MA

The MFI of LDPE/PS blends containing various amounts and types of a third component can be controlled by the change of the blend morphology, the possibility of interchain reaction or interpenetating network developped during processing as well as chain scission. The MFI of blends containing PE-*g*-MA and PS-*g*-MA is presented in Table 3.19.

From Figure 3.41, it is found that an increase in the amount of PE-*g*-MA results in a decrease in MFI of the compatibilised blends while those of the blends containing PS-*g*-MA show approximately similar MFI to the uncompatibilised LDPE/PS blend. This may be due to the inherent properties of each copolymer. In addition, the enhancement in compatibility between the components is probably responsible for the decrease in MFI. PE-*g*-MA is presumed to have a crosslinked structure because its MFI cannot be measured due to too high melt viscosity. An addition of PE-*g*-MA into the LDPE/PS blends affects the resistance to flow of the blends, due possibility to the semi-interpenetrating network structure. It may be possible that the residual MA and peroxide initiator in PE-*g*-MA cause a linkage formation between LDPE and PS pure components, leading to an increase in melt viscosity. The residual MA and peroxide in PS-*g*-MA copolymer might not be able to induce such highly crosslinked structure because of the higher stability of PS than

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LDPE and therefore, no significant change in MFI is observed as PS-*g*-MA was added to the LDPE/PS blend.

Table 3.19 MFI of the blends containing various copolymers with variation loadings

Copolymer	Loading (phr)	MFI (g/10 min)	
		Average	Variance
Control	0	6.5	0.3
PE-*g*-MA	1	6.0	0.1
	3	5.0	0.1
	5	3.9	0.0
PS-*g*-MA	1	6.2	0.1
	3	6.6	0.0
	5	6.6	0.1
PE-*g*-PS	1	6.4	0.2
	3	6.7	0.1
	5	6.7	0.1
PE-MA-PS	1	6.2	0.1
	3	5.2	0.5
	5	4.3	0.1
PE-HMM-PS	1	6.1	0.1
	3	5.8	0.1
	5	5.3	0.1

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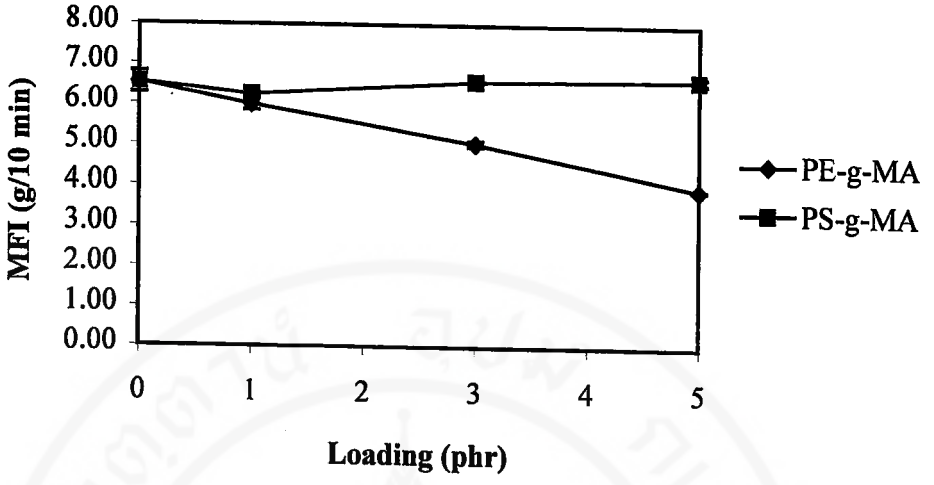

Figure 3.41 MFI of 75:25 LDPE/PS blends filled with various loadings of PE-*g*-MA and PS-*g*-MA

3.8.3 Effects of PE-*g*-PS, PE-MA-PS and PE-HMM-PS

Figure 3.42 shows the influences of the PE-*g*-PS, PE-MA-PS and PE-HMM-PS at various loadings on MFI of the corresponding blends. It is found that the MFI of the blends with PE-*g*-PS is approximately independent of PE-*g*-PS loading. By contrast, the morphology of the blend with PE-*g*-PS shown in Figure D1-D3 and Table 3.15 reveals the reduction in particle size of the dispersed phase, indicating an improvement in compatibility caused by an addition of PE-*g*-PS. The unexpected disagreement in MFI with morphology results is still not understood.

However, in the case of the blends with PE-MA-PS and PE-HMM-PS copolymers, it is found that the MFI decreases with increasing copolymer loading, which is again due to the improvement in compatibility. The higher MFI of the blends with PE-HMM-PS than those with PE-MA-PS suggests the effect of long hydrocarbon fraction of HMM which is more flexible than the MA moiety. The

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crosslinked structure developed during melt processing may also be responsible for the lower MFI of the blend with PE-MA-PS than those with PE-HMM-PS blends, which can be supported by the result of % grafting, as shown in Table 3.20. It is clear that the blends with PE-MA-PS show higher % grafting than the PE-HMM-PS blends.

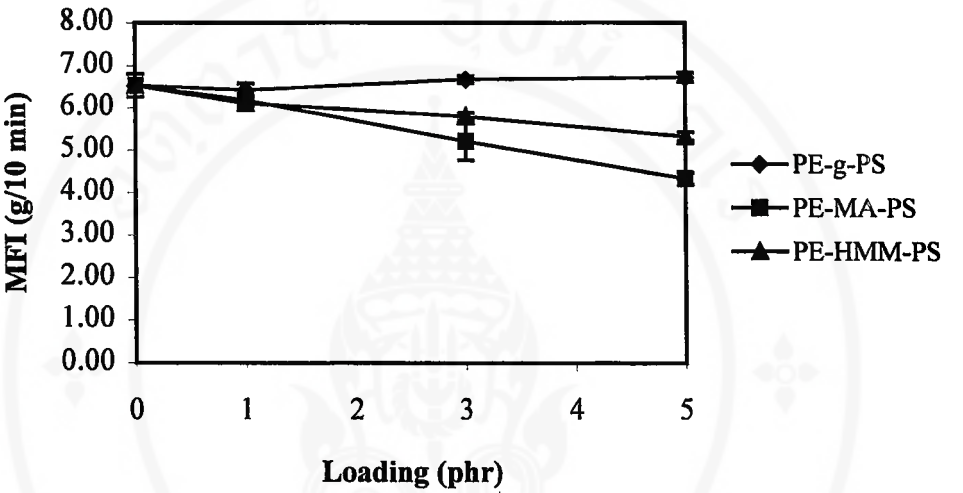

Figure 3.42 MFI of 75:25 LDPE/PS blends filled with various loadings of PE-*g*-PS, PE-MA-PS and PE-HMM-PS

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Table 3.20 % Grafting of 75:25 LDPE/PS blends with various loadings of PE-MA-PS, PE-HMM-PS and PE-*g*-PS

Copolymer	Loading (phr)	% LDPE	% PS	% Grafting
Control	0	73.52	26.46	0.02
PE-MA-PS	1	72.38	25.54	2.08
	3	62.45	24.28	13.27
	5	50.6	21.62	27.78
PE-HMM-PS	1	73.19	24.87	1.94
	3	73.26	23.49	3.25
	5	68.29	20.48	10.87
PE-*g*-PS	1	74.89	24.54	0.57
	3	72.03	25.08	2.89
	5	71.84	24.89	3.27

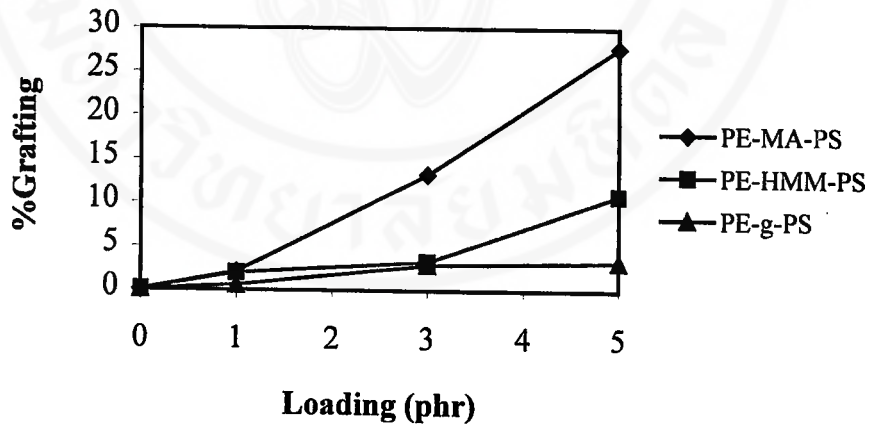

Figure 3.43 % Grafting of blends filled with various loadings of PE-MA-PS, PE-HMM-PS and PE-*g*-PS copolymers

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3.8.4 Effects of PP-*co*-PS

It is found in Figure 3.44 that no significant difference in flowability of the LDPE/PS blends containing various loadings of PP-*co*-PS was observed. Similar to

the case of PE-g-PS as mentioned earlier, the disagreement in MFI with a reduction in dispersed phase shown in Figure 3.39 is again not understood.

The result of grafting yield as illustrated in Table 3.22 and Figure 3.45 reveals the increase in grafting yield with copolymer loading. The result is unexpectedly not in agreement with the MFI result and still not understood. Also, it must be noted that the PP with low MFI (i.e. high MW.) gives greater gel content of the blends than the PP with high MFI.

Table 3.21 MFI of blends with PP-*co*-PS

Copolymer	Loading (phr)	MFI (g/10 min)	
		Average	Variance
Control	0	6.5	0.3
2SP55	1	6.0	0.1
	3	6.5	0.2
	5	6.7	0.1
2SP3.5	1	6.3	0.1
	3	6.5	0.1
	5	6.7	0.1
4SP3.5	1	6.1	0.1
	3	6.6	0.0
	5	6.8	0.0
4SP12	1	6.4	0.1
	3	6.5	0.1
	5	6.5	0.0

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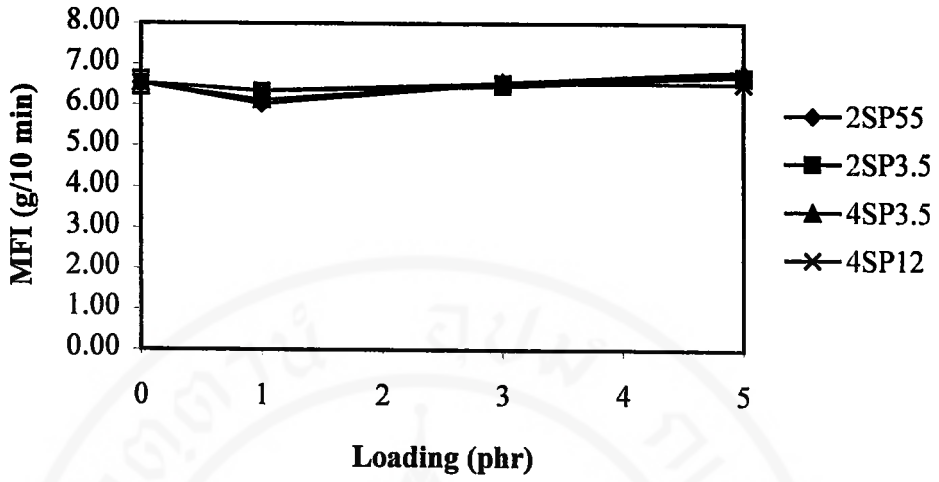

Figure 3.44 MFI of 75:25 LDPE/PS blends with various loadings of PP-*co*-PS

Table 3.22 % Grafting of the blends that contain with various loadings of PP-*co*-PS

Copolymer	Loading	% LDPE	% PS	% Grafting
Control	0	73.52	26.46	0.02
2SP55	1	74.35	25.47	0.18
	3	73.73	25.43	0.84
	5	72.85	26.28	0.87
2SP3.5	1	68.9	26.08	5.02
	3	49.43	22.14	28.43
	5	44.85	19.34	35.81
4SP3.5	1	67.89	23.77	8.34
	3	52.43	23.04	24.53
	5	47.76	22.37	29.87
4SP12	1	72.43	24.11	3.46
	3	68.79	23.42	7.79
	5	57.78	21.25	20.97

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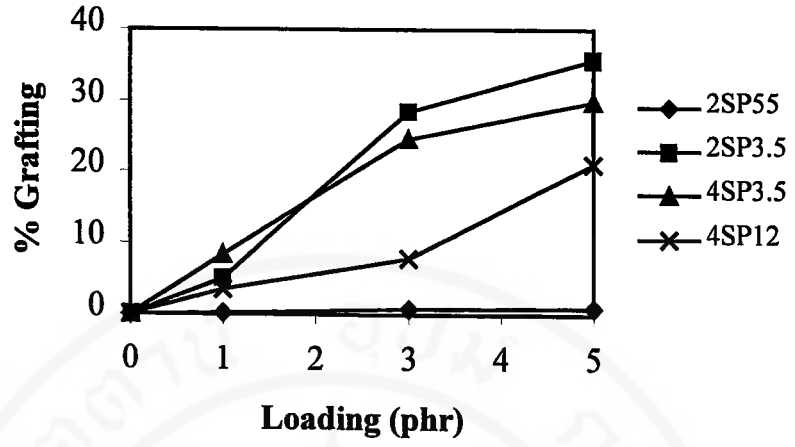

Figure 3.45 % Grafting of blends filled with various loadings of PP-*co*-PS

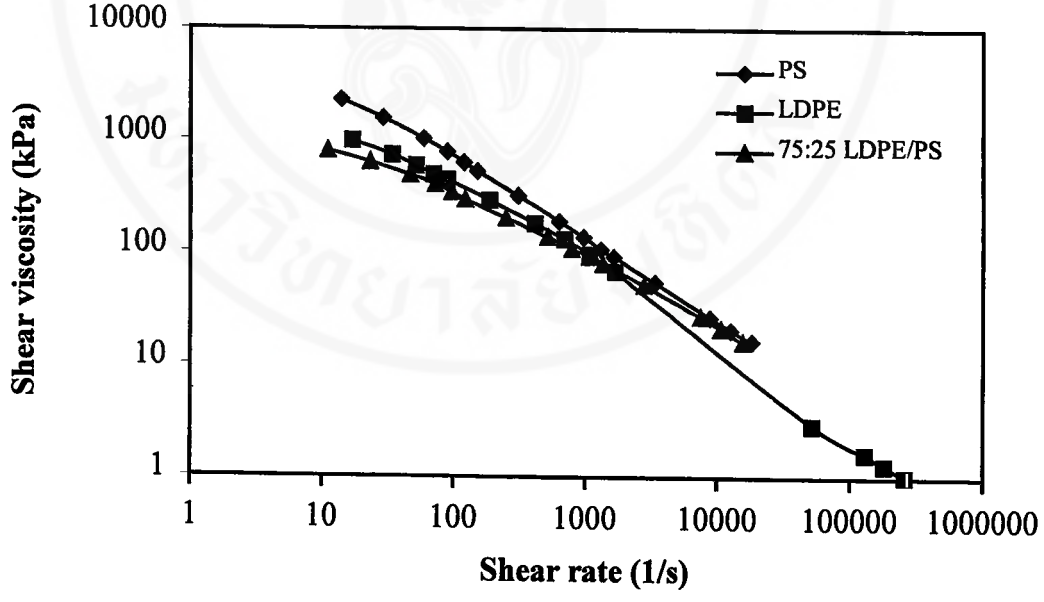

Figure 3.46 Shear viscosity of the homopolymer LDPE, PS and 75:25 LDPE/PS blends versus the shear rate

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As mentioned earlier that the melt rheology of polymer blends can be represented by flow curves. Thus, rheological properties of homopolymers, LDPE/PS blends and blends containing various amounts of PP-*co*-PS were investigated using

the capillary rheometer at 190°C, as shown in Figures 3.46-3.50. Figure 3.46 reveals that at the shear rate up to 1000 sec^{-1}, the viscosity of LDPE/PS blend is lower than those of the pure components, which is typical characteristic of the immiscible blend. This behaviour is related to the interlayer slip associated with the repulsive forces between immiscible polymers leading to a reduction in density at the interface.[19]

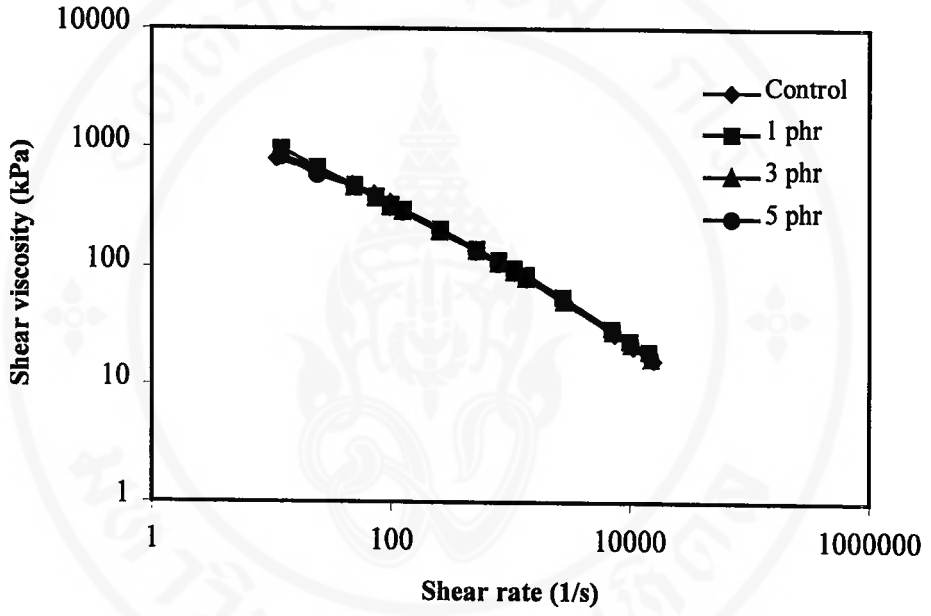

Figure 3.47 Shear viscosity of 75:25 LDPE/PS blends with various loadings of 2SP55

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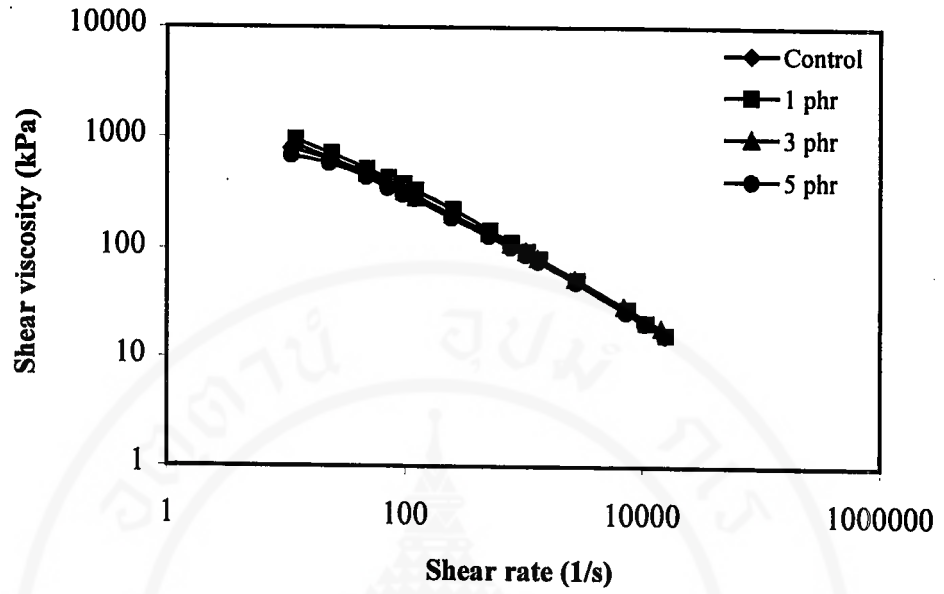

Figure 3.48 Shear viscosity of 75:25 LDPE/PS blends with various loadings of 2SP3.5

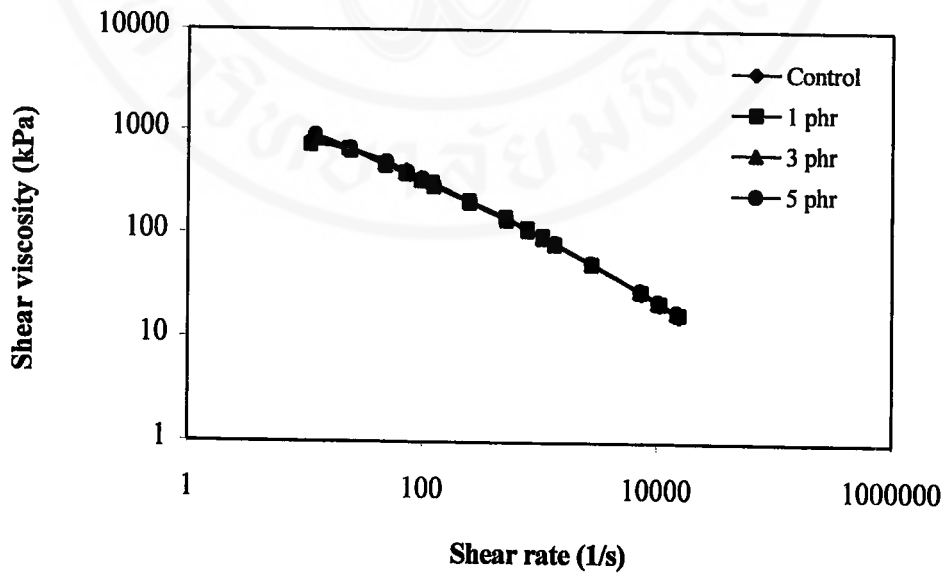

Figure 3.49 Shear viscosity of 75:25 LDPE/PS blends with various loadings of 4SP3.5

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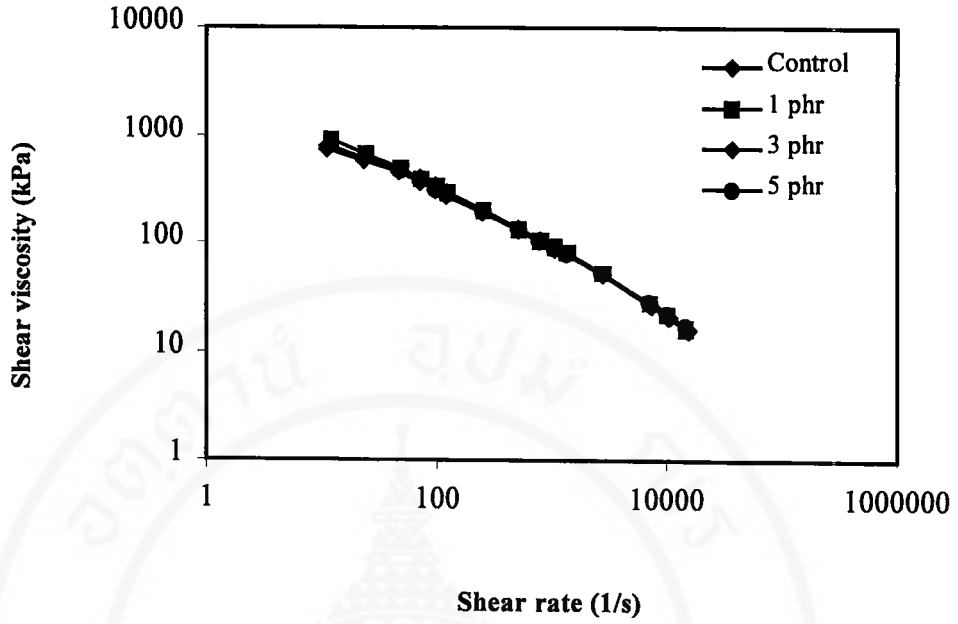

Figure 3.50 Shear viscosity of 75:25 LDPE/PS blends with various loadings of 4SP12

It is obvious from Figures 3.47-3.50 that no significant difference in melt viscosity of the blends compatibilised with the PP-*co*-PS compared to the LDPE/PS blend. These results are in accordance with the results of MFI. However, the data from MFI and capillary rheological measurement are not in agreement with the gel contents. As stated previously, the disagreement is still not understood.

3.8.5 The rheological properties of *in-situ* compatibilised blend

The MFI of the EgSMA3, EgSMA3H and EgSMA3D blends is shown in Table 3.23 and Figure 3.51. It is evident that the addition of diamine, either aliphatic or aromatic type, does not affect the melt viscosities of the blend. In theory, the addition of diamine should give imide linkage and thus an increase in melt viscosity. However, in the present study, the amount of copolymers used might be so small that the imide linkages taking place do not influence the MFI.

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Table 3.23 The MFI of *in-situ* compatibilised blends

Copolymer	MFI (g/10 min)	
	Average	Variance
EgSMA3	5.9	0.0
EgSMA3H	5.7	0.1
EgSMA3D	5.5	0.0

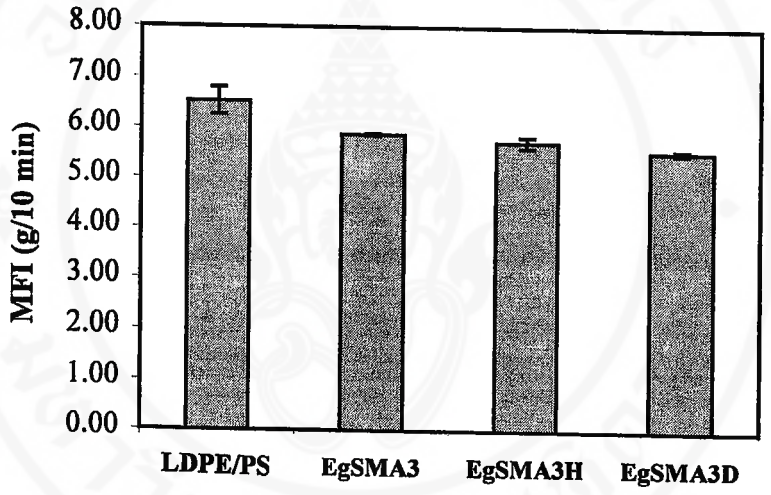

Figure 3.51 MFI of EgSMA3, EgSMA3H and EgSMA3D blends

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CHAPTER IV

CONCLUSIONS

In the present thesis, the following conclusions could be made.

1. Functionalisation of polyethylene and polystyrene with maleic anhydride (PE-*g*-MA and PS-*g*-MA) could be carried out by reactive processing. The MA content was successfully quantified by titration method using cresol red as an indicator. The grafting yield of MA was about 40% and 10% for PE and PS respectively. During the reaction in the melted state, crosslinking of PE and chain scission of PS were noticed.

2. Utilisation of PE-*g*-MA and PS-*g*-MA as reactive compatibilisers in PE-rich LDPE/PS blend gave a slight improvement in mechanical properties of the blends. This may be due to the inherent properties of the added copolymer and slight improvement of interfacial adhesion between the phases. However, side reactions such as crosslinking in the case of PE-*g*-MA and chain scission reaction in the case of PS-g-MA might inhibit the potential formation of copolymer between the matrix and the dispersed phase.

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3. When PE-*g*-PS, PE-MA-PS and PS-HMM-PS copolymers were used as compatibilisers, they may stabilise the PS dispersed phase and inhibit the coalescence, resulting in a reduction of the particle size of the PS compared to the uncompatibilised blend. The domain size of PS droplets was decreased with loading of the copolymer.

The PE-MA-PS and PE-HMM-PS could improve the yield stress and modulus. The MFI decreases with increasing the amounts of the PE-MA-PS and PE-HMM-PS copolymers while PE-*g*-PS compatibilised blends give a slight increase in MFI.

4. The addition of PE-*g*-MA and PS-*g*-MA with amine crosslinkers in PE/PS blends, result in the *in-situ* formation of linkage between reactive functionalities during processing. It was found that the utilisation of HMD (EgSMA3H) affected the mechanical properties and the rheological properties of the blend more significantly than DAPS (EgSMA3D). By contrast, DAPS could reduce the domain size of the dispersed phase more efficiently than HMD due to the rigidity of aromatic ring in DAPS.

5. Mechanical properties of the LDPE/PS blends were improved by the use of PP-*co*-PS series. The 4SP12 were the most efficient copolymer in this series. It was found that the compatibilisation effectiveness of the copolymer did not alter the rheological properties of the blends.

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6. In the case of blends containing PE-MA-PS, PE-HMM-PS and PP-*co*-PS, the average particle size of the dispersed phase was reduced when a small amount of the copolymer was added, but further loading of the copolymers causes the phase separation of partial crosslinked LDPE and PP and the particle size distribution of the dispersed phase become broader. However, the average particle sizes of these blends were still smaller than the uncompatibilised blend.

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APPENDICES

Appendix A: DSC thermogram of various polymers and copolymers

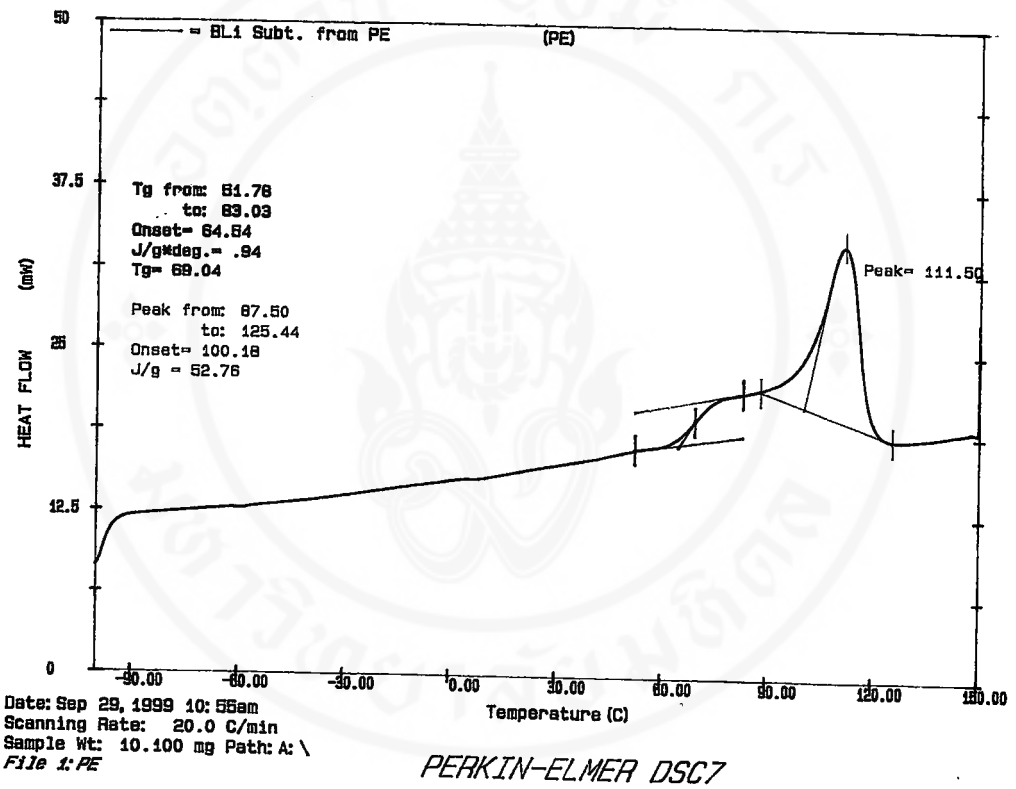

Figure A1 DSC thermogram of LDPE

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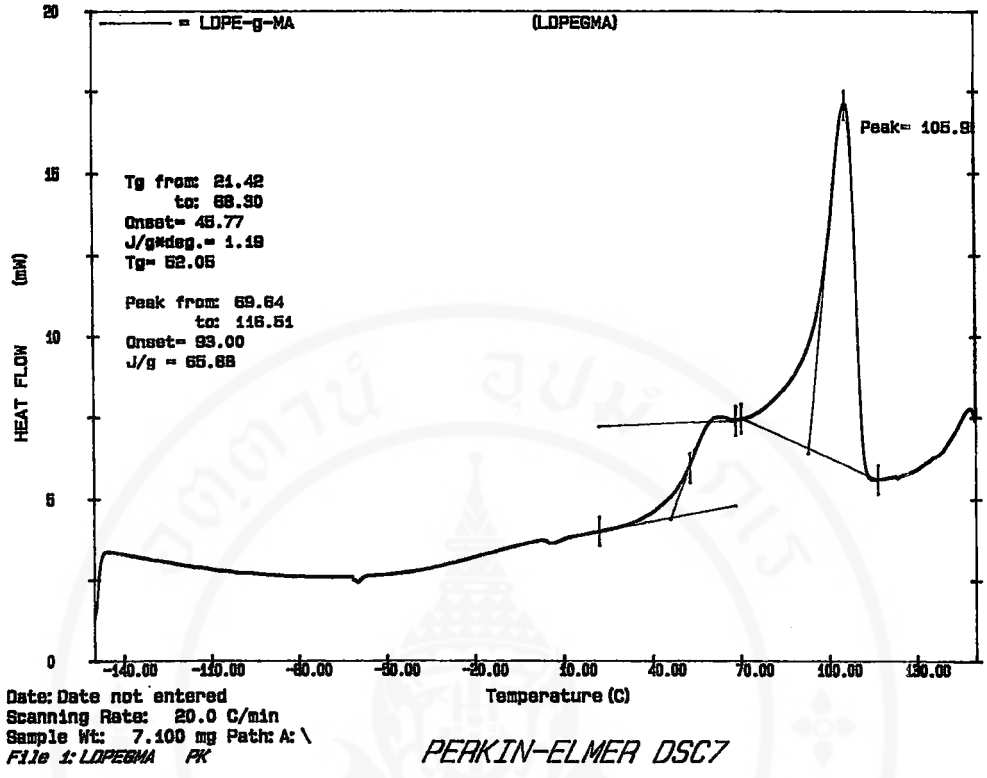

Figure A2 DSC thermogram of PE-g-MA

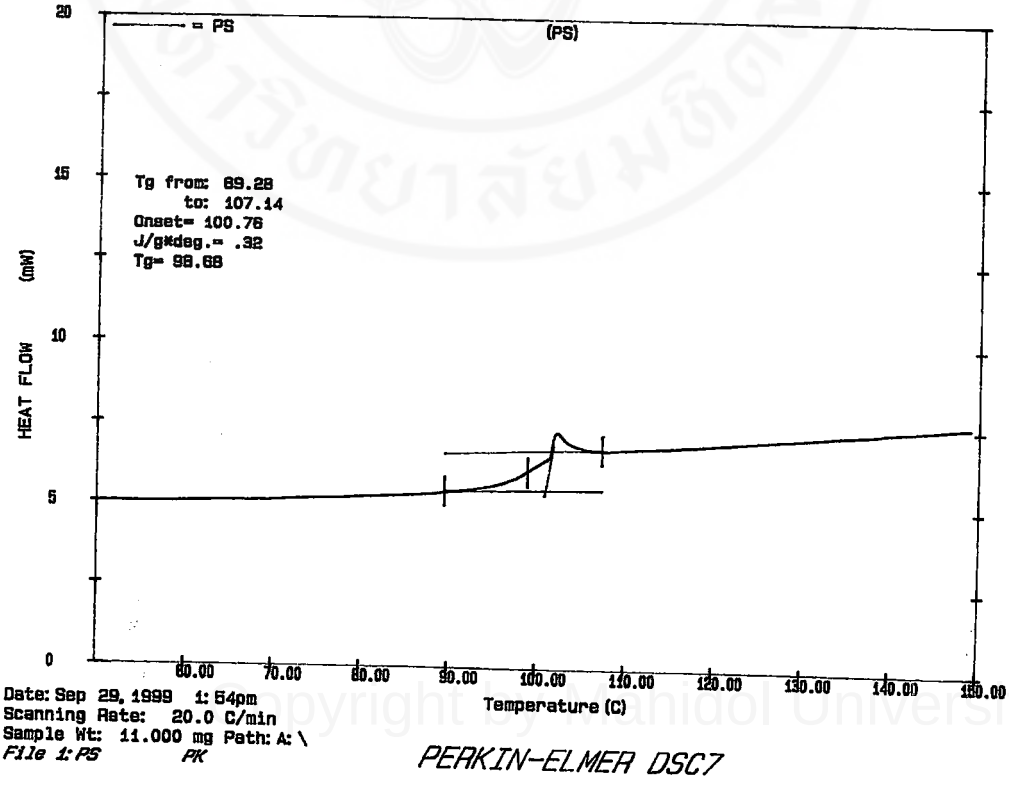

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Figure A3 DSC thermogram of PS

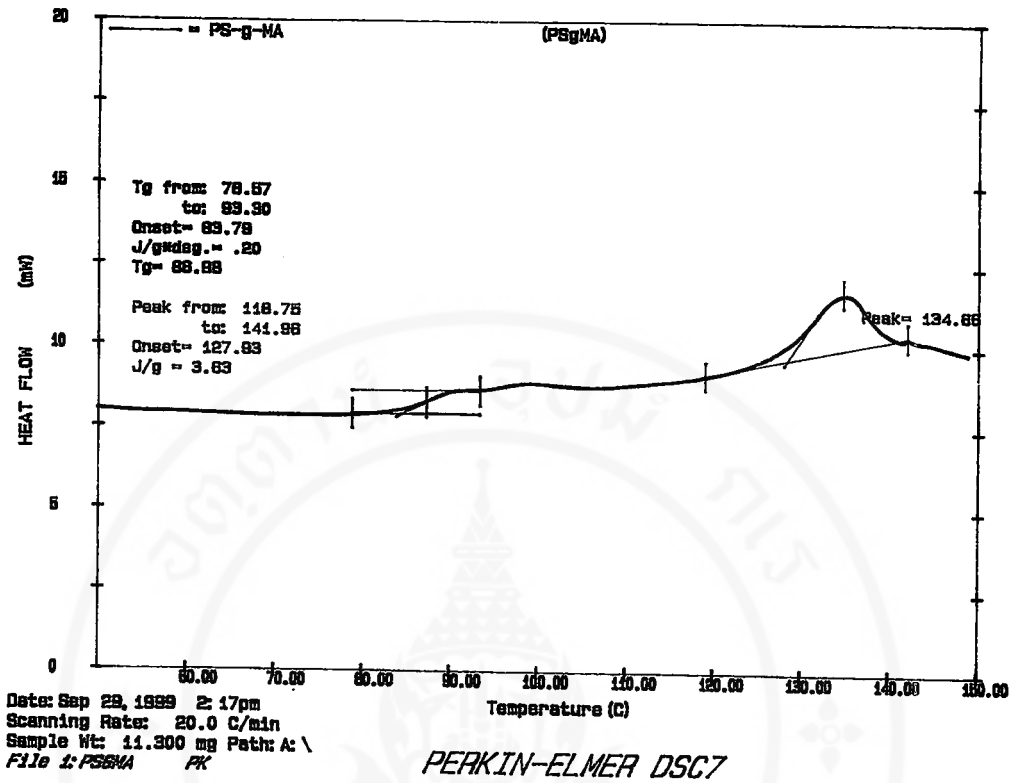

Figure A4 DSC thermogram of PS-g-MA

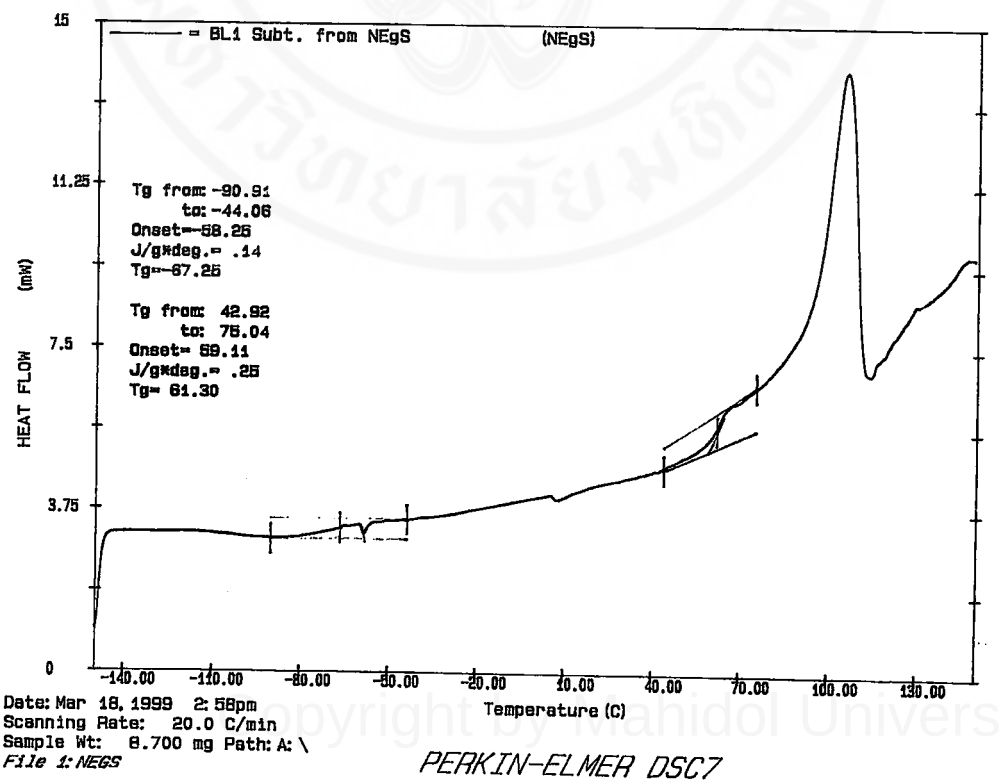

Figure A5 DSC thermogram of PE-MA-PS

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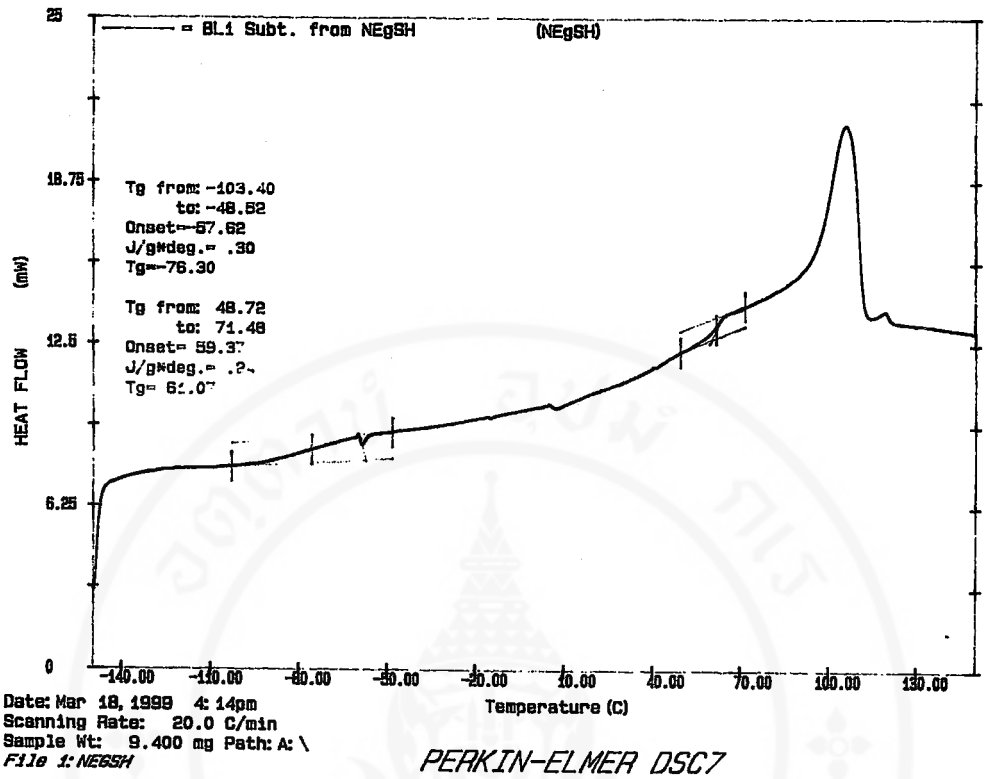

Figure A6 DSC thermogram of PE-HMM-PS

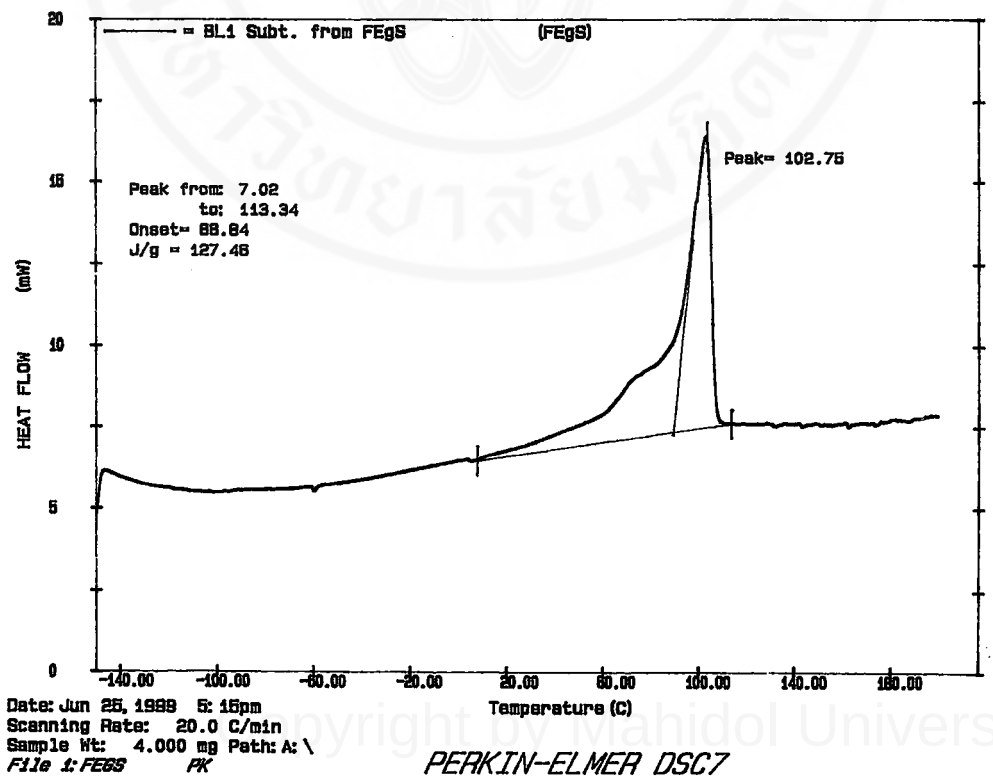

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Figure A7 DSC thermogram of PE-g-PS

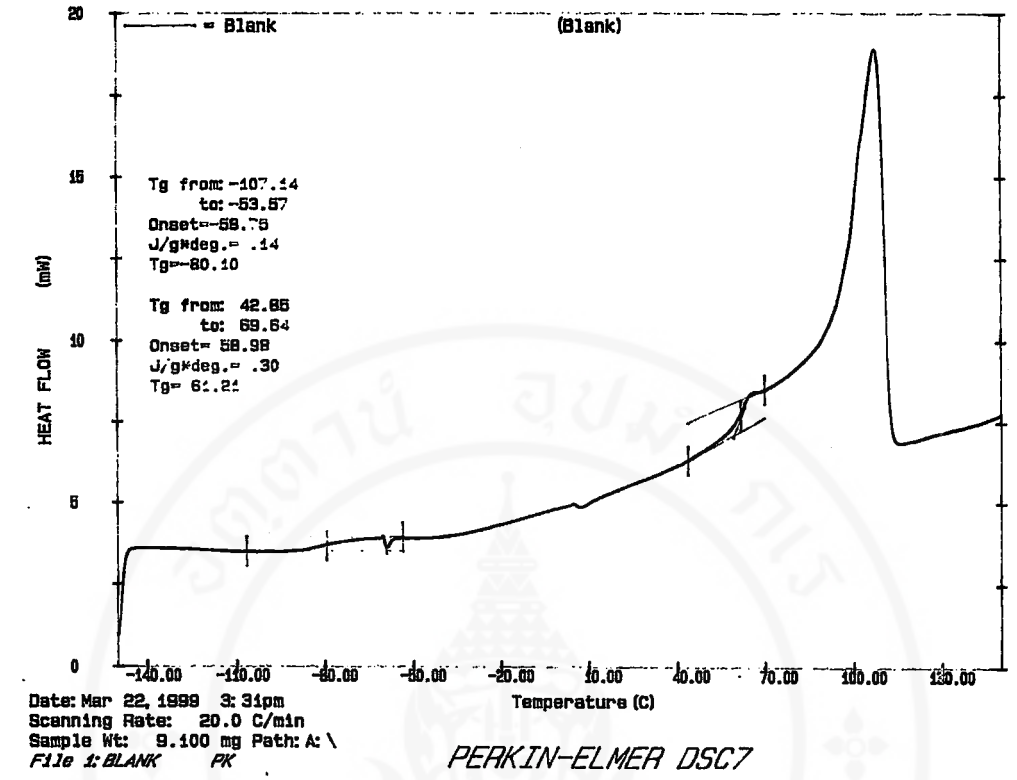

Figure A8 DSC thermogram of 75:25 LDPE/PS blend

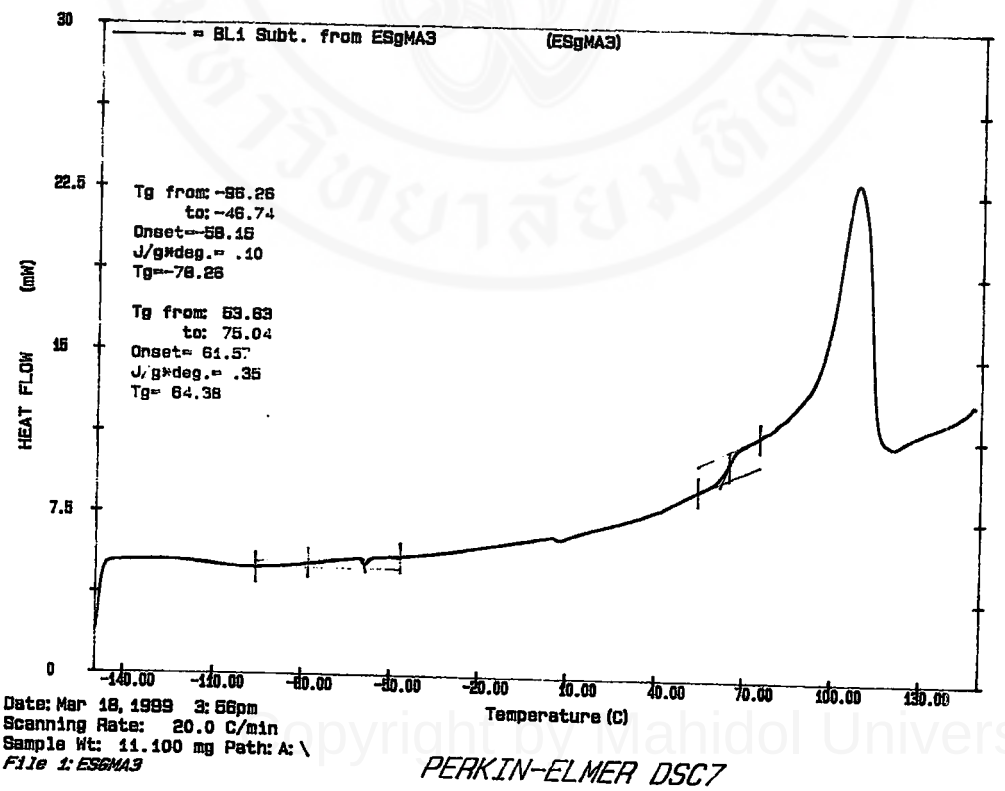

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Figure A9 DSC thermogram of EgSMA3

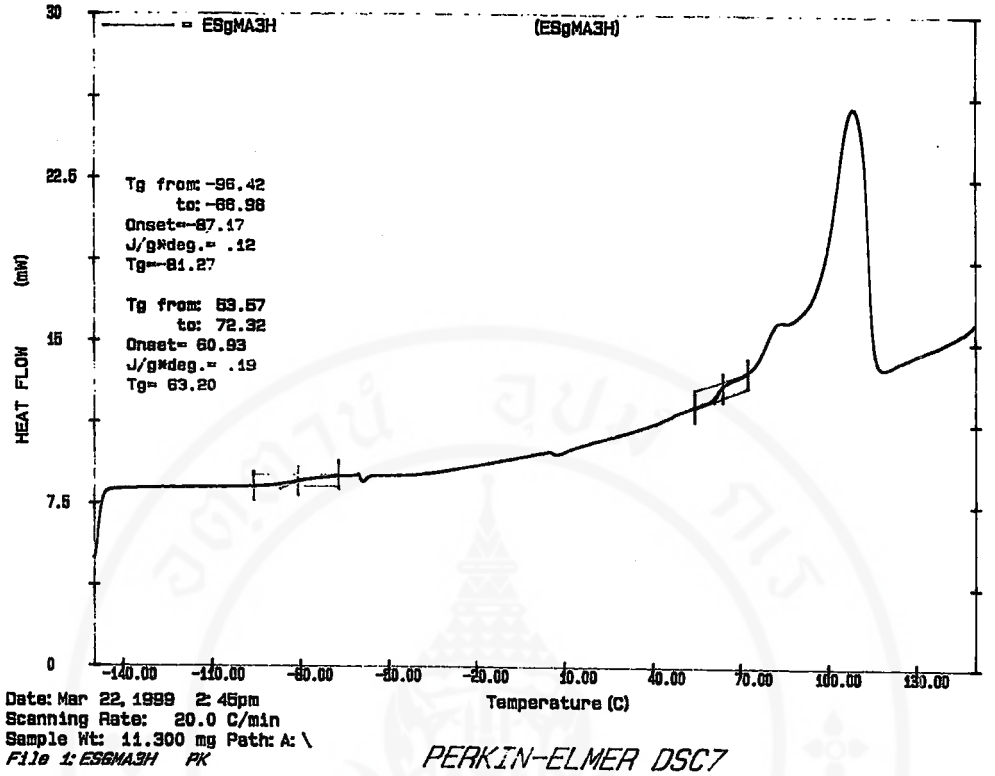

Figure A10 DSC thermogram of EgSMA3H

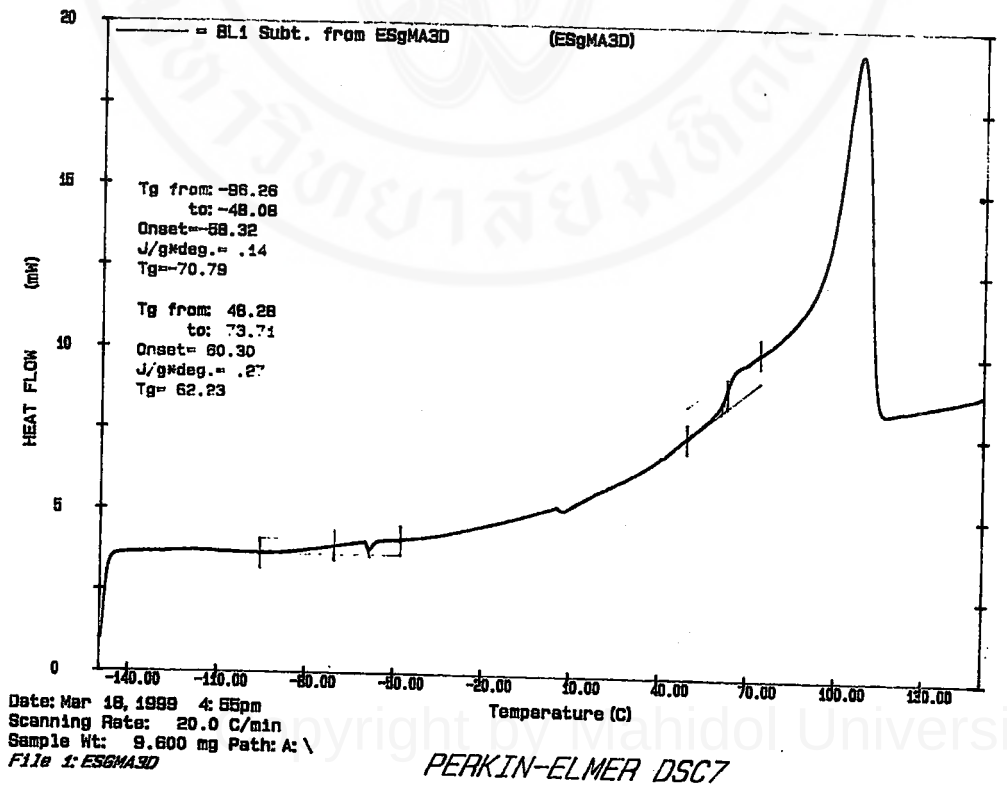

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Figure A11 DSC thermogram of EgSMA3D

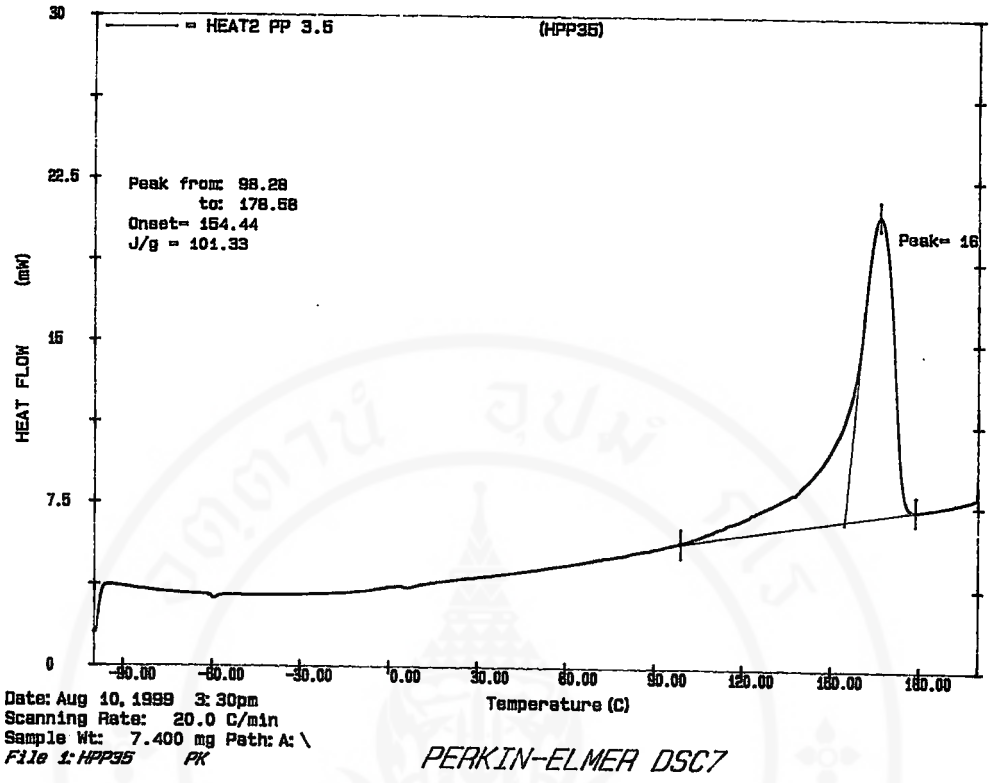

Figure A12 DSC thermogram of PP3.5

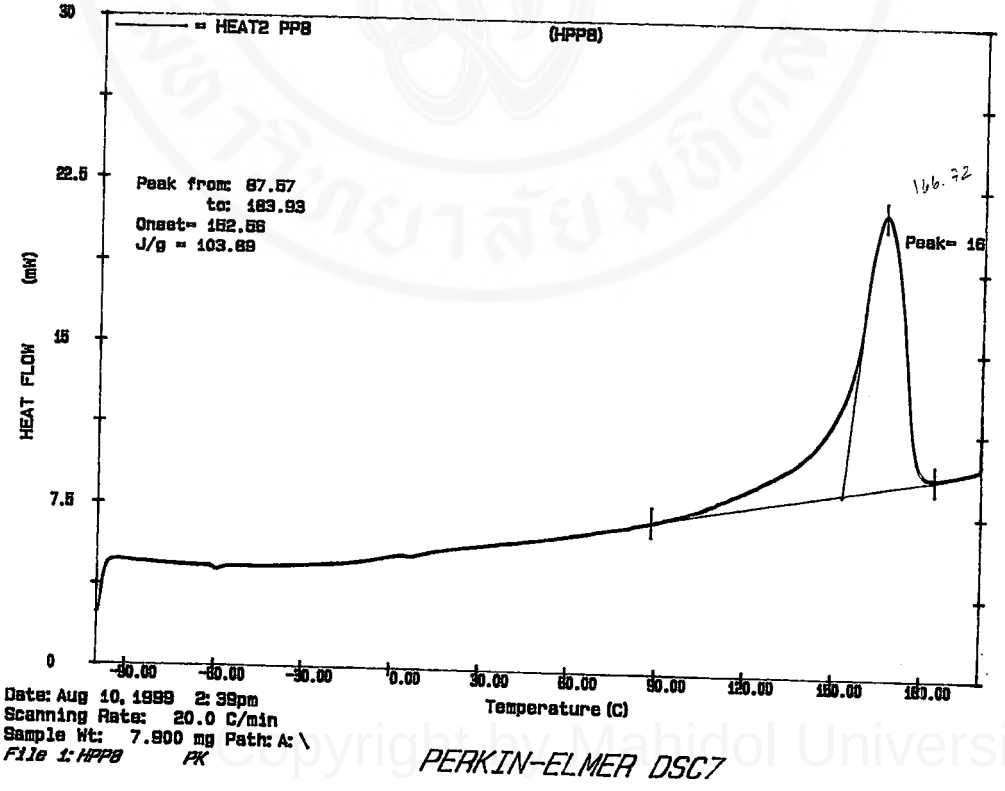

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Figure A13 DSC thermogram of PP8

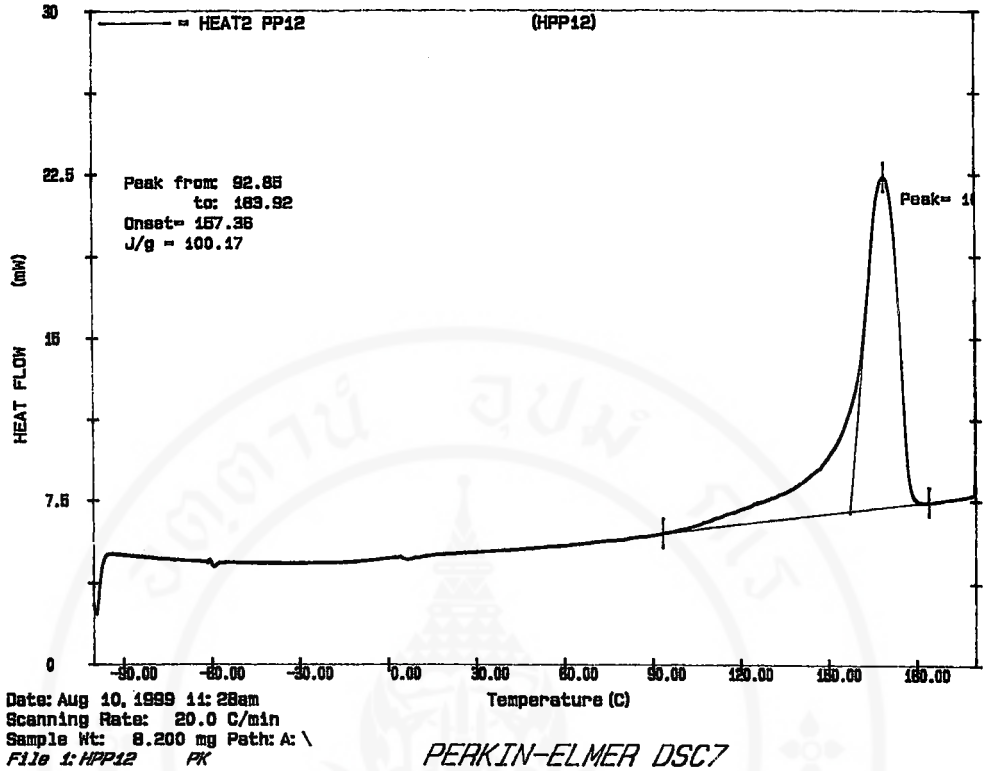

Figure A14 DSC thermogram of PP12

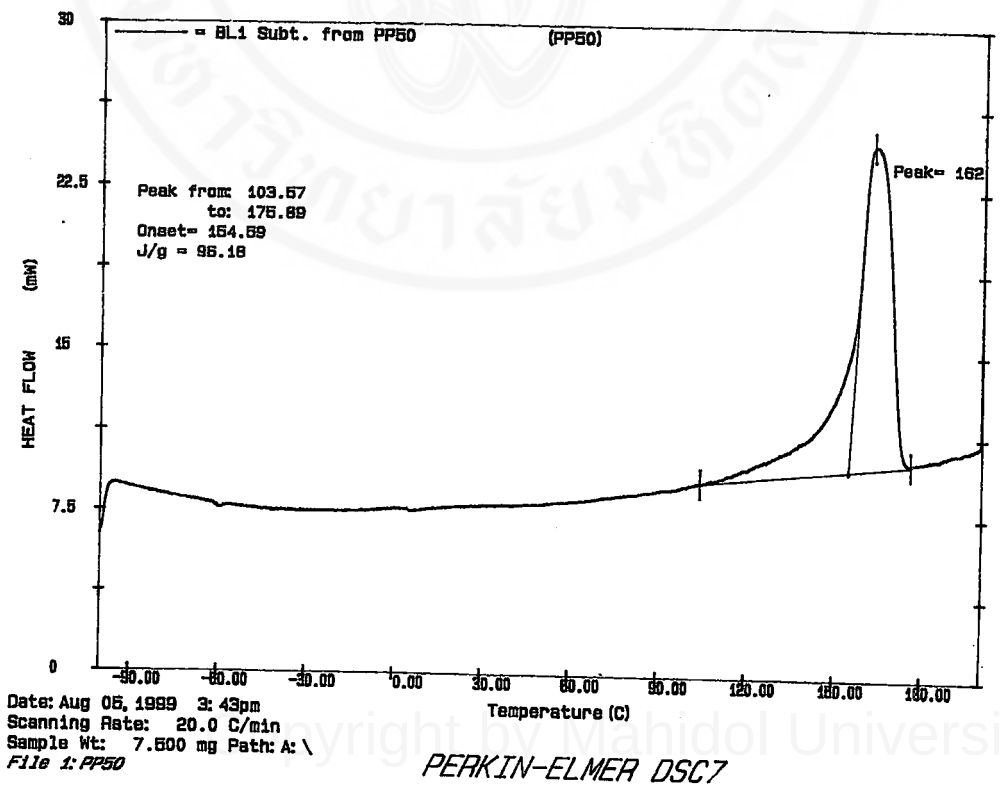

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Figure A15 DSC thermogram of PP55

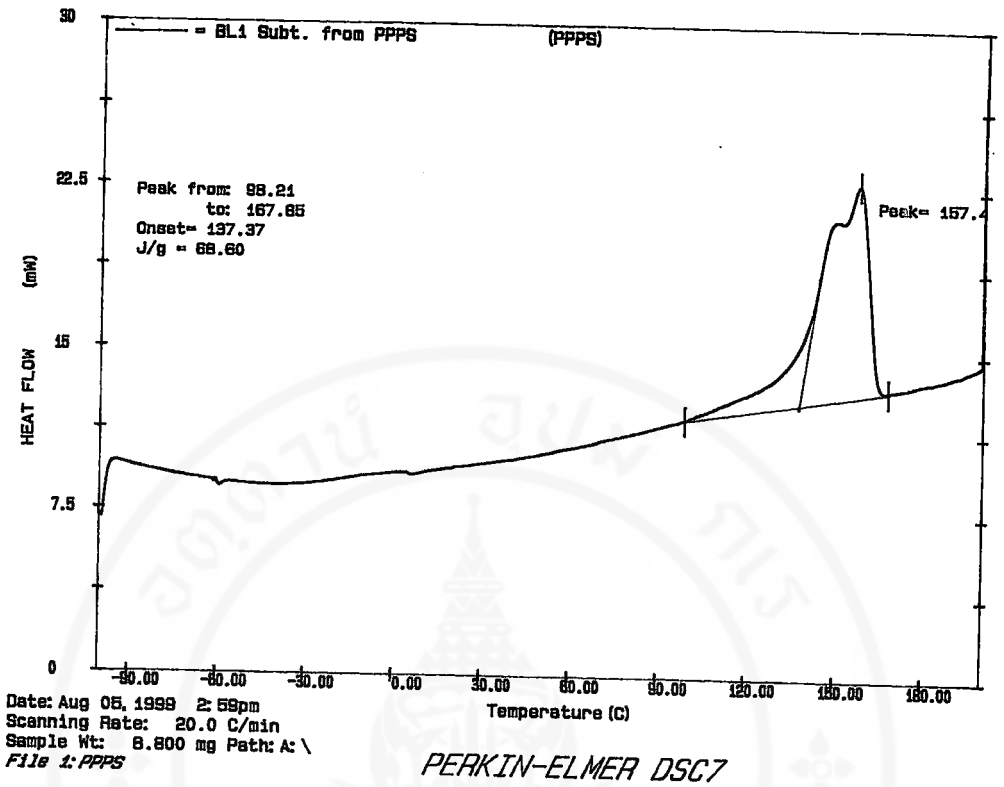

Figure A16 DSC thermogram of 50/50 PP/PS blend

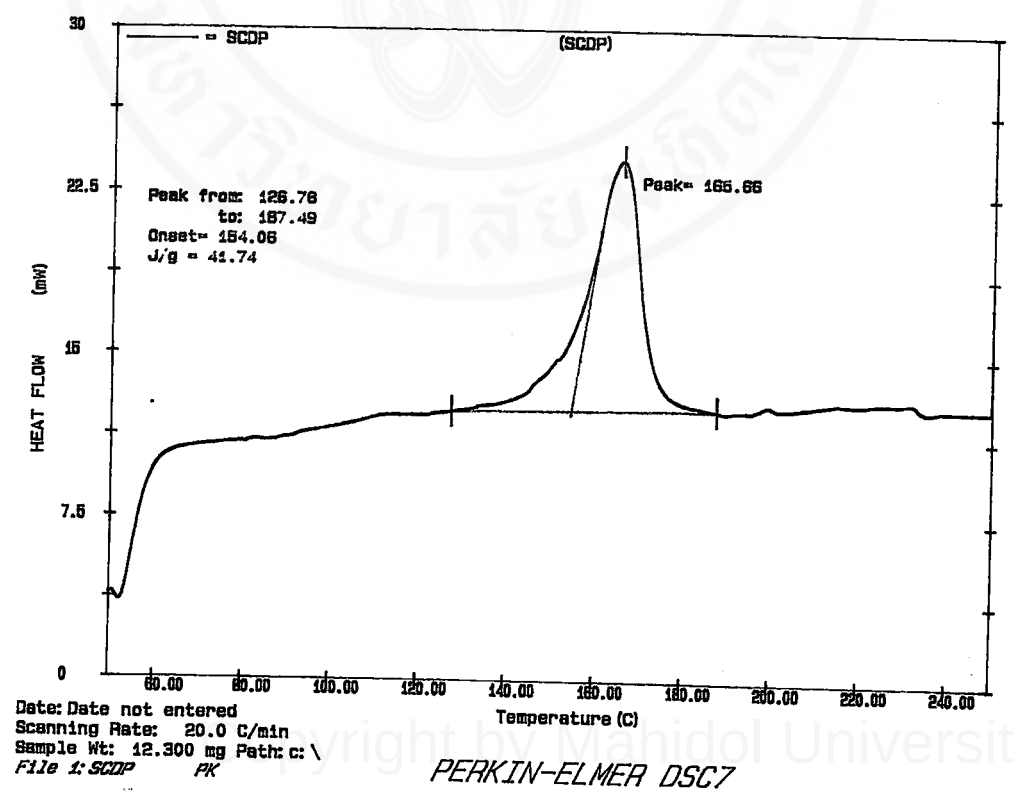

Figure A17 DSC thermogram of 2SP55

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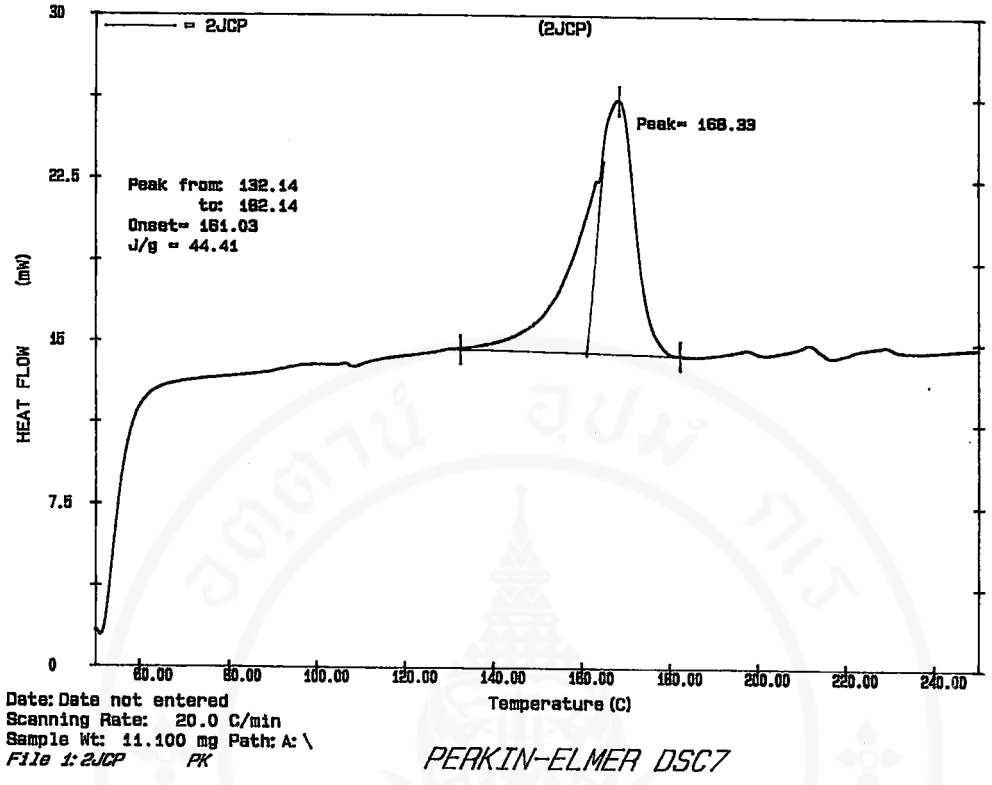

Figure A18 DSC thermogram of 2SP3.5

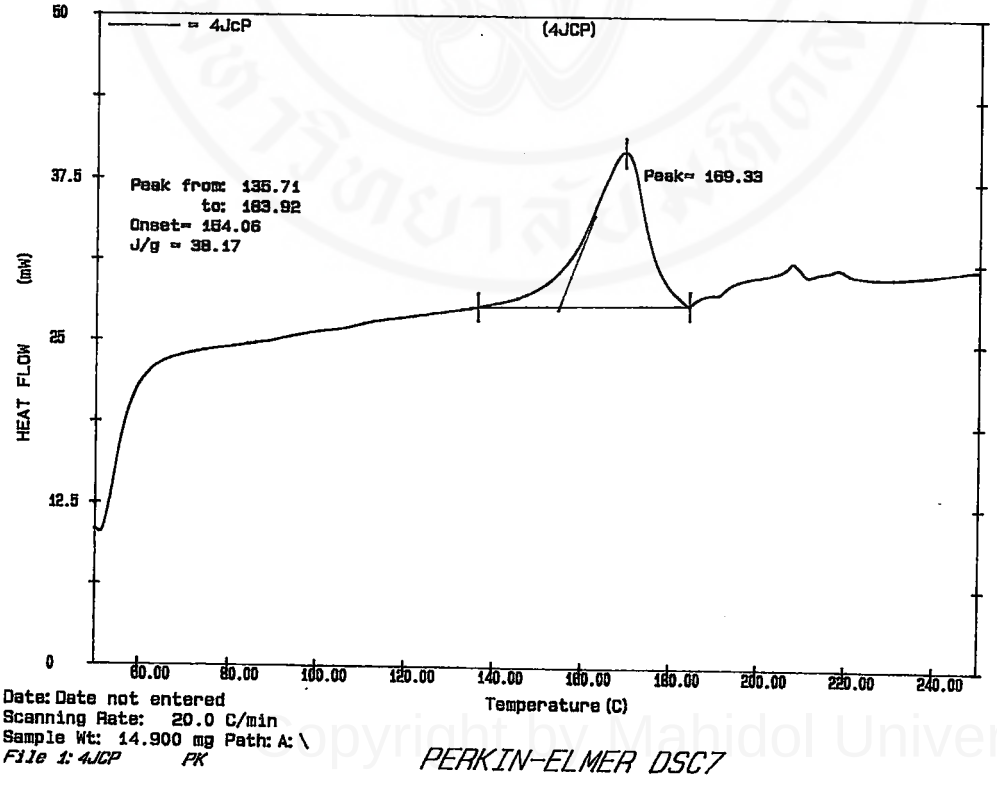

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Figure A19 DSC thermogram of 4SP3.5

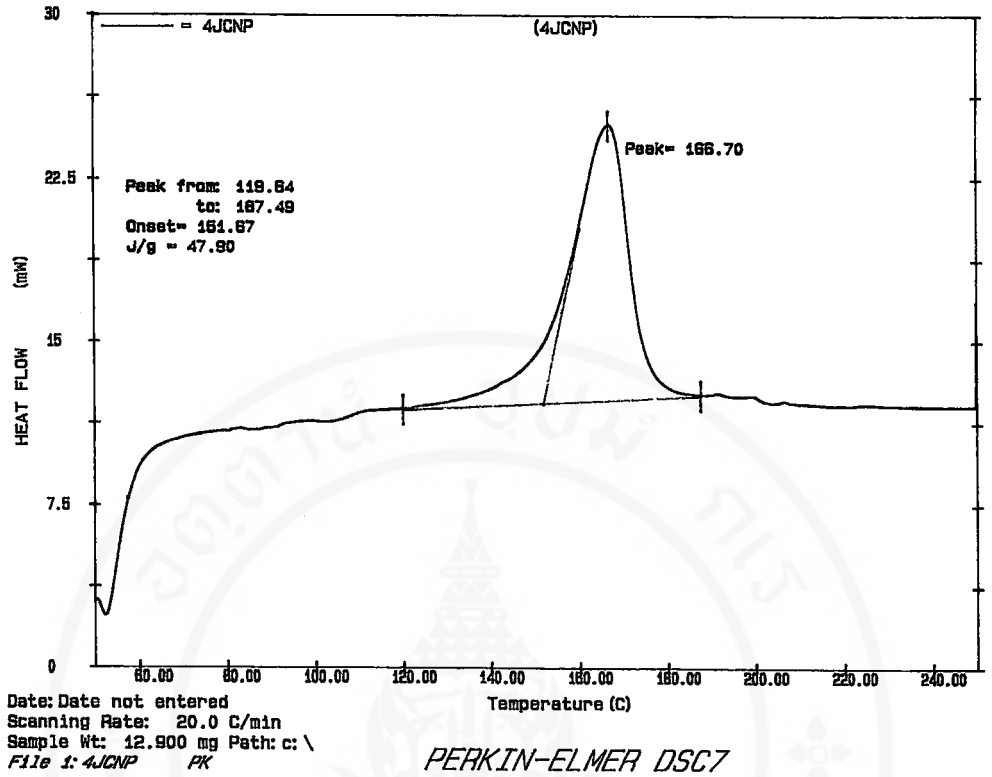

Figure A20 DSC thermogram of 4SP12

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Appendix B: Mechanical properties of various blends.

Table B1 Tensile properties of uncompatiblised LDPE/PS blend and compatibilised blends with PE-*g*-MA and PS-*g*-MA

Copolymer	Loading (phr)	Yield stress (MPa)		Secant modulus at 1% strain (MPa)		% Elongation at break	
		average	variance	average	variance	average	variance
Control	0	12.58	0.12	609.4	16.61	35.03	2.76
PE-g-MA	1	12.73	0.27	589.73	4.85	42.57	3.57
	3	12.32	0.11	555.13	8.93	51.69	3.45
	5	12.04	0.1	526.11	18.11	56.16	1.88
PS-g-MA	1	13.24	0.104	612.37	12.54	40.18	3.21
	3	13.65	0.14	637.4	39.93	31.27	2.98
	5	15.15	0.25	732.34	19.34	23.93	2.49

Table B2 Impact strengths of uncompatiblised LDPE/PS blend and compatibilised blends with PE-*g*-MA and PS-*g*-MA

Sample	loading	Impact strength (kJ/mm^2)	
		Average	Variance
Control	0	6.66	0.22
PE-g-MA	1	7.04	0.18
	3	7.33	0.37
	5	7.97	0.37
PS-g-MA	1	6.42	0.14
	3	5.98	0.6
	5	4.75	0.51

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Table B3 Tensile properties of the blends containing various amounts of PE-*g*-PS, PE-MA-PS and PE-HMM-PS compatibilisers

Copolymer	Loading (phr)	Yield stress (MPa)		Secant modulus at 1% strain (MPa)		% Elongation at break	
		Average	Variance	Average	Variance	Average	Variance
Control	0	12.58	0.12	609.4	16.61	35.03	2.76
PE-g-PS	1	12.11	0.24	583.05	17.68	40.98	3.72
	3	12.35	0.10	543.73	16.27	50.03	3.12
	5	12.45	0.18	583.05	12.13	52.26	2.89
PE-MA-PS	1	12.99	0.14	601.23	15.42	37.05	4.78
	3	13.07	0.12	607.82	17.58	31.48	4.59
	5	13.23	0.14	634.25	14.26	25.42	6.28
PE-HMM-PS	1	12.87	0.07	589.65	19.63	36.78	5.75
	3	13.00	0.18	612.23	26.41	31.63	4.30
	5	13.19	0.08	628.96	15.64	28.74	3.12

Table B4 Impact strengths of blends containing various amounts of PE-*g*-PS, PE-MA-PS and PE-HMM-PS compatibilisers

Copolymer	Loading (phr)	Impact strength (kJ/mm^2)	
		Average	Variance
Control	0	6.66	0.22
PE-g-PS	1	7.45	0.17
	3	8.45	0.54
	5	7.84	0.69
PE-MA-PS	1	9.10	0.90
	3	7.44	0.79
	5	8.56	0.56
PE-HMM-PS	1	8.91	0.59
	3	7.78	0.51
	5	9.24	0.06

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Table B5 Tensile properties of the blends containing the PP-*co*-PS series

Copolymer	Loading (phr)	Yield stress (MPa)		Secant modulus at 1% strain (MPa)		% Elongation at break	
		Average	Variance	Average	Variance	Average	Variance
Control	0	12.58	0.12	609.40	16.61	35.03	2.76
2SP55	1	12.42	0.29	580.79	18.91	34.44	5.39
	3	13.27	0.13	629.83	16.17	26.03	5.75
	5	13.66	0.19	651.53	10.26	30.85	5.69
2SP3.5	1	13.02	0.14	643.31	17.63	39.41	2.28
	3	13.09	0.28	642.03	19.66	30.37	6.17
	5	13.80	0.29	694.92	20.40	25.15	5.24
4SP3.5	1	13.66	0.19	651.53	10.26	30.85	5.69
	3	12.77	0.19	627.97	12.66	36.27	4.44
	5	12.97	0.32	633.52	25.59	34.99	4.30
4SP12	1	13.31	0.24	607.46	22.78	38.62	2.96
	3	14.21	0.02	624.41	14.95	29.94	2.02
	5	14.09	0.19	650.85	17.59	28.75	2.51

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Table B6 Impact strength of blends containing various types of PP-*co*-PS

Copolymer	Loading (phr)	Impact strength (kJ/mm^2)	
		Average	Variance
Control	0	6.66	0.22
2SP55	1	8.47	0.57
	3	7.77	0.77
	5	7.07	0.61
2SP3.5	1	7.50	0.50
	3	6.42	0.40
	5	5.92	0.45
4SP3.5	1	7.40	0.49
	3	7.09	0.59
	5	6.72	0.63
4SP12	1	9.64	0.68
	3	8.04	0.66
	5	7.87	0.59

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Table B7 Tensile properties of the blends containing both of PE-*g*-MA and PS-*g*-MA with and without diamine compounds

Sample	Yield stress (MPa)		Secant modulus at 1% strain (MPa)		% Elongation at break	
	Average	Variance	Average	Variance	Average	Variance
Control	12.58	0.12	609.40	16.61	35.03	2.76
EgSMA3	13.12	0.42	620.23	10.23	36.45	5.87
EgSMA3H	12.54	0.18	631.53	11.48	37.61	2.98
EgSMA3D	12.88	0.21	624.79	18.32	32.74	7.61

Table B8 Impact strengths of the blends containing both PE-*g*-MA and PS-*g*-MA with and without diamine compounds

Sample	Impact strength (kJ/mm^2)	
	Average	Variance
Control	6.66	0.22
EgSMA3	6.54	0.15
EgSMA3H	5.42	0.19
EgSMA3D	5.89	0.27

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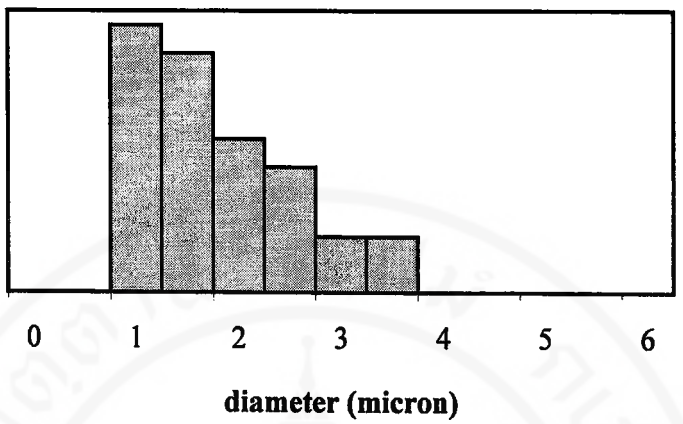
Appendix C: Dispersed phase size distribution of the blends



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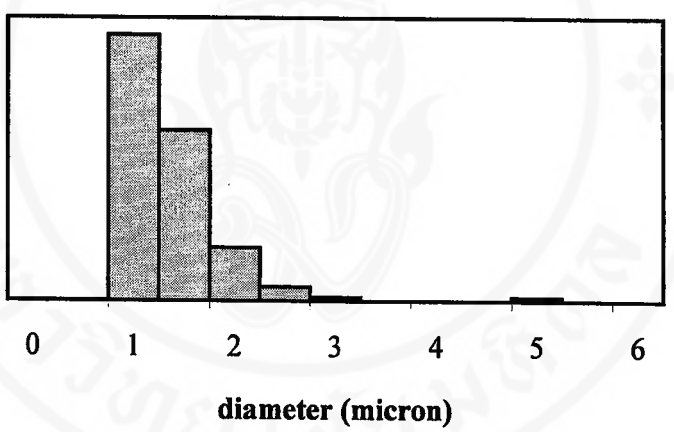
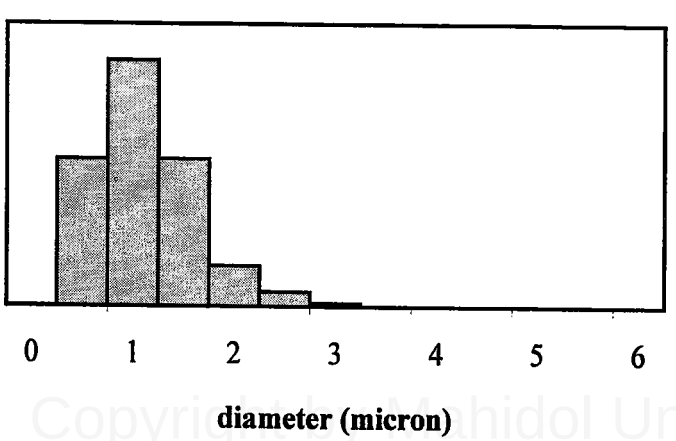


B)



C)

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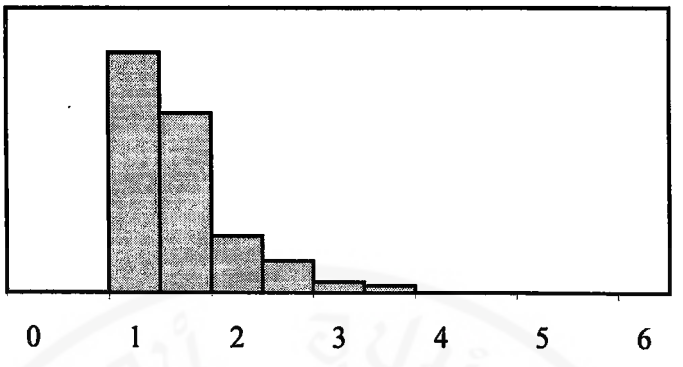
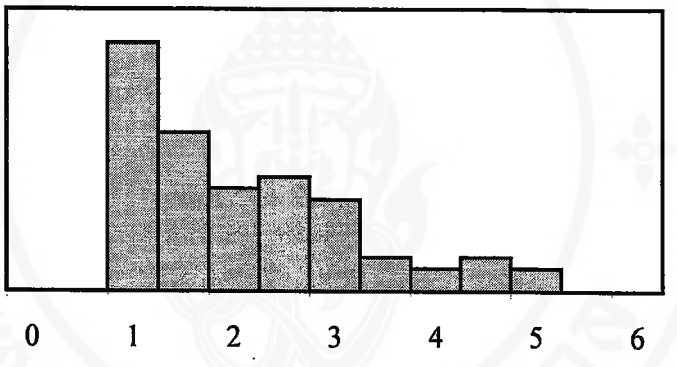
Figure C1 Particle size distribution of the 75/25 LDPE/PS blends with PE-*g*-PS ; A) 1 phr; B) 3 phr; C) 5 phr



A)



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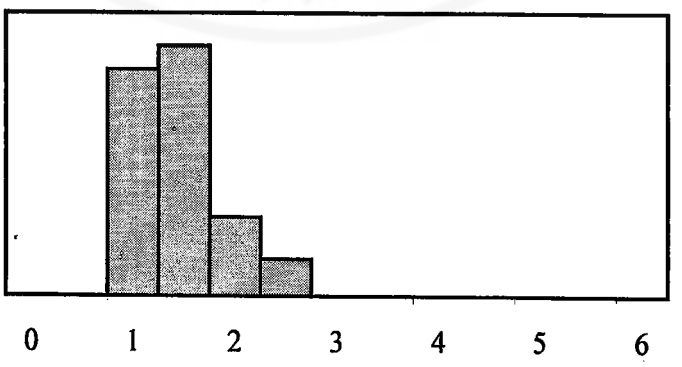

C)

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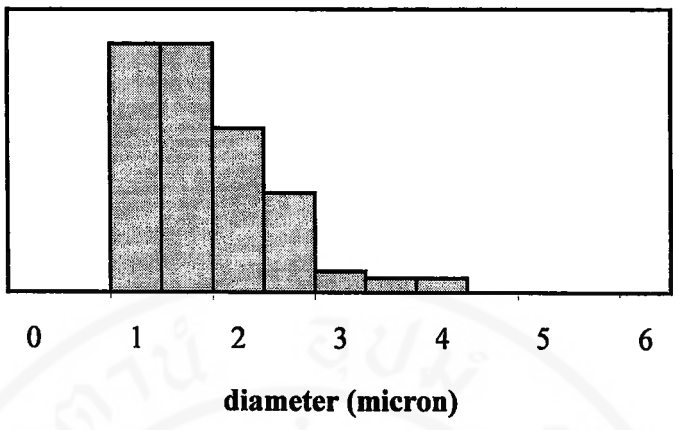
Figure C2 Particle size distribution of the 75/25 LDPE/PS blends with PE-MA-PS; A) 1 phr; B) 3 phr; C) 5 phr



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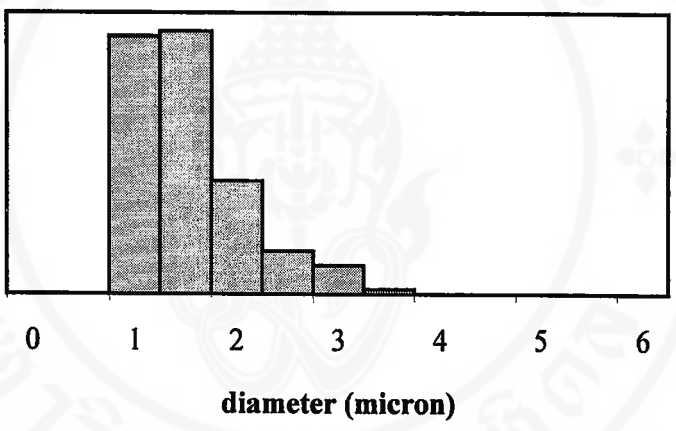

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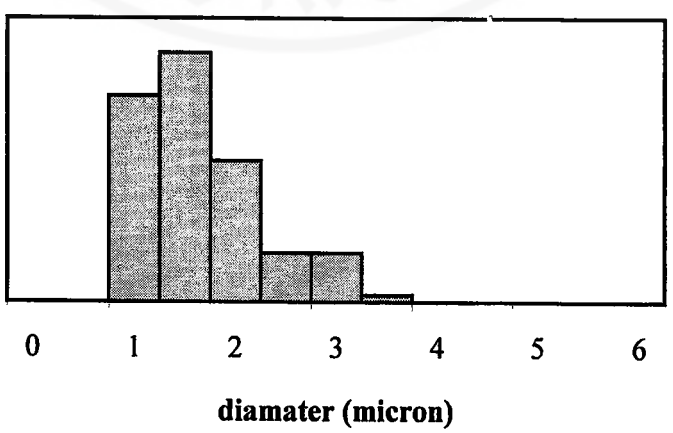

C)

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Figure C3 Particle size distribution of the 75/25 LDPE/PS blends with PE-HMM-PS; A) 1 phr; B) 3 phr; C) 5 phr

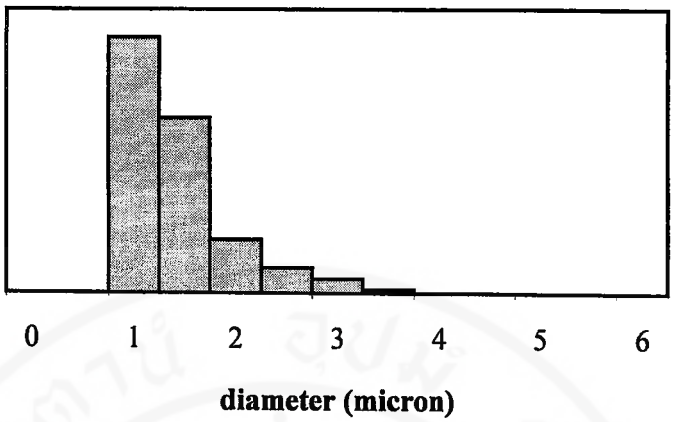

Figure C4. Particle size distribution of EgSMA3

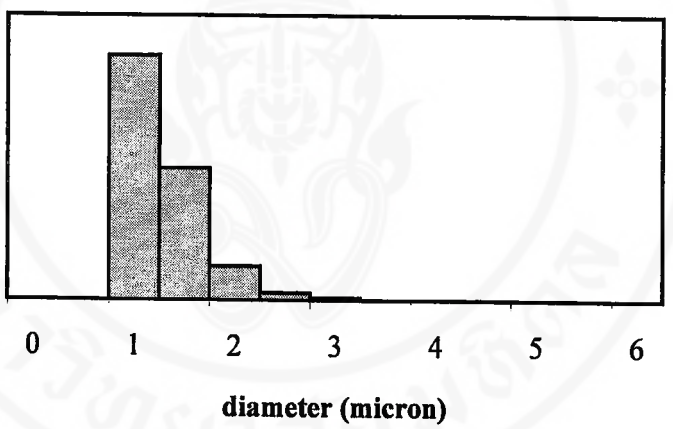

Figure C5. Particle size distribution the EgSMA3H

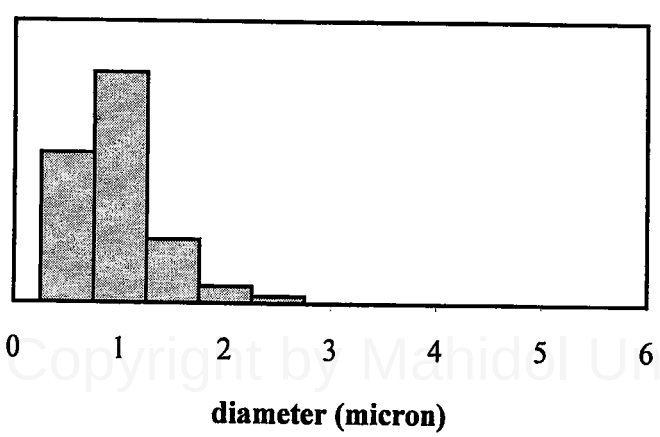

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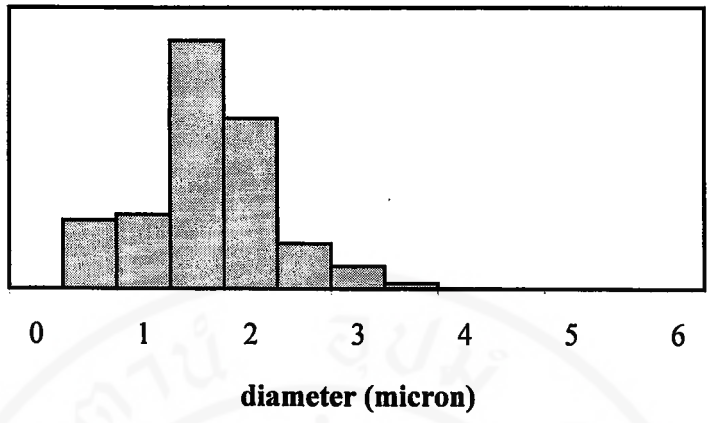
Figure C6. Particle size distribution the EgSMA3D



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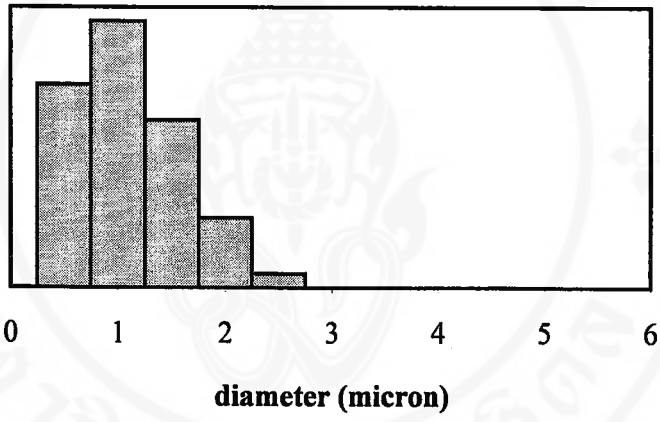

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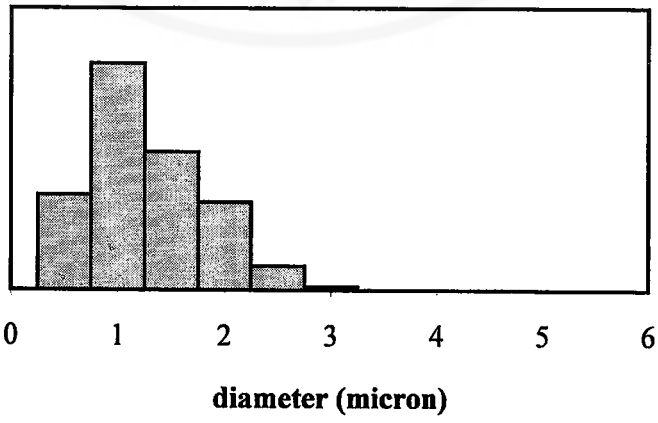

C)

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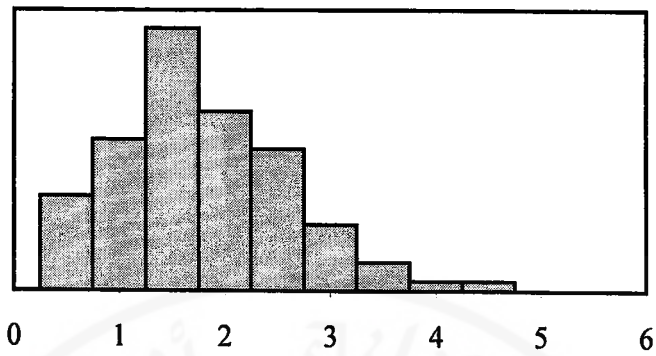
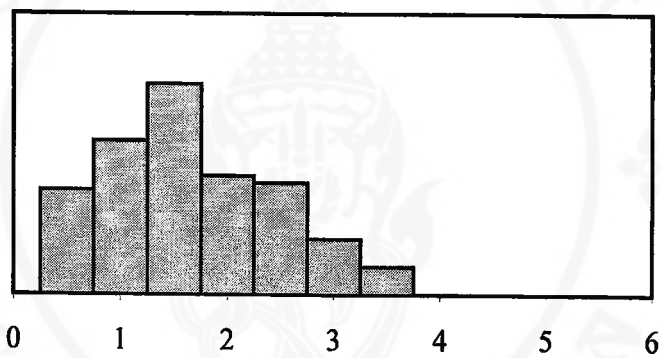
Figure C7 Particle size distribution of the 75/25 LDPE/PS blends with 2SP55 ;

A) 1 phr; B) 3 phr; C) 5 phr



A)



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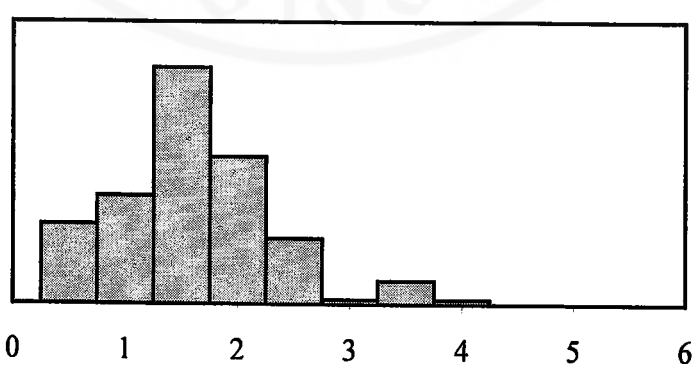

C)

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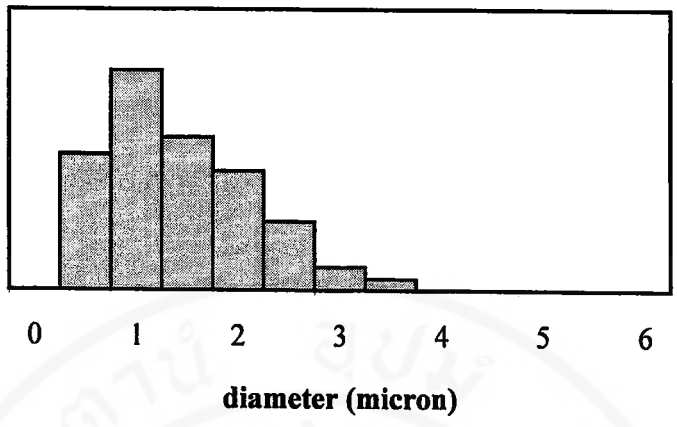
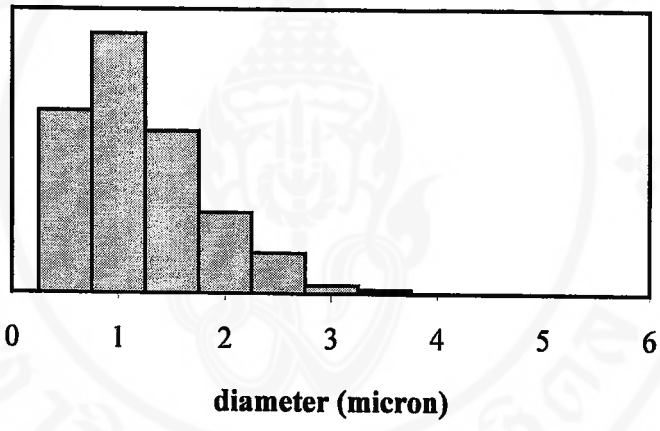
Figure C8 Particle size distribution of the 75/25 LDPE/PS blends with 2SP3.5;

A) 1 phr; B) 3 phr; C) 5 phr



A)



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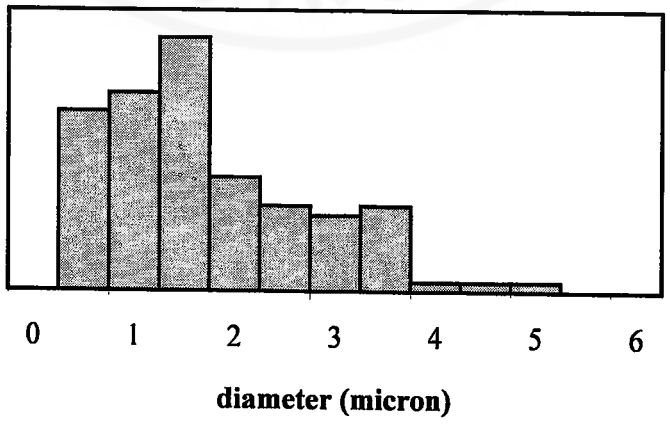

C)

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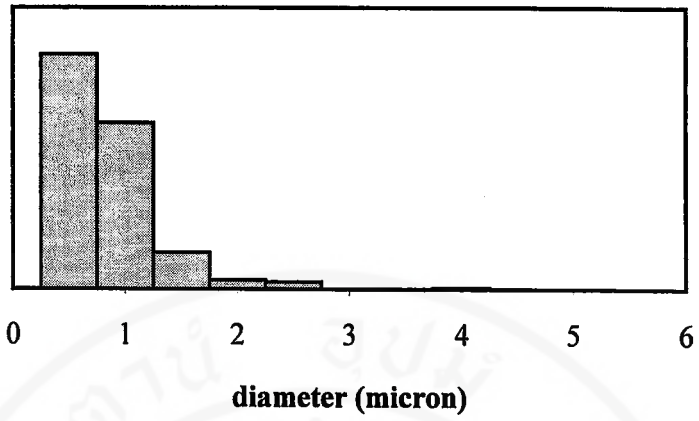
Figure C9 Particle size distribution of the 75/25 LDPE/PS blends with 4SP3.5 ;

A) 1 phr; B) 3 phr; C) 5 phr



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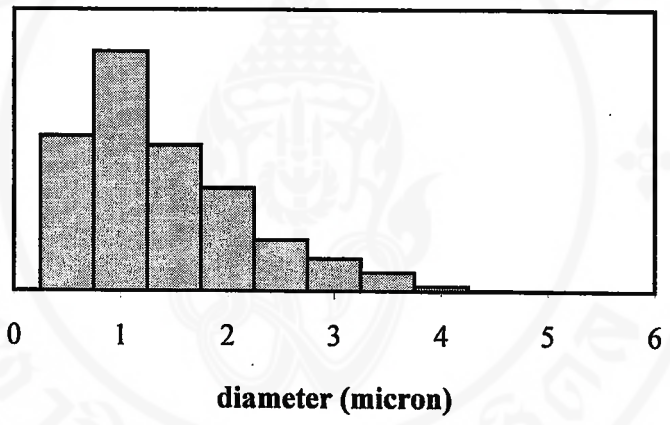

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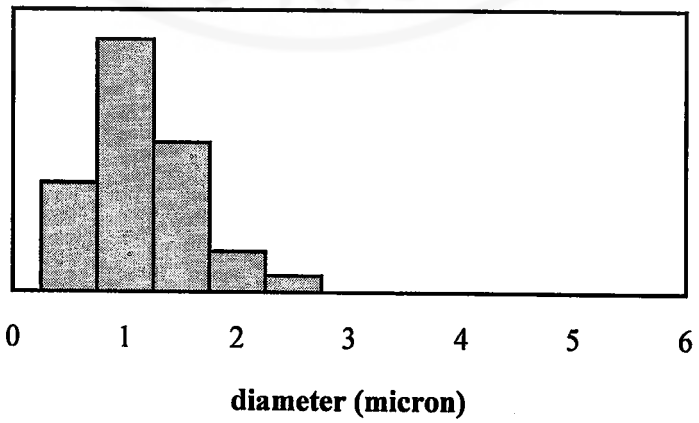

C)

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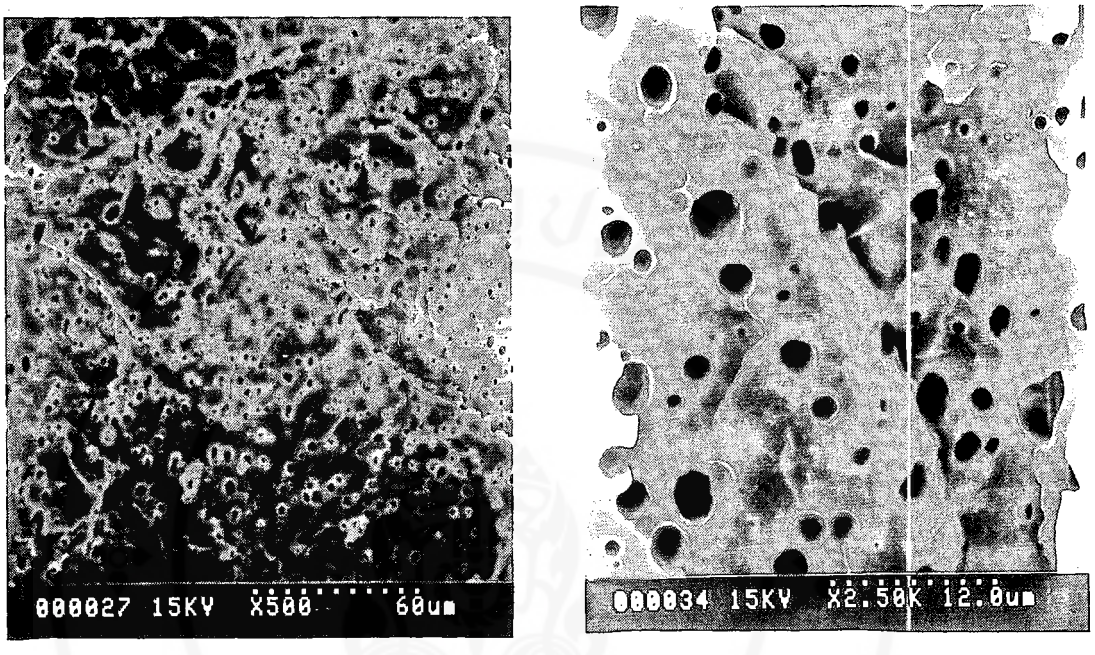
Figure C10 Particle size distribution of the 75/25 LDPE/PS blends with 4SP12;

A) 1 phr; B) 3 phr; C) 5 phr

Appendix D: Scanning electron micrograph of the blends with various compatibilisers.



A) B)

Figure D1 SEM micrograph of 75:25 LDPE/PS blend with PE-*g*-PS 1 phr:

A) x 500; B) x 2500

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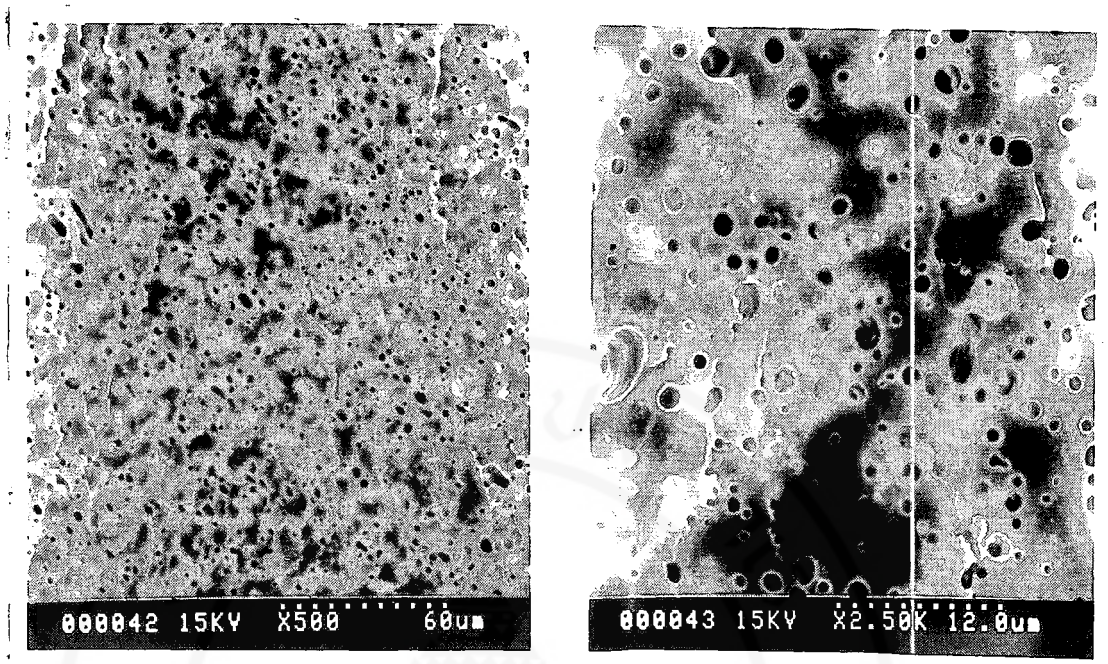
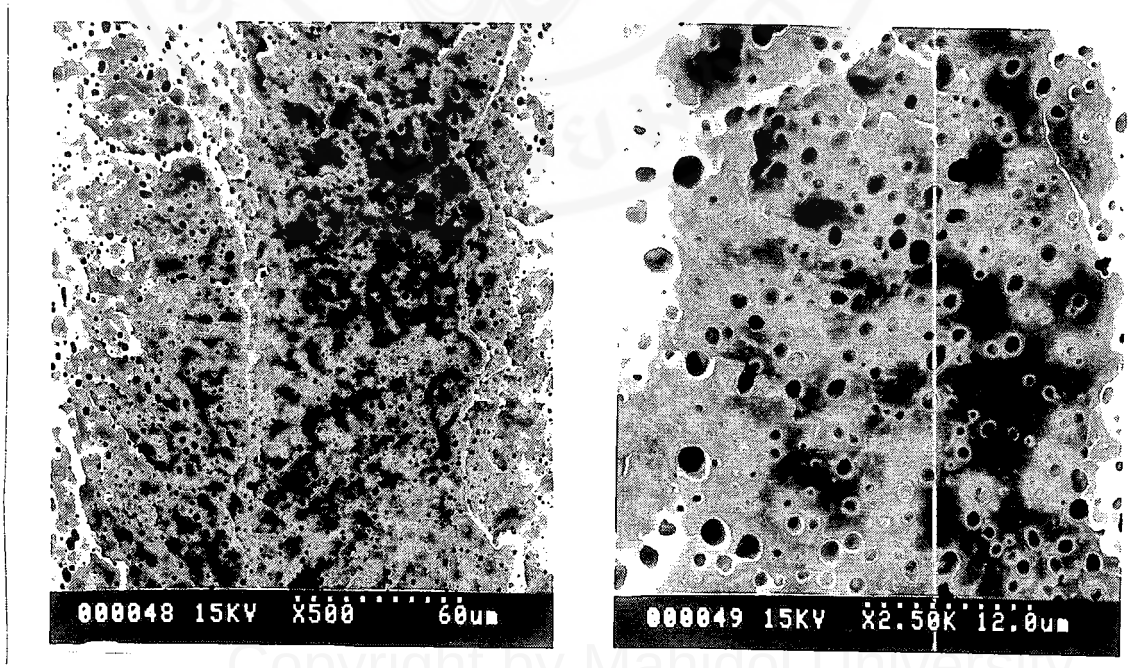


A) B)

Figure D2 SEM micrograph of 75:25 LDPE/PS blend with PE-*g*-PS 3 phr:

A) x 500; B) x 2500



A) B)

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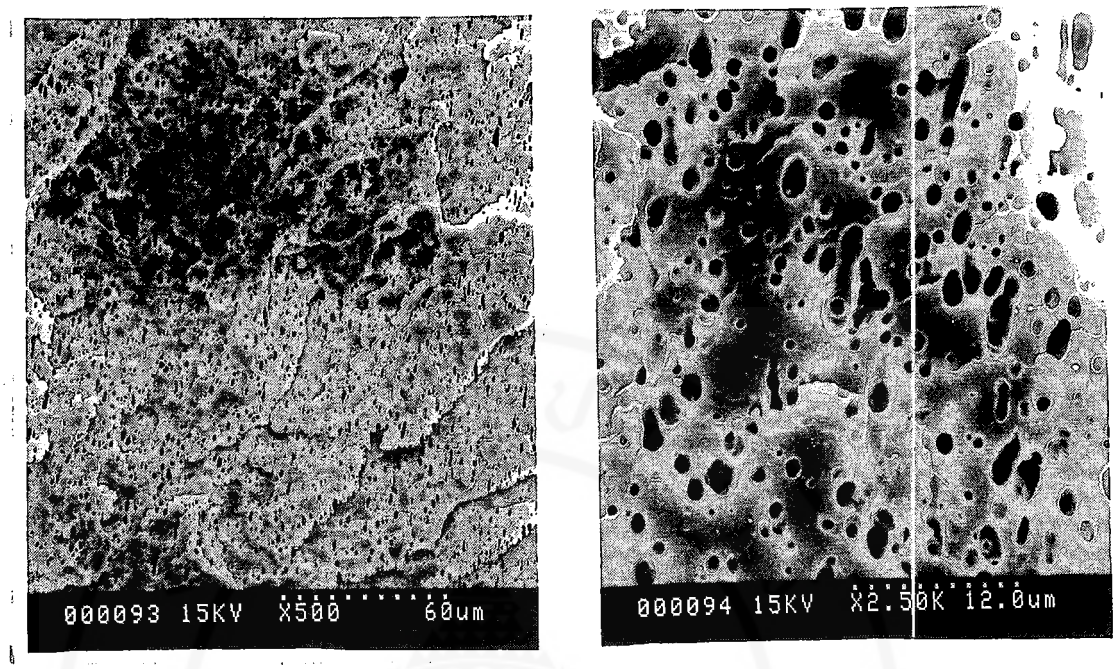
Figure D3 SEM micrograph of 75:25 LDPE/PS blend with PE-*g*-PS 5 phr:

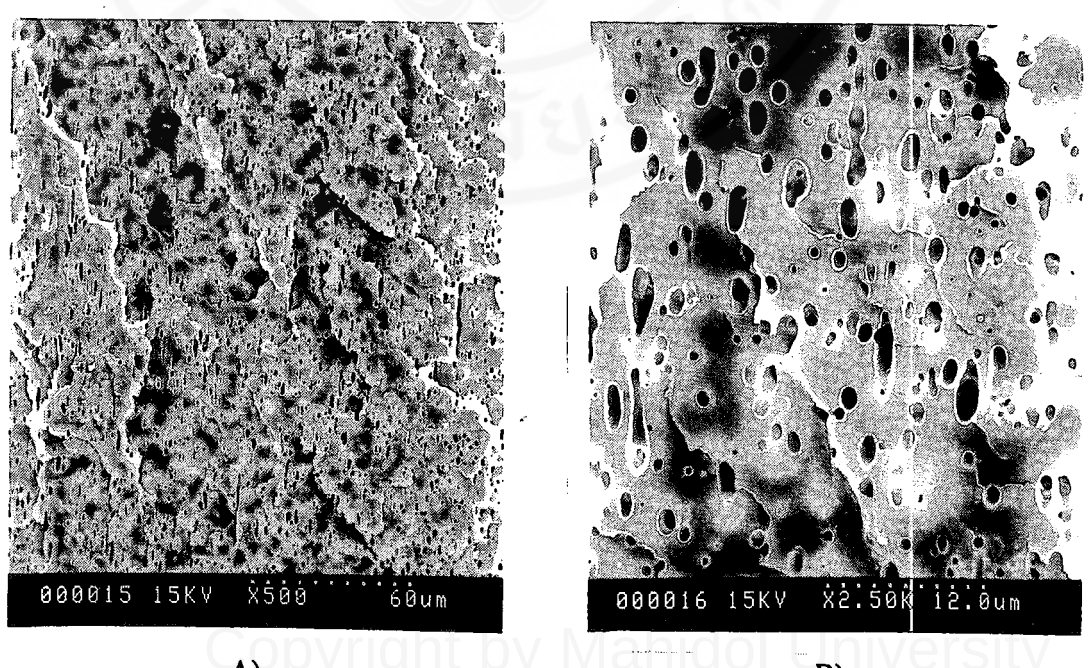
A) x 500; B) x 2500



A) B)

Figure D4 SEM micrograph of 75:25 LDPE/PS blend with PE-MA-PS 1 phr:

A) x 500; B) x 2500



A) B)

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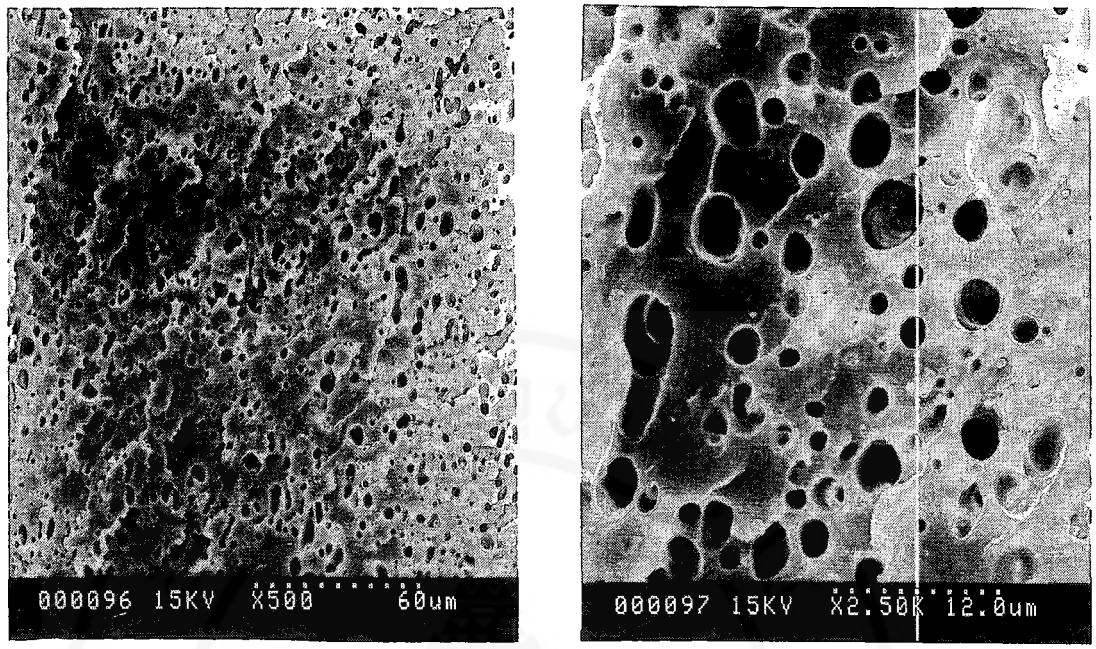
Figure D5 SEM micrograph of 75:25 LDPE/PS blend with PE-MA-PS 3 phr:

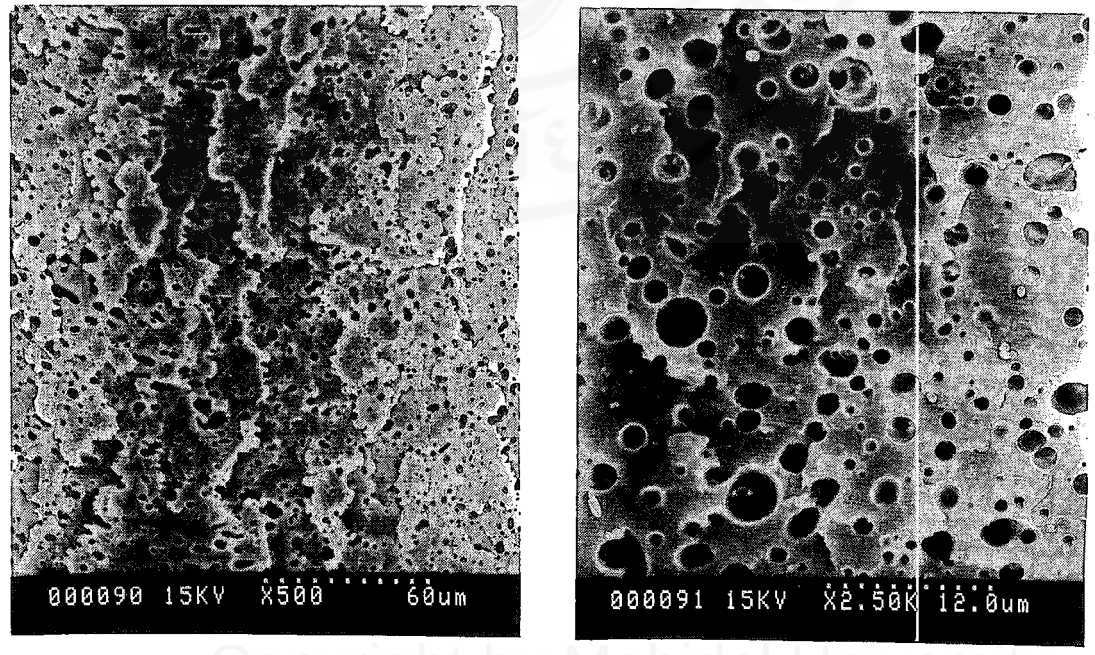
A) x 500; B) x 2500



A) B)

Figure D6 SEM micrograph of 75:25 LDPE/PS blend with PE-MA-PS 5 phr:

A) x 500; B) x 2500



A) B)

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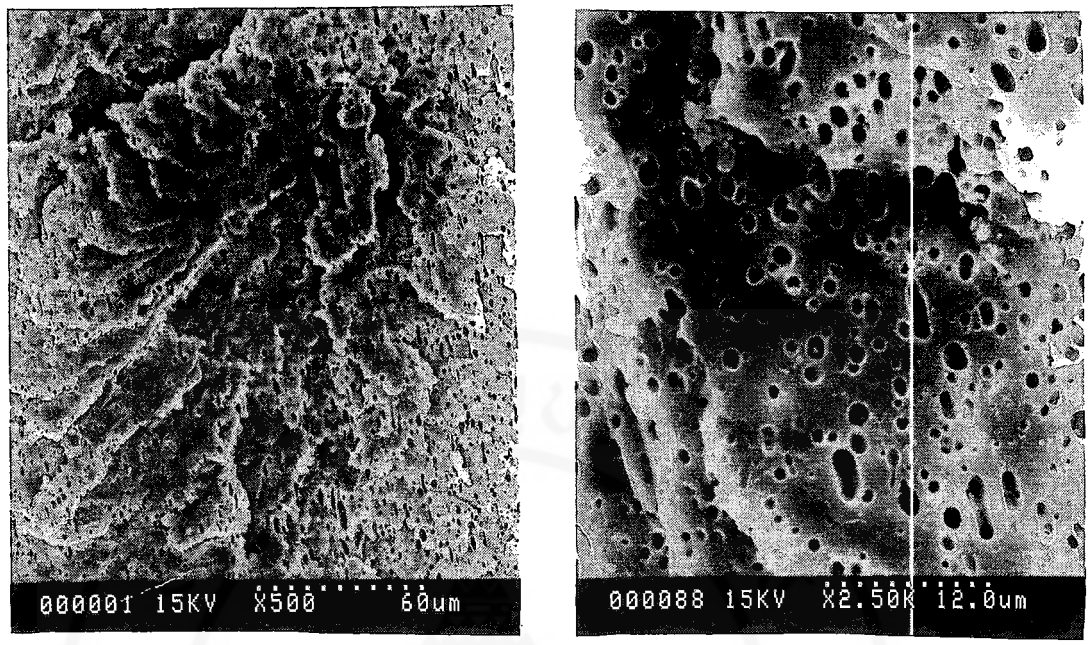
Figure D7 SEM micrograph of 75:25 LDPE/PS blend with PE-HMM-PS 1 phr:

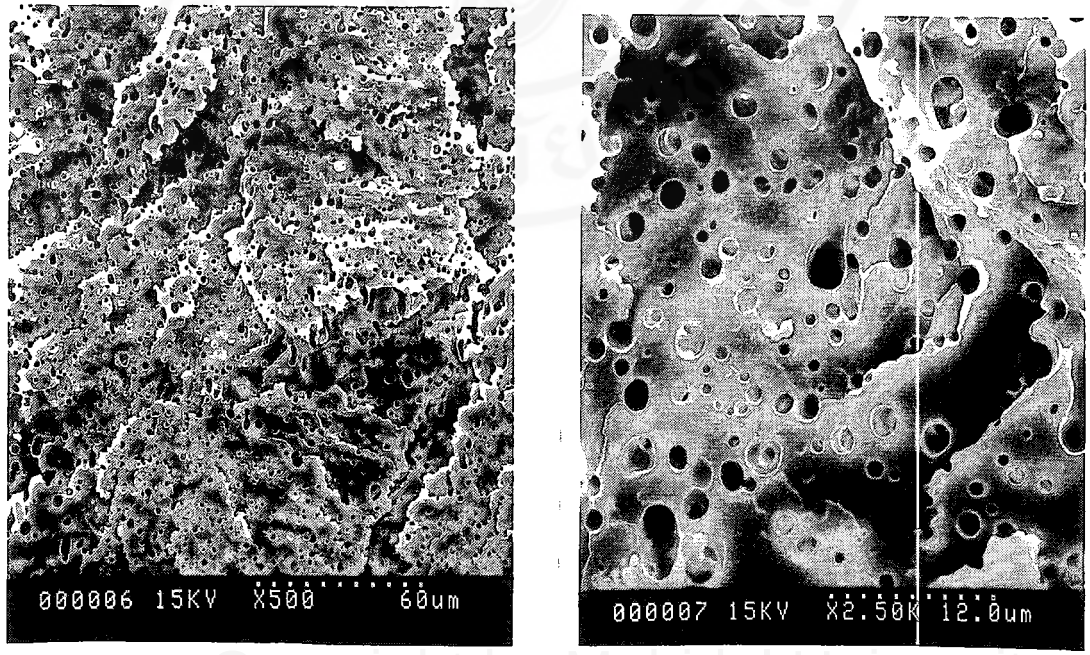
A) x 500; B) x 2500



A) B)

Figure D8 SEM micrograph of 75:25 LDPE/PS blend with PE-HMM-PS 3 phr:

A) x 500; B) x 2500



A) B)

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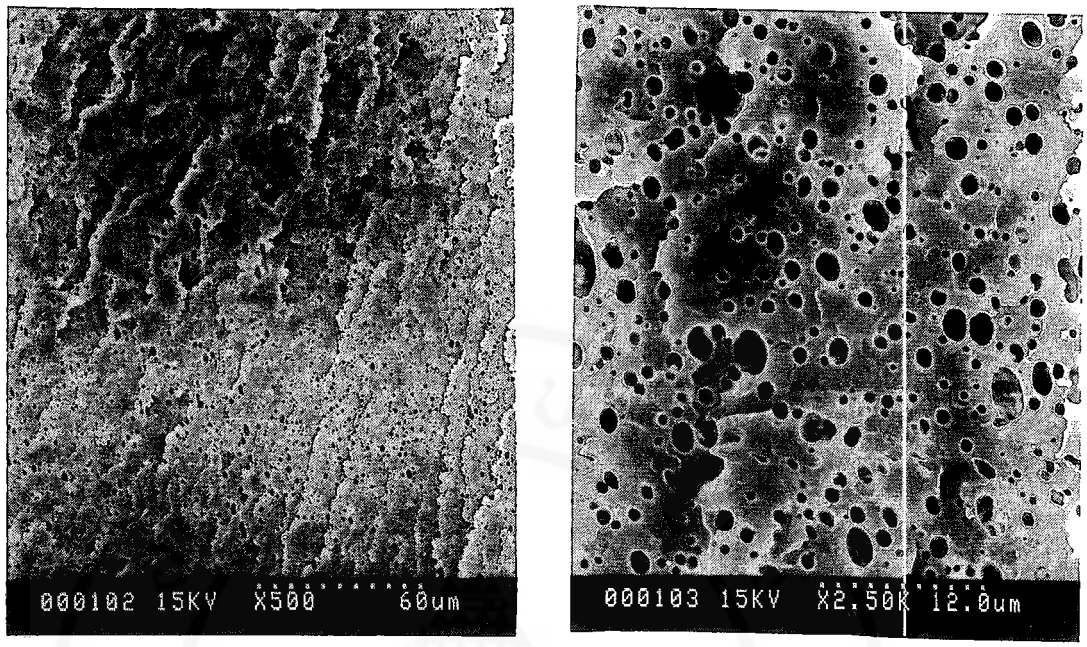
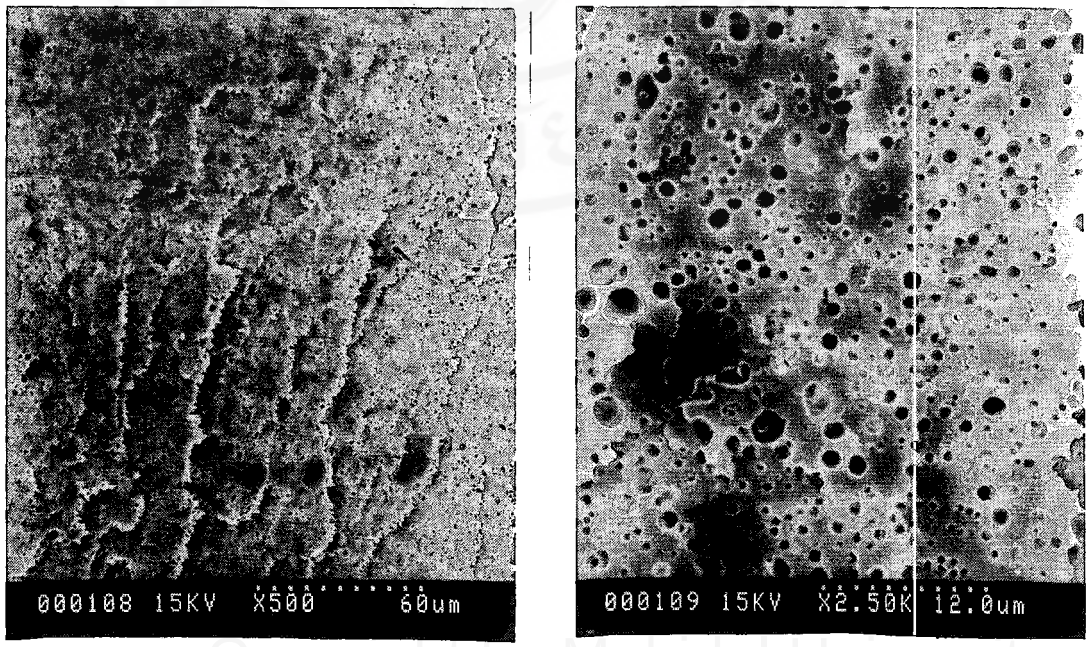
Figure D9 SEM micrograph of 75:25 LDPE/PS blend with PE-HMM-PS 5 phr:

A) x 500; B) x 2500



A) B)

Figure D10 SEM micrograph of EgSMA3: A) x 500; B) x 2500



A) B)

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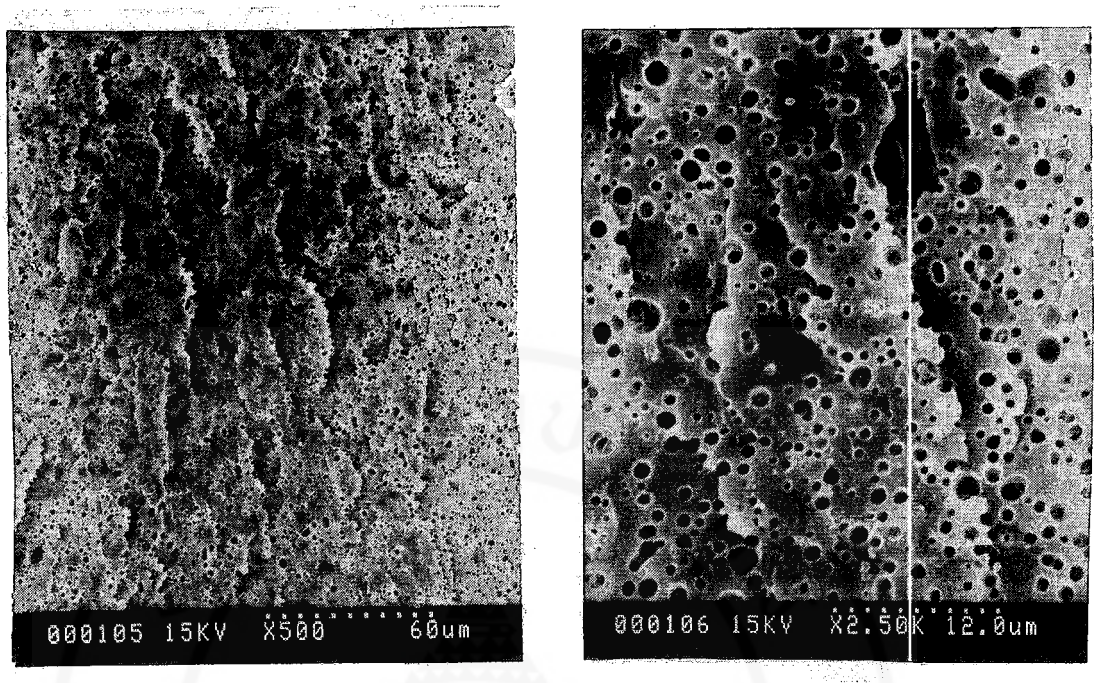
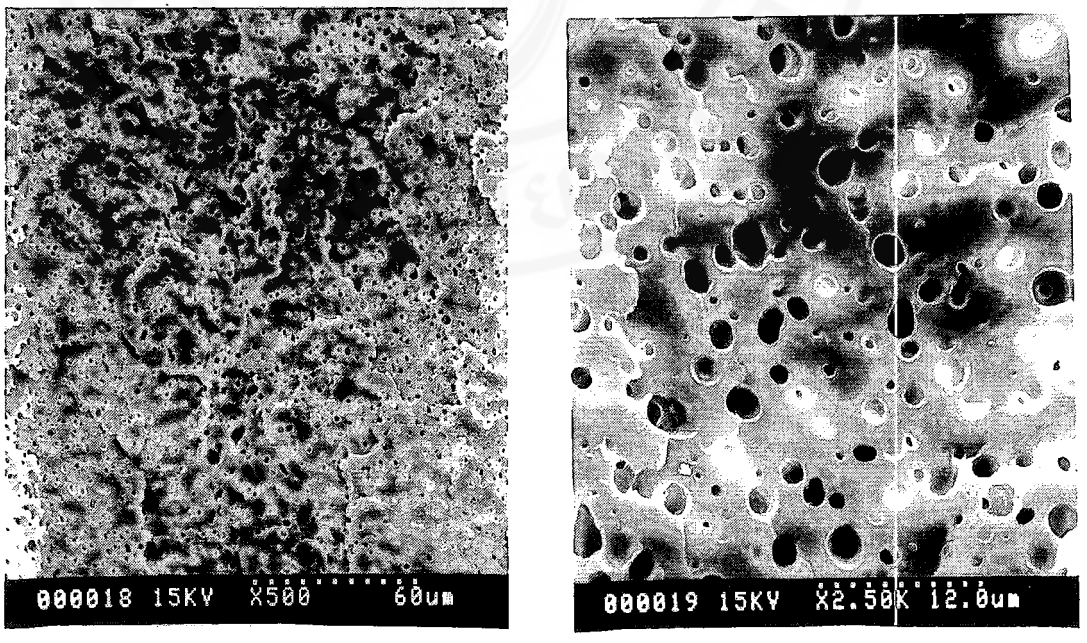
Figure D11 SEM micrograph of EgSMA3H: A) x 500; B) x 2500



A) B)

Figure D12 SEM micrograph of EgSMA3D: A) x 500; B) x 2500



A) B)

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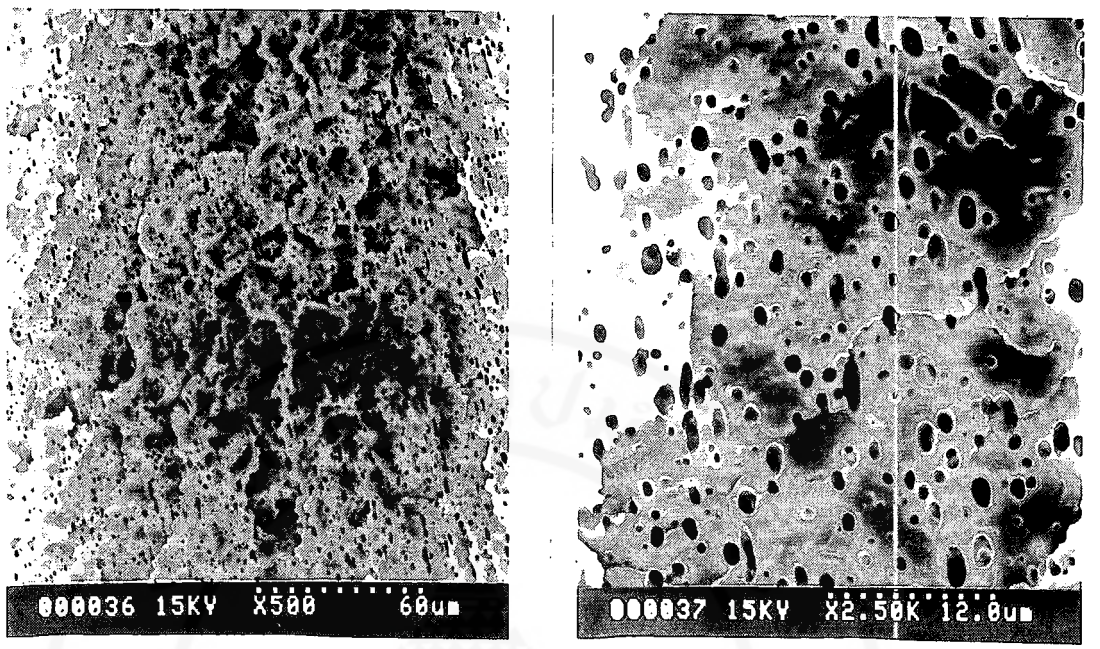
Figure D13 SEM micrograph of 75:25 LDPE/PS blend with 2SP55 1 phr:

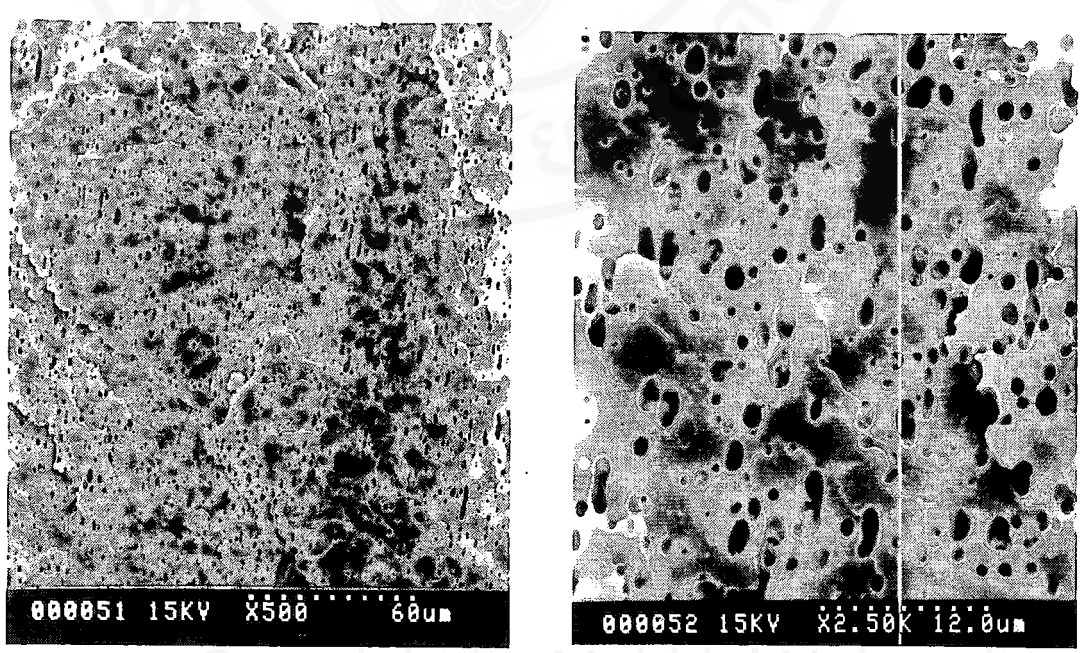
A) x 500; B) x 2500



A) B)

Figure D14 SEM micrograph of 75:25 LDPE/PS blend with 2SP55 3 phr:

A) x 500; B) x 2500



A) B)

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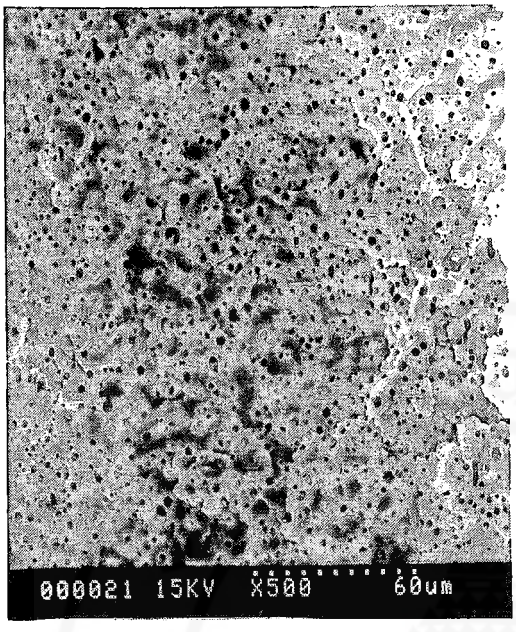
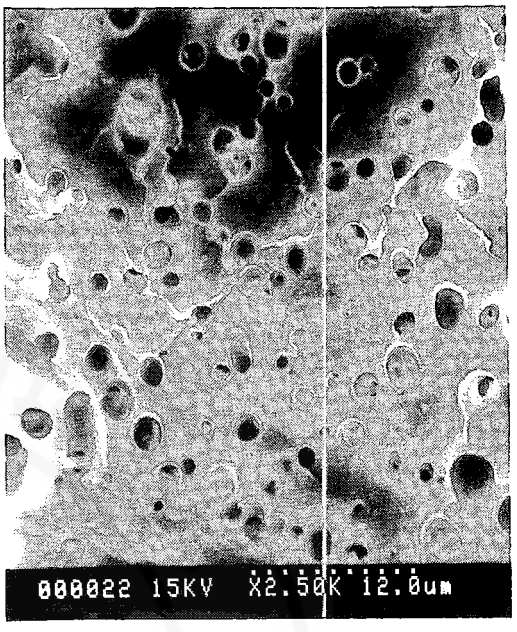
Figure D15 SEM micrograph of 75:25 LDPE/PS blend with 2SP55 5 phr:

A) x 500; B) x 2500

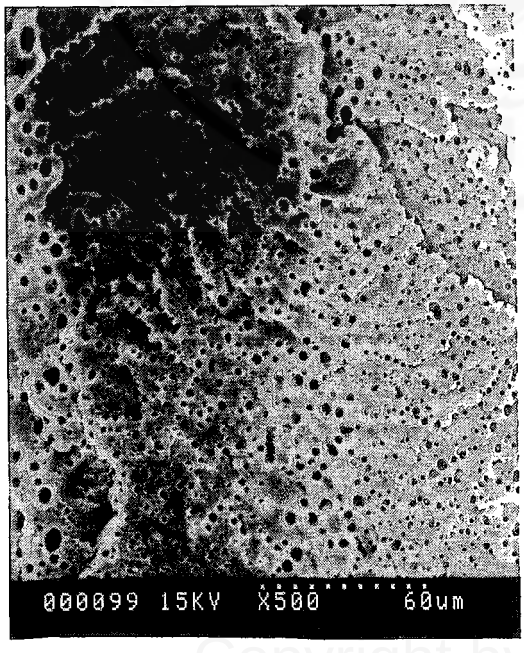


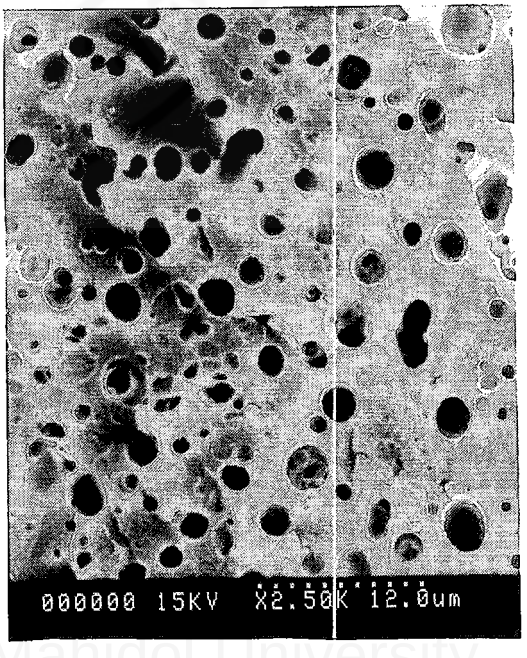


A) B)

Figure D16 SEM micrograph of 75:25 LDPE/PS blend with 2SP3.5 1 phr:

A) x 500; B) x 2500





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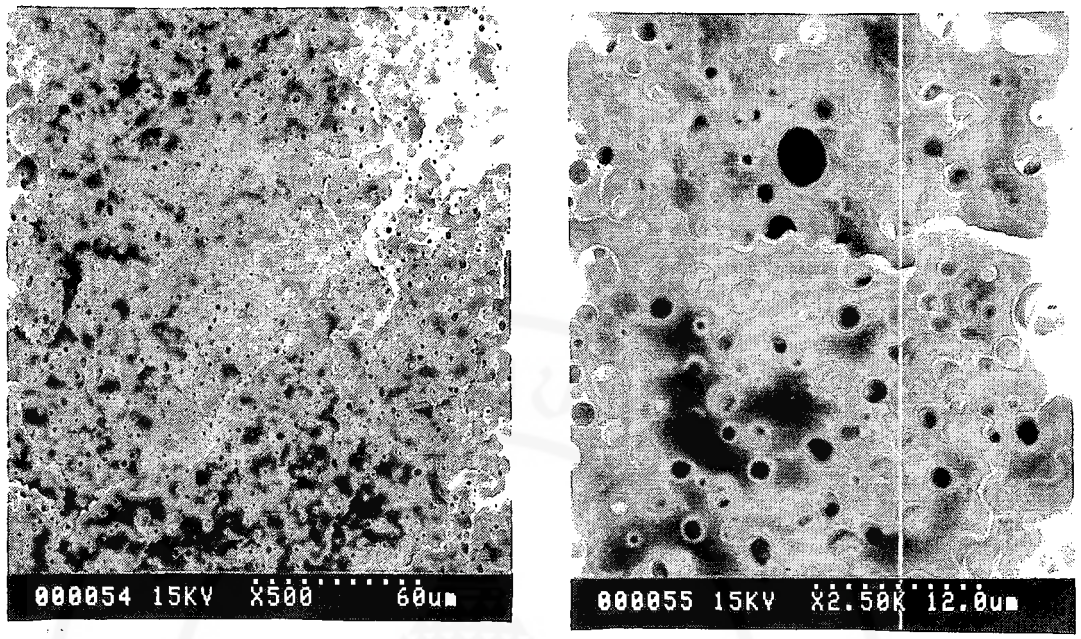
A) B)

Figure D17 SEM micrograph of 75:25 LDPE/PS blend with 2SP3.5 3 phr:

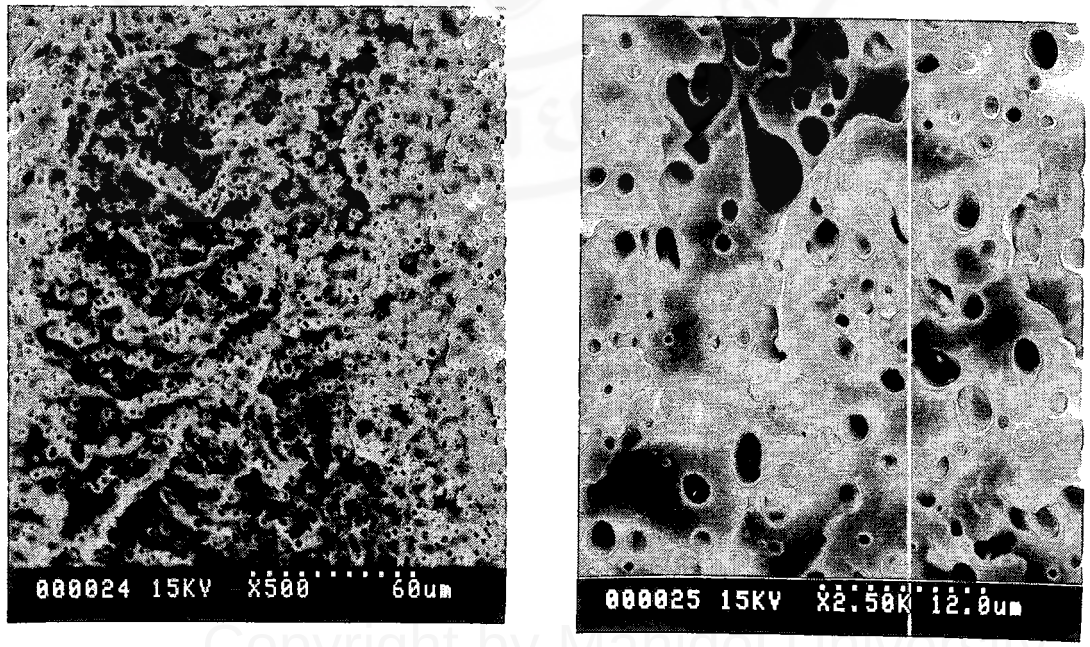
A) x 500; B) x 2500



A) B)

Figure D18 SEM micrograph of 75:25 LDPE/PS blend with 2SP3.5 5 phr:

A) x 500; B) x 2500



A) B)

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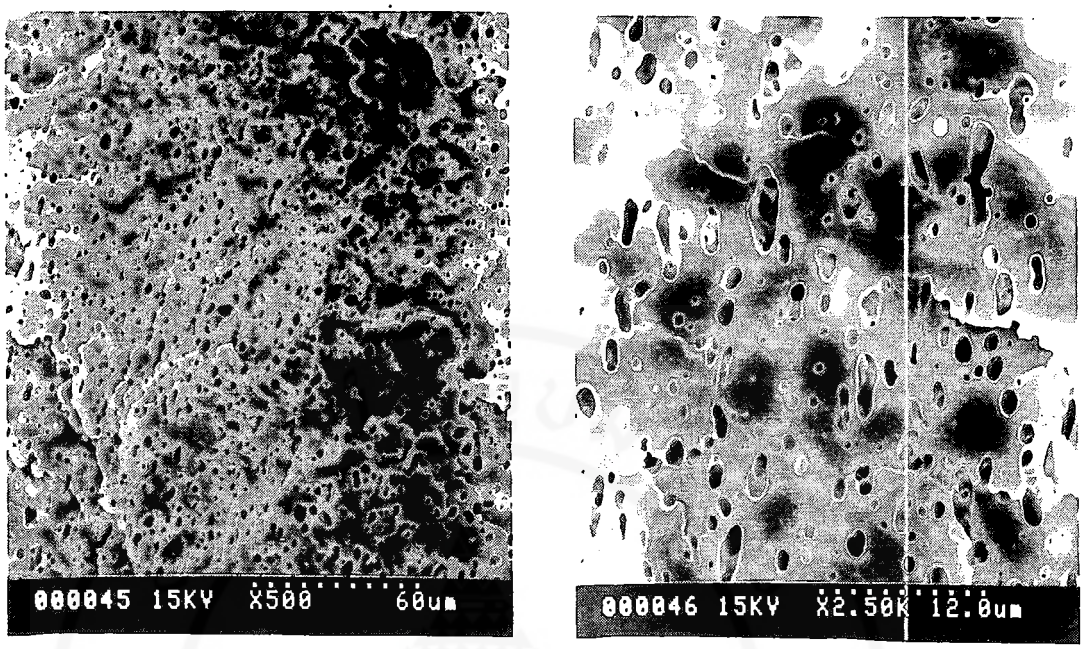
Figure D19 SEM micrograph of 75:25 LDPE/PS blend with 4SP3.5 1 phr:

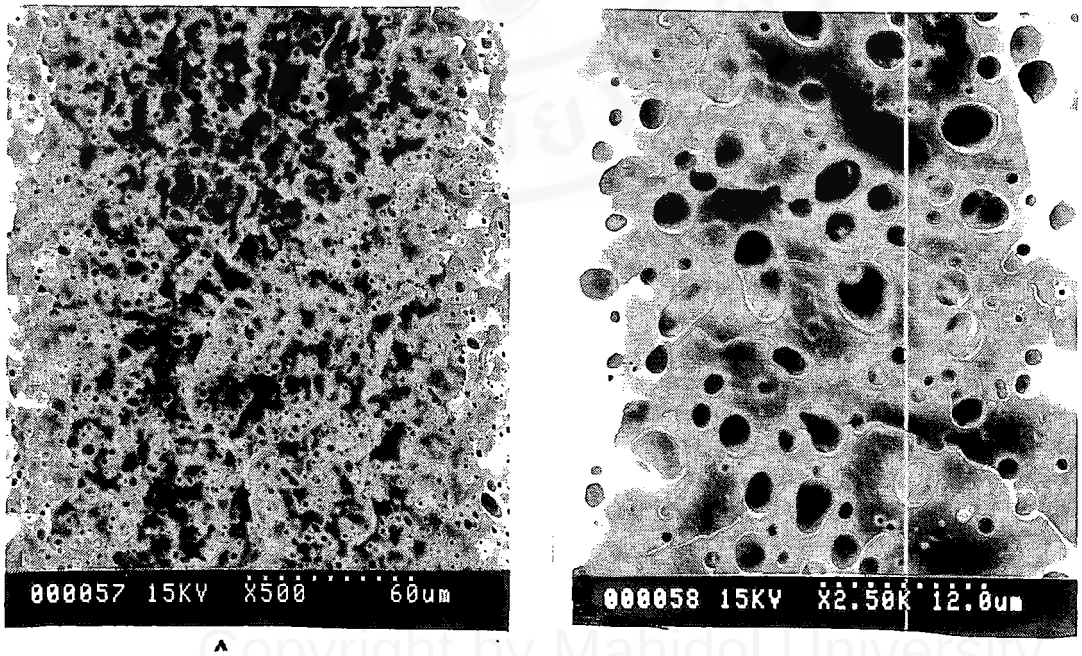
A) x 500; B) x 2500



A) B)

Figure D20 SEM micrograph of 75:25 LDPE/PS blend with 4SP3.5 3 phr:

A) x 500; B) x 2500



A) B)

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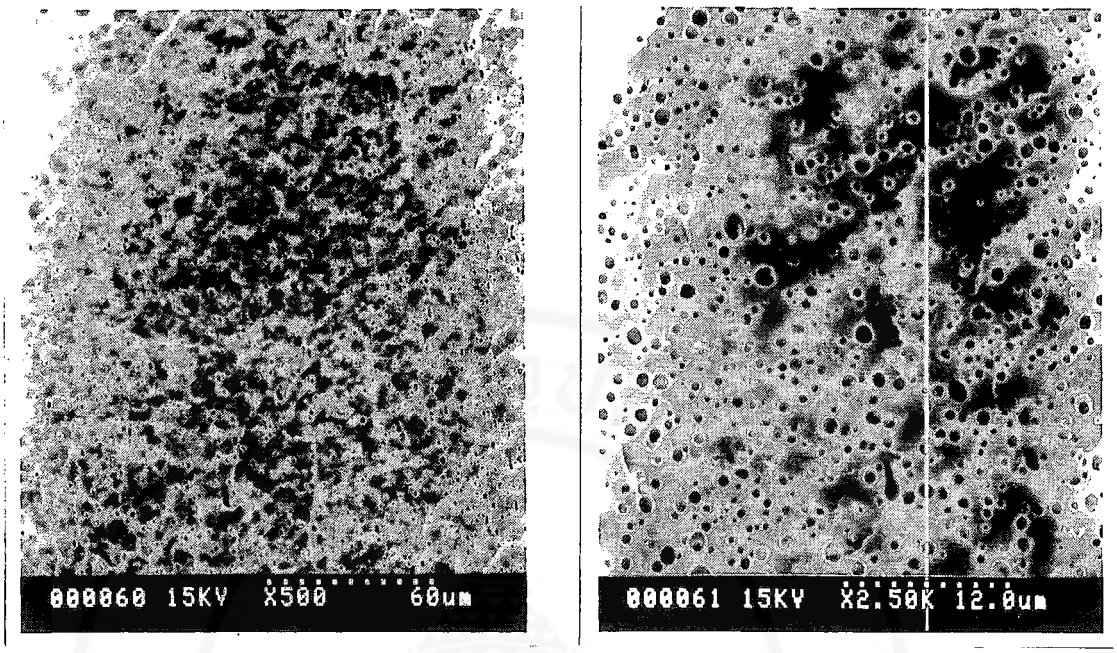
Figure D21 SEM micrograph of 75:25 LDPE/PS blend with 4SP3.5 5 phr:

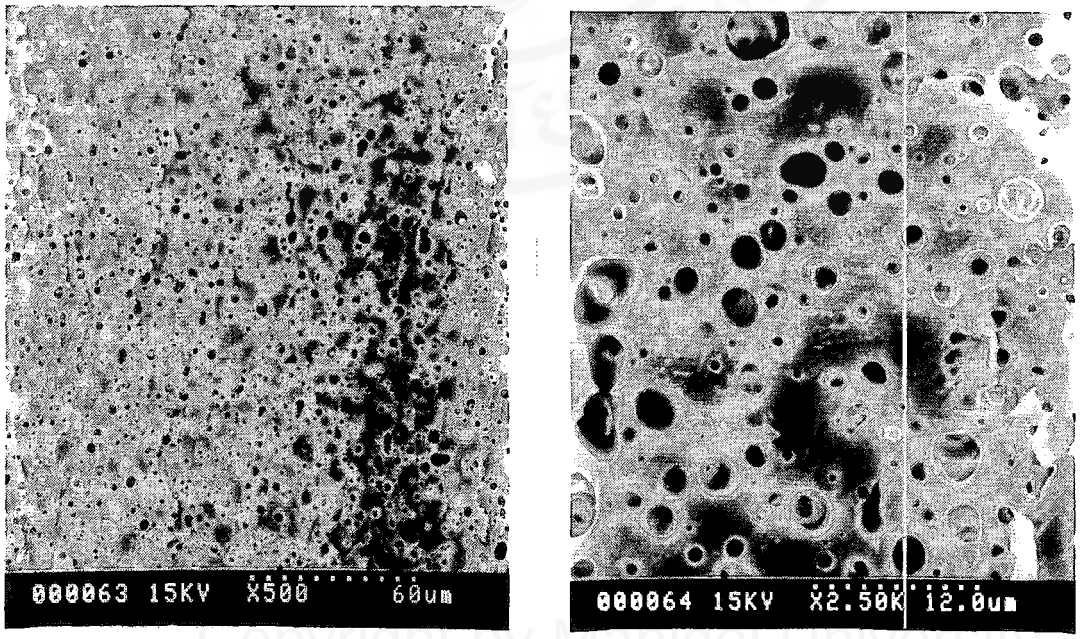
A) x 500; B) x 2500



A) B)

Figure D22 SEM micrograph of 75:25 LDPE/PS blend with 4SP12 1 phr:

A) x 500; B) x 2500



A) B)

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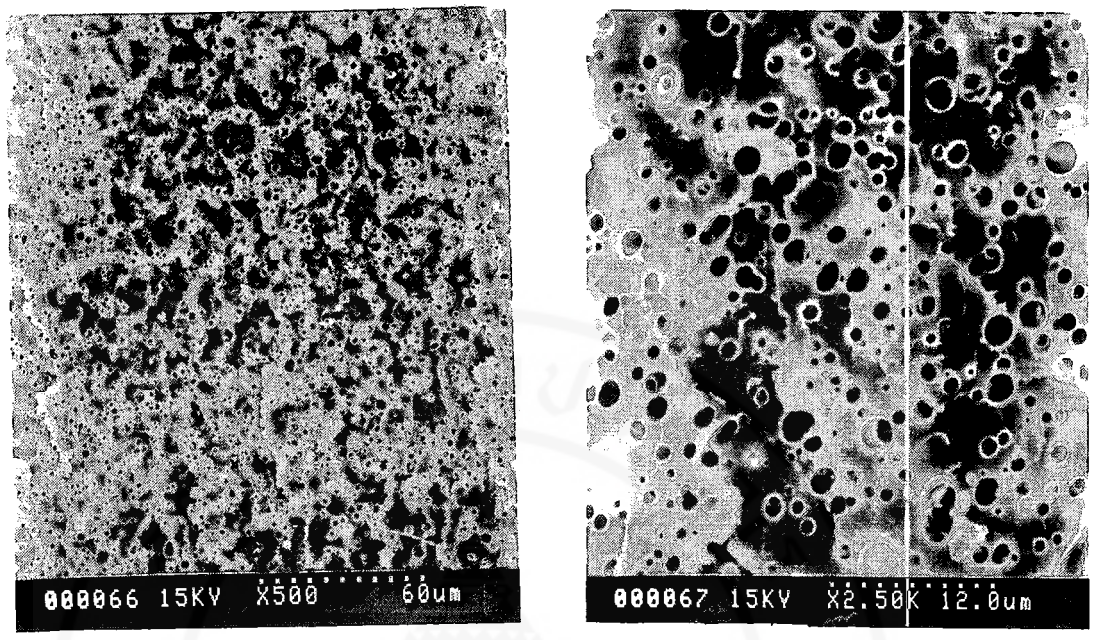
Figure D23 SEM micrograph of 75:25 LDPE/PS blend with 4SP12 3 phr:

A) x 500; B) x 2500



A) B)

Figure D24 SEM micrograph of 75:25 LDPE/PS blend with 4SP12 5 phr:

A) x 500; B) x 2500

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BIOGRAPHY

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