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นางสาวสวนิต อนันตธนวนิชย์

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NATURAL RUBBER – POLYSTYRENE
INTERPENETRATING POLYMER NETWORKS AS IMPACT MODIFIER

Miss Sawanit Anuntathanawanich

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สวนิต อนันตธนวนิชย์ : ยางธรรมชาติ–พอลิสไตรีน อินเทอร์เพนิเทรติงพอลิเมอร์เนตเวิร์ค เพื่อเป็นสารดัดแปรทนแรงกระแทก อาจารย์ที่ปรึกษาวิทยานิพนธ์ : รศ. ดร. โสภณ เริงสำราญ ; 116 หน้า. ISBN 974-334-066-1

ยางธรรมชาติ (NR) – พอลิสไตรีน (PS) อินเทอร์เพนิเทรติงพอลิเมอร์เนตเวิร์ค (IPNs) ถูกสังเคราะห์โดยใช้กระบวนการพอลิเมอไรเซชันในภาวะอิมัลชัน น้ำยางธรรมชาติที่มีสารเชื่อมขวางถูกเคลือบด้วยเปลือกของพอลิสไตรีน ใช้สารริเริ่มระบบรีดอกซ์ประกอบด้วยเทอร์เชียรี่บิวทิวไฮโดรเพอร์ออกไซด์ และเททราเอทิลีนเพนตะมีน ทำให้มีการจัดเรียงตัวแบบเปลือกหุ้มแกนกลาง (core-shell) ปฏิกิริยาพอลิเมอไรเซชันของ IPNs ถูกศึกษาปัจจัยต่าง ๆ อันได้แก่ ความเข้มข้นของตัวริเริ่ม สารเชื่อมขวาง สารก่ออิมัลชัน อุณหภูมิของปฏิกิริยา และเวลาที่ใช้ในการทำปฏิกิริยา พบว่าภาวะที่เหมาะสมคือ ภาวะที่ใช้ความเข้มข้นตัวริเริ่ม 1.5 ส่วนต่อ 100 ส่วนของยาง ความเข้มข้นของสารเชื่อมขวางร้อยละ 0.25 ของมอนอเมอร์ ความเข้มข้นของสารก่ออิมัลชันร้อยละ 1.5 ของมอนอเมอร์ และอุณหภูมิ 60°ซ เป็นเวลา 2 ชั่วโมง ทั้ง IPNs และ semi-IPNs ถูกสังเคราะห์และวิเคราะห์ลักษณะโดยศึกษาโครงสร้างของผลิตภัณฑ์และสมบัติเชิงกล โครงสร้างของผลิตภัณฑ์ IPNs ถูกวิเคราะห์โดยทรานมิสชันอิเลกตรอนไมโครสโคป (TEM) และสแกนนิงอิเลกตรอนไมโครสโคป (SEM) จากการศึกษาพบว่า IPNs มีค่าความทนแรงดึง มอดุลัส ความทนแรงฉีกขาด และการกระจายตัวของพอลิเมอร์ที่ดีกว่า semi-IPNs ในขณะที่ semi-IPNs มีค่าการยืดออกจนขาดสูงกว่า

ผลิตภัณฑ์ IPNs ถูกใช้เป็นสารดัดแปรทนแรงกระแทกในพอลิโพรพิลีน (PP) ผลิตภัณฑ์ผสมของ IPNs (10, 15, 20 และ25 ส่วนต่อ 100 ส่วนของยาง) กับ PP ถูกเตรียมขึ้น ผลของปริมาณผลิตภัณฑ์ IPNs ต่อค่าความทนแรงดึง และความแข็ง คือมีค่าลดลงเมื่อเพิ่มปริมาณผลิตภัณฑ์ IPNs แต่ค่าความทนแรงกระแทกเพิ่มขึ้นเมื่อเพิ่มปริมาณผลิตภัณฑ์ IPNs ปริมาณผลิตภัณฑ์ IPNs ที่เหมาะสม คือ 10 และ 15 ส่วนต่อ PP 100 ส่วน

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต สวนิต อนันตธนวนิชย์
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KEYWORD: INTERPENETRATING POLYMER NETWORKS (IPNs) / EMULSION POLYMERIZATION / CORE-SHELL PATICLE / IMPACT MODIFIER / NR/PS COMPOSITE

SAWANIT ANUNTATHANAWANICH: NATURAL RUBBER – POLYSTYRENE INTERPENETRATING POLYMER NETWORKS AS IMPACT MODIFIER. THESIS ADVISOR : ASSOC. PROF. SOPHON ROENGSUMRAN, Ph.D. 116 pp. ISBN 974-334-066-1

Natural rubber - polystyrene interpenetrating polymer networks (IPNs) were synthesized by emulsion polymerization process. A prevulcanized natural rubber latex was coated with a shell of polystyrene (PS). The bipolar redox initiating system tert-butyl hydroperoxide/tetraethylene pentamine promoted a core-shell arrangement. IPNs polymerization was carried out by varying concentrations of the initiator, emulsifier, crosslinking agent, reaction time, and reaction temperature. The optimum conditions were the initiator concentration of 1.5 phr, the crosslinking agent concentration of 0.25 % wt of monomer, emulsifier concentration of 1.5 % wt of monomer, and temperature of 60°C for 2 hours. Both IPNs and semi-IPNs were prepared and characterized by evaluating their morphology and mechanical properties. The morphologies of resulting latex IPNs were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). From this experiment, IPNs showed higher tensile strength, modulus, tear strength and finer phase distribution than the corresponding semi-IPNs, while the latter exhibited higher elongation at break.

IPNs products were used as an impact modifier in polypropylene (PP). The IPNs products (10, 15, 20, and 25 phr) and PP blends were prepared. The effects of IPNs products content on tensile strength and hardness decreased with increasing the IPNs product content, but impact strength increased with the increasing IPNs product content. The appropriate amounts of IPNs products used were 10 and 15 phr.

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต สุวนิต อนันตธนวนิชย์
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ABBREVIATIONS

°C	Degree Celsius
CU	Chulalongkorn University
DSC	Differential Scanning Calorimetry
DVB	Divinyl Benzene
EPDM	Ethylene Propylene Diene Monomer
IPNs	Interpenetrating Polymer Networks
MTEC	National Metal and Materials Technology Center
NR	Natural Rubber
phr	Part per Hundred Rubber
PP	Polypropylene
PS	Polystyrene
RRIT	Rubber Research Institute of Thailand
SEM	Scanning Electron Microscopy
St	Styrene Monomer
STREC	Scientific and Technological Research Equipment Centers
t-BuHP	Tertiary-Butylhydroperoxide
TEM	Transmission Electron Microscopy
TEPA	Tetraethylene Pentamine
Tg	Glass Transition Temperature
TGA	Thermogravimetric Analysis

CHAPTER I

INTRODUCTION

Statement of Problems

Natural rubber latex is present in a range of plants, but *Hevea brasilliensis* is the only rubber tree that is truly considered to be the important commercial source of the polymer cis-polyisoprene. In addition to its botanical, and hence, renewable origins, natural rubber (NR) has an attractive portfolio of properties which is unmatched by most synthetic rubbers. Nonetheless, many attempts have been made to modify this rubber. The backbone unsaturation makes certain types of chemical modification relatively easy. Moreover, natural rubber is a resource of Thailand that has high potential of production during each year. The Rubber Research Institute of Thailand reported that Thailand produced 2,065,202 tons of natural rubber and exported 1,839,396 tons or 89.07% of total production in 1998, the remaining 10.93% were used in the country [1]. However, in present, the export of ribbed smoke sheet rubber and block rubber has had the tendency to decrease [2].

Therefore, it is extremely necessary to find a new approach to use more natural rubber products. In thesis research natural rubber, reinforced with thermoplastic,was produced by emulsion polymerization process. This experiment was designed to yield NR-based latex interpenetrating polymer networks (IPNs) and semi-IPNs, in which the second component is polystyrene (PS).

Since ethylene propylene diene monomer (EPDM) is expensive and imported from abroad, using natural rubber in replacement of EPDM in an impact modifier should help reduce the capital of production. The product of this research is expected to act as an impact modifier because it has hard segment, polystyrene, and elastomer segment, natural rubber. This assumption is due to the fact that impact modifier from natural rubber has only been slightly developed to be used in the automotive part of industry [3]. Currently, EPDM is used as an impact modifier of polypropylene (PP), which is used as bumper.

This investigation was concerned with the preparation of impact modifier from natural rubber-polystyrene interpenetrating polymer networks by emulsion polymerization. Many different parameters such as the initiator, crosslinking agent and surfactant concentrations, reaction time and temperature were taken into account. Furthermore, the morphology and mechanical property were considered. Finally, the blends of IPNs product and PP were also studied.

Objectives

1. To prepare natural rubber-polystyrene composites by means of emulsion polymerization method. The effects of such influential parameters as the concentrations of initiator, crosslinking agent, emulsifier, and reaction time and temperature, finally ratio of natural rubber and styrene monomer were studied.

2. To characterize the morphology and mechanical properties of the resulting natural rubber-polystyrene composites.

3. To prepare the blends of the composite products and EPDM and to investigate the mechanical properties of the blends as an impact modifier for PP.

Scope of the Investigation

For the preparation of the natural rubber-polystyrene composite, the appropriate conditions were studied. The suitable ratio of natural rubber and polystyrene, which yielded the best mechanical properties was determined. The investigation procedures were carried out as follows:

1. Literature survey and in-depth study of this research work.

2. Design and preparation of apparatus and chemical substance.

3.Preparation of the natural rubber-polystyrene composite by emulsion polymerization. The appropriate reaction conditions were determined by changing the following parameters:

(a) The optimum concentrations of the initiator/activator, crosslinking agent, emulsifier.

(b) The effect of reaction temperature and time.

4. Study the effect of parameters on the degree of monomer conversion.

5.Characterize the morphology of the resulting interpenetrating polymer networks by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

6. Test mechanical properties such as tensile strength, tear strength and hardness.

7. Evaluate the miscibility between components of polymer blends by differential scanning calorimetry (DSC).

8. Study the stability of product by thermogravimetric analysis (TGA).

9. Blend the composite product and PP. The properties such as tensile strength, impact strength, tear strength and hardness were investigated.

10. Summarize the results.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber

The recorded history of western civilization contains no mention of rubber or the plants that have produced rubber prior to the discovery by Christopher Columbus. During the course of his second voyage to the Americas, Columbus saw Itaitian natives playing games with balls produced from latex of the rubber (*Hevea brasiliensis*) tree. Early explorers of South America found that natives, living in areas where the rubber tree grew, used latex, which had the capability of fabrication rubber goods such as waterproof clothing, water bottle, and shoes from latex [4].

Today it is known that the rubber tree was not indigenous to South America alone. Rubber tree grew wild in many regions of Africa and mainly in Southeast Asia including Thailand, Indonesia, Malaysia [5].

2.1.1 Agriculture

It has been estimated that some 2,000 different plant species yield polymer akin to natural rubber and use sorts have been obtained from some 500 of them. To all purposes and intents the natural rubber of commerce is obtained from the latex of *Hevea brasiliensis*. It requires temperatures of 25-30°C, a well-distributed annual rainfall at least 180-250 cm., and high atmospheric humidity. An initial growth period of 5-7 years is needed before a tree gives latex for as long as 25-30 years. Advantages of *Hevea brasiliensis* is very suitable for rubber extraction for the following reasons [6]:

1) It can be tapped because of its milk vessels.
2) It does not form resins on tapping
3) Polyisoprene with almost 100% cis double bonds is produced.
4) It tolerates tapping very well for over a period of many years.

2.1.2 Exploitation

Natural rubber occurs as particles dispersed in and aqueous serum. i.e., latex. which is contained in bundles of tubular vessels in the tissue of the tree (Figure 2.1). Latex is harvested from the tree by a process called tapping, which can be described as controlled wounding of the tree. A specially designed tapping knife is used to remove shavings of bark from the surface of groove made into the tree to a depth ca 1 mm from the cambium. The groove is made downward from left to right at an angle of ca 30° to the horizontal across half the tree.

The tapper begins tapping in the morning. There is latex prevention by using a few drops of ammonia solution in the tapping cup prior to tapping to prevent premature coagulation from attacking the sugars in the latex of bacteria; this generates low molecular weight fatty acids. The tapper collects the latex and takes it to a central bulk station where it is preserved further, usually with the addition of ammonia gas to ca 0.40% before transportation to the factory [7].

Natural rubber arrives at the processing factory field latex or field coagula. About 7-10% of the world's natural rubber is converted into latex concentrate. Concentration is achieved by centrifugation (most commons), by creaming, or by evaporates. The centrifuged latex is shipped as latex concentrate containing 60% dry rubber content. The remainders of latex and field coagulum are processed into conventional types of rubber such as ribbed smoke sheets (RSS), pale crepes, and brown crepes, into the newer forms of technically specified 'block' rubber (TSR). These are the basic raw materials for all types and grades of natural rubber [8].

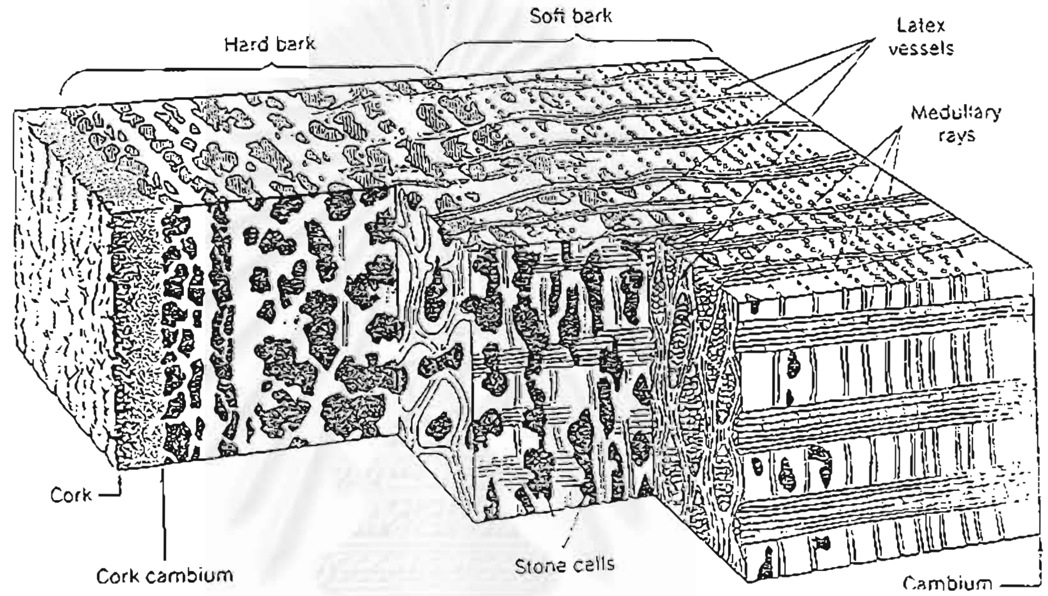
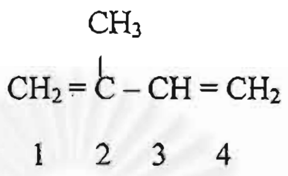


Figure 2.1 The bark of *Hevea brasiliensis*. Hard bark consists of stone cells, parenchyma, and disorganized sieve tubes and latex vessels.

2.1.3 Chemical Formula

The chemical name for natural rubber is polyisoprene, which is a homopolymer of isoprene. Isoprene has the formula C_5H_8, which structure is as follows:

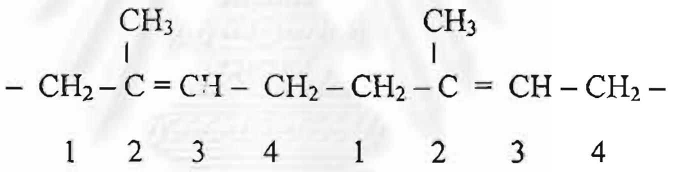


$$CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2$$

1 2 3 4

Isoprene

Natural rubber is a polymer of isoprene, in which essentially all the isoprene units are linked together at carbon atoms 1 and 4 in a head-to-tail arrangement.

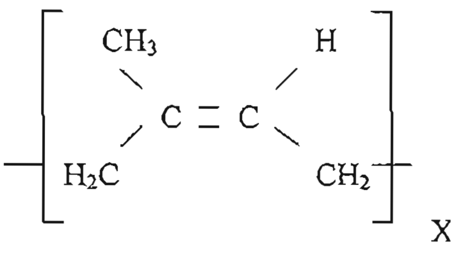


$$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-$$

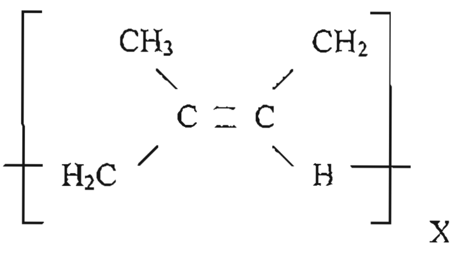
1 2 3 4 1 2 3 4

Head-to-tail arrangement of polyisoprene

Commercial grades of *Hevea* natural rubber contain 93-94 %wt. cis - 1,4 configuration, which means that carbon atoms 1 and 4 are both on the same side of double bond. In the trans-1,4 configuration, these two carbon atoms are on opposite sides of the double bond.



Cis-1,4-polyisoprene NR/IR



Trans-1,4-polyisoprene gutta-percha

The cis-polymer structure of natural rubber and the unit cell of the crystalline stretched rubber are shown in Figure 2.2:

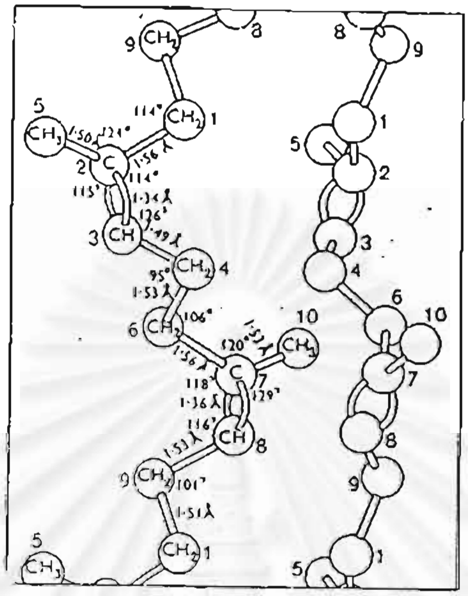


Figure 2.2 Unit cell structure of the natural rubber molecule [9].

2.1.4 Composition

The latex of the *Hevea brasiliensis* tree has been described as a cytoplasmic system containing rubber and non-rubber particles dispersed in an aqueous serum phase.

Freshly tapped *Hevea* latex has a pH of 6.5 – 7.0, a density of 0.98 g/cm^3 and surface free energy of 4.0-4.5 μJ/cm^2 (0.96-1.1 μcal/cm^2). The total solids of fresh field latex vary typically from 30 to 40%, depending on the clone, weather, stimulation, tapping frequency, and other factors. The dry rubber content is ca 3 %wt. less than the total solids. The non-rubber portion is made up of a large number of substances with protein and the cyclic polyol quebranchitol predominating. The solid, both rubber and non-rubber, in freshly tapped latex are distributed through three phases, which are separated by ultracentrifugation. They are the top or rubber phase, the middle or serum phase, and the bottom or lutoid phase.

The rubber phase typically contains 96 %wt rubber hydrocarbon, 1%wt protein, and 3%wt lipids, along with trace amounts of magnesium, potassium, and copper. The rubber particles are stabilized by an absorbed layer of protein and phospholipids. The serum phase is a dilute aqueous solution with a density slightly over 1.0 g/cm^3. The serum contains many different classes of compounds, including carbohydrates, protein, amino acids, enzymes, and nitrogenous bases. The bottom fraction of lutoid phase consists mainly of lutoid particles [7].

2.1.5 Physical Properties

The physical properties of unvulcanized natural rubber very slightly depends on the clone mix, non-rubber content, degree of crystallinity and storage hardening. Average physical properties of raw rubber are shown in Table 2.1. Most applications for natural rubber are vulcanized. The physical properties of a vulcanizate are different from those of raw rubber. Table 2.2 gives typical values for the physical content of a gum and a 50 phr carbon black-filled vulcanizate [7].

Table 2.1 Physical properties of unvulcanized natural rubber.

PROPERTIES	VALUE
1. Specific gravity	
At 0°C	0.950
At 20°C	0.934

Table 2.1 (continued)

PROPERTIES	VALUE
2. Refractive index at 20°C	
RSS	1.5195
Pale crepe	1.5218
3. Coefficient of cubical expansion, °C	0.00062
4. Heat of combustion, J/g[a]	44.129
5. Specific heat, J/(g.k)[a]	0.502
6. Thermal conductivity, W/(m.k)	0.13
7. Dielectric constant	0.14-0.20
8. Volume resistivity, ohm.cm	10
9. Dielectric strength, V/mm	3.937
10. Cohesive energy density, J/cm^3	266.5
11. Glass-transition temperature, °C	-72

[a] To convert J to cal, divided by 4.185

Table 2.2 Physical properties of vulcanized rubber.

PROPERTIES	Gum vulcanizate	Black-filled vulcanizate
1. Density, g/ml	0.95	1.12
2. Young's modulus, MPa[a]	2	6
3. Bulk modulus, MPa[a]	2000	2200
4. Poisson's ratio	0.4998	0.4995
5. Sound transmission velocity, m/s	54	37
6. Glass-transition temperature, °C	-70	-70

Table 2.2 (continued)

PROPERTIES	Gum vulcanizate	Black-filled vulcanizate
7. Specific heat, J/(g.k)[b]	1.83	1.50
8. Thermal conductivity, W/(m.k)	0.15	0.28
9. Coefficient of cubical expansion, $10^{-5}/°C$	67	56
10. Volume resistivity, ohm.m	10^{14}	10
11. Dielectric constant	3	15
12. Power constant	0.002	0.1

[a] To convert MPa to psi, multiplied by 145

[b] To convert J to cal, divided by 4.185

2.1.6 Natural Rubber in Thailand

The data from the Rubber Research Institute of Thailand showed that in 1998, Thailand produced 2,065,002 tons of natural rubber and exported 1,839,396 tons 89.07% of total production [8]. The remaining 10.93 % were used in the country. Since 1991, Thailand was the world's largest producer of natural rubber as shown in Table 2.3. Thailand produced 2.0 million tons of natural rubber. It is very uneconomical to transport preserved field latex form before shipment. After the natural rubber latex has been collected from the field, it is processed in many forms of rubber products, as shown in Table 2.4. Natural rubber latex containing 60% dry rubber content (DRC) by a concentration method is usually obtained.

Table 2.3 World production of natural rubber in 1998

Country	Tons (x 10^3)
Thailand	1,763.0
Indonesia	1,449.8
Malaysia	709.8
Sri Lanka	72.1
Vietnam	69.0
Others	368.6
Total	4,430

Source : Rubber Research Institute of Thailand [8]

Table 2.4 Thailand exports of rubber by types in 1998

Types of Rubber	Tons
Smoked sheet (RSS)	1,047,152
Block rubber (STR)	480,222
Crepe rubber	920
Concentrated latex	246,438
Air dried sheet	10,819
Other rubbers	53,856
Total	2,065.002

Source : Rubber Research Institute of Thailand [8]

2.1.7 Rubber Derivatives

Before the 1960s, interest in the chemical modification of natural rubber focused on new materials with unusual properties. In the last 30 years, however, more emphasis has been placed on modifying natural rubber in a controlled way without altering its strength properties. A great number of chemical derivatives have been prepared from natural rubber, but only a few have attained commercial significance, mainly because of the high cost of manufacture [9].

Modification highly affects physical properties. Even thermoplastic or resinous material can be obtained by modification of rubber. The most well known types of modification are hydrogenation, chlorination, hydrohalogenation, cyclization, resin modification, methyl methacrylate grafting, superior-processing N-phenylcarbonylazoformate modification, polystyrene grafting, and epoxidation [10].

Polystyrene – Grafted Natural Rubber

Polystyrene-modified natural rubber was developed for the production of a thermoplastic elastomer. Thermoplastic elastomer frequently has an ABA block structure where A is styrene. The desired structures cannot be obtained by natural rubbers in this fashion. Polystyrene of controlled molecular weight is first prepared by anionic polymerization and terminated with a hydroxyl group. Treatment with phosgene followed by methyl or ethyl carbazate gives a hydrazo terminal group. Oxidation of the latter yields an azo-terminated polystyrene. The azo-tipped polystyrene reacts with natural rubber in solution or by dry blending in an internal mixer at 100-120°C [11]. Since thermoplastic natural rubber is also obtained through blends of natural rubber with polyolefins, the graft products with styrene have not gained any commercial importance [12].

2.2 Interpenetrating Polymer Networks (IPNs)

Interpenetrating polymer networks (IPNs) are defined as a combination of two or more polymers in network form, at least one of which is synthesized or crossliked in the immediate presence of the other [14] .

When two or more polymers are mixed, the resulting composition can be called a multicomponent polymer material. There are several ways to mix two kinds of polymer molecules, see Figure 2.3. Simple mixing, as in an extruder, results in a polymer blend. If the chains are bonded together, graft or block copolymer result; bonding between some portion of the backbone of polymer 1 and the end of polymer 2, the result is called a graft copolymer; chain bonded end to end result in block copolymer. Other types of copolymers include AB-crosslinked copolymer, where two polymers make up one network, and the IPNs, and semi-IPNs (SIPNs).

An IPN is distinct from simple polymer blends, block or grafts in two ways: it swells but does not dissolve in solvent, and creep and flow are suppress.

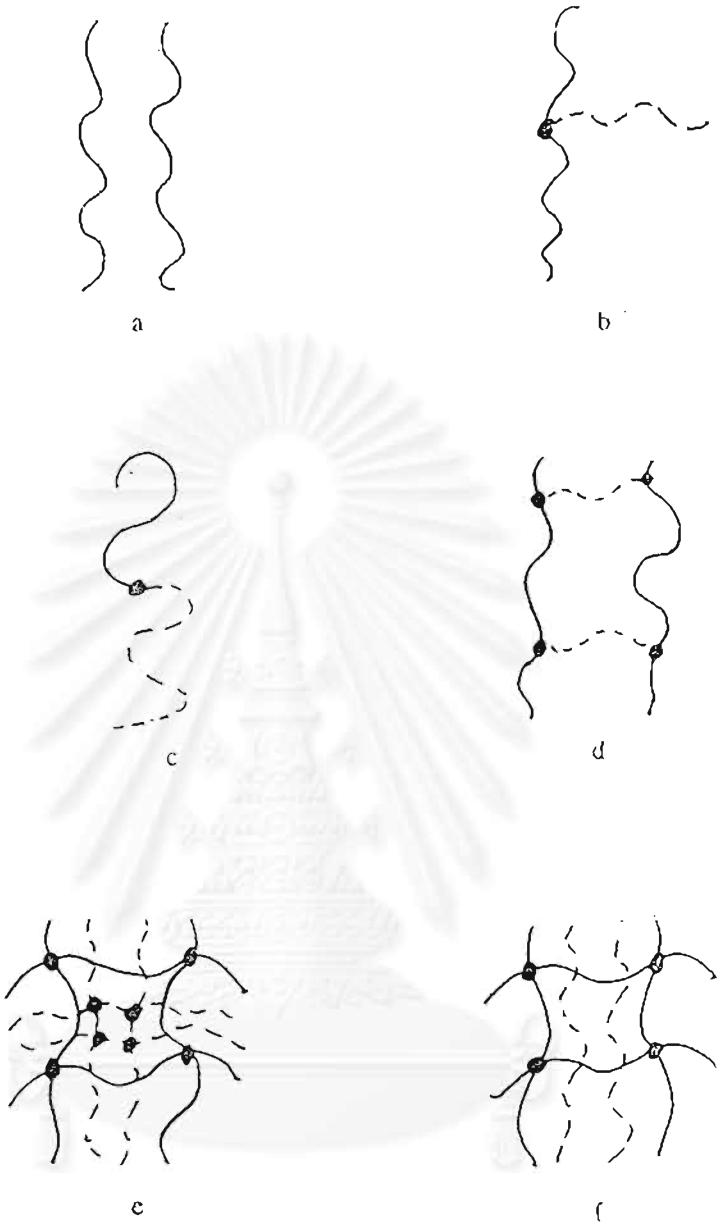


Figure 2.3 Six basic combinations of two polymers.; a, Polymer blend. no bonding between chains; b, a graft copolymer; c, a block copolymer; d, an AB-graft copolymer; e, an IPN; f, a SIPN. Structures a –c are thermoplastic; structures a-f are thermoset.

2.2.1 History of IPNs

In 1914, the first invention of an IPNs was discovered by Aylsworth. He combined the new phenol-formaldehyde compositions with natural rubber and sulfur. In effect, by adding natural rubber and sulfur, Aylsworth made the world's first rubber-toughed plastic, decades before rubber-toughed styrenics were commercial. The next known discovery of IPNs was by Stuadinger et. al in 1941. To smooth the surface of transparent plastic sheeting for esthetic reasons, he took sheets of crosslinked polystyrene or poly(methyl methacrylate) and swelled sheets with the same monomer mix as network 1. After polymerization, the swelled sheets were stretched to reduce the waviness or surface imperfections of the original material. The next independent invention of IPNs was by Solt in 1955. He developed cationic-anionic ion exchange resin using suspension-sized particles and both networks oppositely charged. The idea of both charges on the same particle was that the exchange efficiency would be improved if both charges were in juxtaposition, but still separated in space. Indeed, the charges must be separated, even by a fraction of a nanometer, to prevent coaccerration. The term 'interpenetrating polymer networks' was coined by Millar in 1960. Several investigating terms found IPNs independently in the 1960s.

2.2.2 Kinds of IPNs

IPNs can be made in many different ways. Brief definitions of some of the more important IPNs material are in Table 2.5

Table 2.5 Classification of IPNs

Category	Definition
• Sequential IPNs	• Polymer network1 is made. Monomer2 plus crosslinker and activator are swollen into network1 and polymerized in situ.
• Simultaneous Interpenetrating networks (SIN)	• Monomers or prepolymers plus cross-linkers and activators of both networks are mixed. The reaction is carried out simultaneously, but by noninterfering reaction.
• Latex IPNs	• The IPNs are made in the form of latex, frequently with a core and shell structure. A variation is to mix two different latex and then form a film, which crosslinks both polymers. This variation is sometimes called an interpenetrating elastomer network (IEN).
• Gradient IPNs	• Gradient IPNs are materials in which the overall composition of crosslink density of the material varies from location on the macroscopic level. For example, a film can be made with network1 predominantly on one surface, network 2 on the other surface, and a gradient in composition throughout the interior.
• Thermoplastic IPNs	• Thermoplastic IPN materials are hybrids between polymer blends and IPNs that involve physical crosslinks rather than chemical crosslinks. Thus, these materials flow at elevated temperatures, similar to the thermoplastic elastomers, and at use temperature, they are crosslinked and behave like IPNs.
• Semi IPNs	• Composition in which one or more polymers are crosslinked and one or more polymers are linear or branched.

2.2.3 Polybutadiene – Polystyrene IPNs

Polybutadiene-polystyrene sequential IPNs and semi-IPNs are synthesized by thermal polymerization. The elastomeric component is prepared by dissolving linear polybutadiene in tetrahydrofuran (THF), adding dicumyl peroxide (DCP) for crosslinking, and evaporating the solvent. The polybutadiene matrix is partially cured by compression molding at 120°C and 130 kPa (45 psi) for 20 min, followed by ca 4 hrs at 130°C in a nitrogen atmosphere.

The IPN and semi-IPN morphologies of polybutadiene-polystyrene materials are compared in Figure 2.4. In each case, polybutadiene-rich elastomer phase is stained dark with osmium tetroxide, where as the PS-rich plastic phase is white. The electron micrograph of the semi-I IPN (0.1% DCP) shows that the elastomeric phase is more continuous, where as the PS-phase domains exhibit a bimodal distribution.

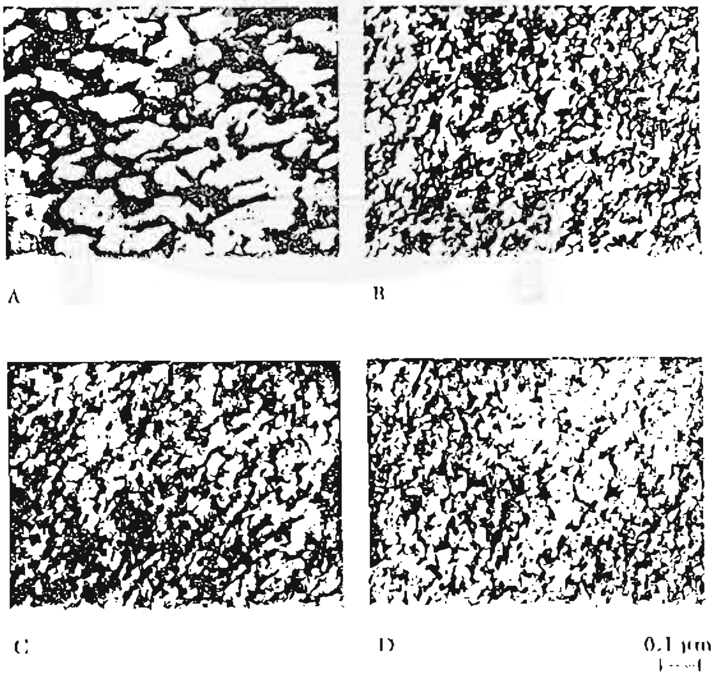


Figure 2.4 Polybutadiene-polystyrene IPN morphologies via TEM; phase stained with OsO_4. A semi I IPN (0.1% DCP); B semi I IPN (0.2% DCP); C full IPN (0.1% DCP); D full IPN (0.2% DCP). Increased crosslinker reduces domain sizes [15].

2.2.4 EPDM-PP thermoplastic IPNs

The most important commercial system involves ethylene-propylene-diene-monomer (EPDM) in combination with isotactic-polypropylene (i-PP). The EPDM is blended with the PP under condition where the EPDM undergoes crosslinking through the diene moiety.

Fischer invented this new class of IPNs in the early 1970s. Ficher blended i-PP and EPDM during the shearing action. The two phases in this system have remarkably different properties. The first phase is the disperse phase, it contains a component which is above its glass transition temperature (Tg) and melting temperature (Tm), so that chain is very mobile. Another phase is the matrix phase, it contains segments which are rigidity locked in place, because the service temperature is below both Tm and Tg [16]. The result is a series of leathery materials that have great energy absorbing capacity. End use includes automotive bumpers.

2.2.5 Application

The IPNs have many applications, both proposed and in practice. Many types of IPNs, SINs, semi-IPNs, etc, are available in commercial products, some commercial materials are shown in Table 2.6.

Table 2.6 IPNs commercial materials.

Manufacture	Trade name	Composition	Application
Shell chemical	Kraton IPN	SEBS-polyester	Automotive parts
ICI Americans	ITP	PU-polyester-styrene	Sheet molding compounds
DSM N.V.	Kelburon	PP-PE, rubber-PE	Automotive parts
Shell Reserch	-	Rubber-PP	Tough plastic
Reichold Chemical	TRP	EPDM-PP	Auto bumper parts, wire, and cable
Monsanto	Santoprene	EPDM-PP	Tire, hoses, belts, and basket
Du Pont	Somel	EPDM-PP	Outdoor weathering
BF Goodrich	Telcar	EPDM-PP or PE	Tubing, liners, wire, and cable
Exxon	Vitalon	EPDM-PP	Paintable automotive parts

2.3 Seeded Emulsion Polymerization (Core-Shell)

Latex particles with different morphological structures can be prepared from a seeded emulsion polymerization technique. These particles typically comprise an inner soft polymer sphere, i.e., the 'core' and an outer hard polymer 'shell'. Although particles may be prepared in two consecutive stages, a core-shell structure does not necessarily result. In the literature, many examples of other phase arrangements like. e.g., 'raspberrylike', 'acornlike', 'sandwichlike', 'poow', and inverted structures are found [17-20]. Figure 2.5 schematically represents these structures.

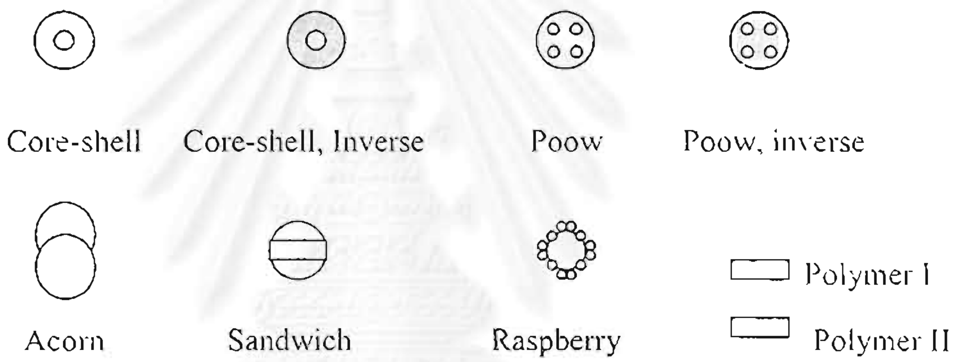


Figure 2.5 Possible morphologies of composite latex particles

Many different parameters , e.g. the monomer addition sequence, the hydrophilicity of the monomers and polymers. the used initiating systems, and the viscosity with in the monomer swollen seed latex particles. have to be taken into account. The last factor is primarily determined by the reaction temperature. the degree of crossslinking of the polymer chains, the monomer concentration in the seed latex particle during the reaction, and the molecular weight of the polymer. Furthermore. thermodynamic and kinetic aspects have to be considered. A morphology with the lowest free energy G is only achieved when the mobility of polymer chains is not too much reduced by a very high viscosity within the monomer swollen latex particle [21].

Core-shell, polymers such as polybutadiene (PB), styrene-butadiene rubber (SBR) and poly (butyl acrylate) (PBA), are usually chosen as the soft components, whereas the polymers of methyl metahcrylate (MMA), styrene (St), acrylonitrile (AN), vinyl chloride (VC), vinyl acetate (VAc), and so on are chosen as the hard components. They exist as graft polymers on the interface between the core and the shell. Polymers with a soft core and a hard shell are used as impact modifiers, toughened plastics, and damped oscillation materials, whereas polymers with a hard core and a soft shell are usually applied in the coating and adhesive fields [22].

2.4 Toughening by Rubber Addition

The impact resistance of glassy plastics may be increased by the addition of small quantities of rubber in the form of a polymer blend or graft copolymer. The rubber promotes crazing in the material, which absorbs the energy locally. This may be seen in everyday life as the white spot that results after a plastic has been hit accidentally. This is called stress whitening.

The characteristic of the rubber additive which is of critical importance, is determining the toughness of the final product. Typical values for Izod impact strengths are summarized in Table 2.7. Several important factors include the size of the droplets, the phase structure within the rubber particles (see Figure 2.6 and 2.7), grafting of the rubber to the plastic, and glass transition of the rubber.

Table 2.8 Izod impact strengths of several plastics.

Polymer	Impact strength (ft.lb/in.)
Polystyrene	0.25-0.4
High-impact polystyrene (Hips)	0.5-4
ABS plastics	1-8
Epoxy resin (no filler)	0.2-1.0
Epoxy resin (glass-fiber-filled)	10-30
Cellulose acetate	0.4-5.2
Poly (methyl methacrylate)	0.3-0.5
Phenol-formaldehyde plastics	0.2-0.36
Poly (vinyl chloride)	0.4-1
High-impact poly (vinyl chloride)	10-30

Source : Modern Plastics Encyclopedia (1973); Lannon (1967)

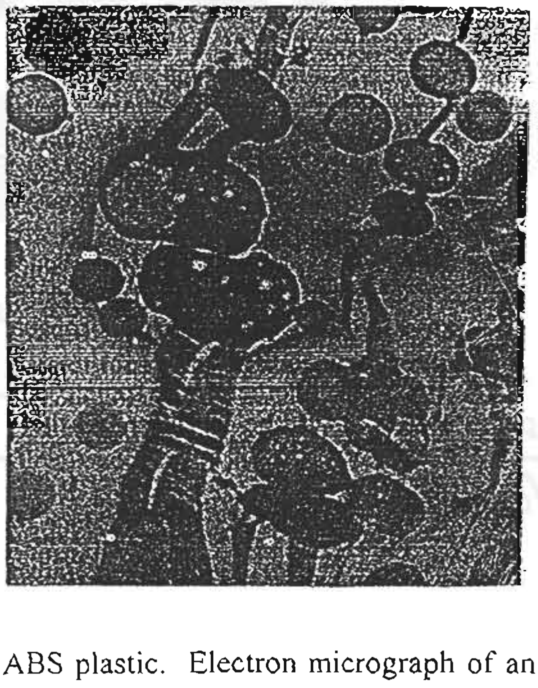


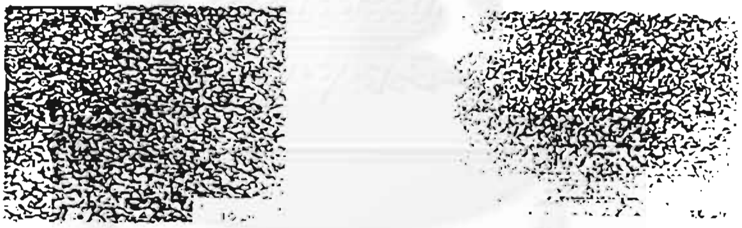
Figure 2.6 Crazing in ABS plastic. Electron micrograph of an ultrathin section cut parallel to the stress-whitened surface. The dark portions gave been stained with OsO_4. The white plastic phase is poly (styrene-stat-acrylonitrile), and the stained phase is poly (butadiene-stat-acrylonitrile).

HIPS
PHASE INVERTED

GRAFT
NO PHASE INVERSION

SEMI – I

SEMI – II



IPN, 0.1% CROSSLINKING

IPN, 0.2% CROSSLINKING

Figure 2.7 Phase morphology of graft copolymers and IPNs of SBR rubber and polystyrene by transmission electron microscopy. Upper two figures, graft copolymers; middle two semi IPNs; bottom two full IPNs. Diene portion stained dark with OsO_4.

The rubber droplets must be at least as large as the crack they are trying to stop. This puts the minimum size at several hundred angstroms, and a maximum size at about 3,000-5,000 °A.

One of the ways of obtaining the greatest overall toughness in a plastic is by combining shear yielding , crazing, and cracking in the proper order to absorb the highest total energy. Usually, it is desirable to have the sample yield in shear first. This absorbs energy without serious damage to the plastic. Then crazing should be encouraged to form within the shear-banded areas. The shear bands tend to stop the propagation of the crazes, limiting their growth. Only lastly does the 'molecular engineer' want an open crack to form, because its propagation will lead to failure [23].

2.5 Polymer Blends

A continuous need for new materials is created by the increasing complexity of products that result from technological breakthroughs and the desire to obtain improved cheaper materials for existing applications. Alongside the development of new improved base polymers and their copolymer, blend technology is one of the most widely used routes to satisfy this need. Polymer blends (also known as alloys) are combinations of two polymers with one or more distinctive properties that contribute to or are required for the proper functioning of a specific application. Their enhanced, especially adapted property profiles provide advantages to the processor and end user such as extra ease of processing, better low-temperature impact performances higher strength, higher or lower gloss, reduced flammability, and higher transparency, often in combination with a lower price.

2.5.1 Polypropylene Blends

Polypropylene (PP) is used as homopolymers, random copolymers and block copolymers. PP is one of the most widely used commodity plastics. It has a good chemical resistance, excellent thermal stability, a low price and high flowability. The polymer has three draw backs : (1) it is sensitive to oxidation during processing and use, (2) it has a poor resistance to UV-induced degradation, and (3) it is rather brittle even though it glass transition temperature (-10°C) is below room temperature.

Thermal oxidation problems have been solved by use of specially developed additive packages. Impact performance can be improved by chemical modification (copolymerization) or blending. Comonomers are mainly ethylene and higher olefins. Rubbers such as ethylene propylene diene monomer (EPDM) are frequently used for blending. The miscibility between polyolefins is extremely limited in spite of their great chemical similarity. However, due to the small interfacial tension the dispersibility is acceptable. Nevertheless, when blends of PP and other polyolefins are being made, they often require a compatibilizing block copolymer to provide the necessary degree of dispersion and to maintain morphological control during processing. The latter is essential for obtaining the desired mechanical properties of the product. Morphological stability can be further enhanced by in situ crosslinking of the dispersed phase (dynamic vulcanization). The main applications of PP and its blends are in bumper systems and dash boards.

2.5.2 Processing Technique

In the processing technique for PP/EPDM blend, in which both PP and EPDM have similar melt viscosity and are in particular form, it may be possible to mix in low shear mixing sections or even directly into the extruder or injection molding machine used to make the final part. However, the most widely used high shear mixing equipment are internal mixers, two-roll mills, brabender mixers, banbury mixers as well as single and twin screw extruders.

A two-roll mill is selected for blending PP and IPNs products of this research. The mill generates a high shear rate in a narrow nip between two heated rolls, which counter-rotate with slightly different velocities. In commercial mills, the rolls are about 1 ft. in diameter by 3 ft long. Once the polymer has banded on one of the rolls, the ingredients are added to the bank between the rolls. (see Figure 2.8) The band is cut off from the roll with a knife, rolled up, and fed back to nip at right angles to its former direction. This is done several times to improve mixing [24].

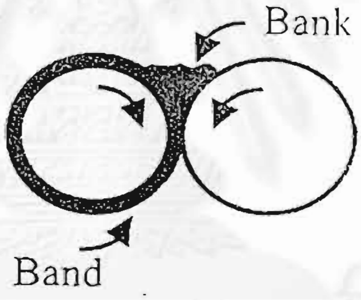


Figure 2.8 Characteristic of two-roll mills.

2.5.3 Morphology

The morphology of a material is its organization on a supermolecular scale, i.e., the form, size, orientation of its crystallites, domains, the structure of group of molecules in the specimen and of their boundaries, and the degree of crystallinity. Most polymer blends are heterogeneous, and the sizes and shapes of the phase domains control mechanical and transport properties. This is especially relevant for elastomeric systems, as many of these are rubber blends, thermoplastic elastomers, thermoplastic olefins such as PP/EPDM blends, and dynamic vulcanizates. The measurement of interfacial tension, which controls phase separation and growth and thus morphology, is also important.

The Scanning Electron Microscopy (SEM) is used to investigate the morphology of blend products. SEM is becoming the most popular method of observation of polymer blends. The great advantages of this technique are its rapidity, range of readily accessible magnifications, and depth of field. In addition, the SEM is considered to be a universal modern machine.

2.6 Literature Review

Natural rubber (NR) has been modified in many different ways, and modified forms have been available commercially. Several monomers can be grafted onto natural rubber (e.g., styrene(St), vinyl acetate, acrylonitrile, and methyl methacrylate (MMA)). The most important graft polymers are NR with MMA that are marketed under the trade name Hevea Plus MG. Emulsion polymerization is used for synthesis. Peroxides or hydroperoxide are used as initiator. Their main areas of use are in self-reinforcing vulcanizates and adhesive. One use of these materials is for PVC adhesion [12].

Polystyrene – modified natural rubber was developed for the production of a thermoplastic elastomer. The desire structures cannot be obtained by common grafting process, as used for grafting with MMA. A longer route, via special PS having azodicarboxylate as the terminal group, must be used. Then polymerized with NR in solvent or dry mix in internal mixer at 100-200°C, the defined structure is formed [11].

Hoursten et al. studied on natural rubber latex. NR latex has been synthesized to yield materials, which may be formally regarded as interpenetrating polymer networks and semi-interpenetrating polymer networks. Styrene was added to a carefully stabilized natural rubber latex and polymerized in situ using amine-activated initiator, t-butyl hydroperoxide. Dynamic mechanical analysis suggests that the blends are highly incompatible and phase-separated. An increasing PS content increases the initial modulus but reduces the tear strength [25]. In addition, the studied natural rubber PMMA composite latex synthesized uses an amine-activated hydroperoxide that uses the same process as styrene. The stress-strain data indicates that the incorporation of PMMA yields, which is a dramatic increase in both initial modulus and tensile strength [26]. Furthermore, their groups also studied using azobisisobutylonotrile as initial material for NR-PS composite latex. The results of the mechanical properties were not outstanding. AIBN does lead to some grafting of PS and causes significant degradation of the natural rubber molecules when the styrene content is low [27].

Das et al. [28] studied sequential IPNs which were synthesized using NR and PS as elastomer and plastomer components, respectively. Benzoyl peroxide was used as the polymerization initiator, dicumyl peroxide (DCP) as the crosslinker for NR and divinyl benzene as the comonomer/crosslinker for PS. Both full IPNs and semi-IPNs were prepared by using dry NR that was masticated in a two-roll mill with crosslinking and cured. Then cured NR sheets were swollen in distilled styrene monomer containing the initiator, and crosslinking took place before polymerization occurred. Morphology of IPNs was studied through scanning electron microscopy. Crosslinking of the plastomer component induced better miscibility and finer morphology. IPNs products were characterized by evaluating their mechanical properties. Full IPNs showed higher tensile strength, modulus, tear strength than the corresponding semi-IPNs while the latter exhibited higher elongation at break and toughness.

Schneider et al. [21] studied different emulsion polymerization processes allowing a variation in the microstructure of composite NR-based latex particles. Prevulcanized and not-crosslinked natural rubber latex were coated with a shell of crosslinked PMMA or PS. The bipolar redox initiating system tert-butyl hydroperoxide/tetraethylene pentamine promoted a core-shell arrangement. Furthermore PS subinclusions were introduced into the NR core. The initiators used for the subinclusion synthesis were azobisisobutyronitile at high temperature and a redox initiator system consisting of tert-butyl hydroperoxide/dimethylaniline at low temperatures. TEM and SEM characterized the morphology of the resulting latex IPNs. Different staining methods allowed an increase the contrast between the NR phase and the secondary polymers in the composite latex particles. A semi-continuous feeding process decreased the PS subinclusions sized by a factor of 6 in comparison with a batch reaction. Differential scanning and DMA confirmed two-or three-phase particle morphology.

Asaletha et al. [29] studied compatibility of NR/PS blend that is poor and can be enhanced by the addition of a graft copolymer of NR-graft-PS. The effect of homopolymer molecular weight, copolymer molecular weight, copolymer concentration, processing condition and mode of addition on the morphology of the dispersed phase have been investigated by means of optical microscopy. The addition of small percentage of the compatibilizer decreases the domain size of the dispersed phase. The effect levels off at higher concentrations the leveling off could be an indication of interfacial saturation. The addition of the graft copolymer improves the mechanical properties of the blend and attempts were made to correlate the mechanical properties of the blend and attempts were made to correlate the mechanical properties with the morphology of the system. Attempts were also made to understand the conformation of the morphology of the graft copolymer at the interface.

Kitikorn C. [30] studied the graft copolymerization of MMA and styrene onto NR in the emulsion process. The optimum condition were 100 parts by weight of monomer per 100 parts by weight of NR latex, the emulsifier concentration of 1.5 parts by weight, the initiator concentration of 1.5 parts by weight and temperature of 70°C for 8 hours. The grafted natural rubber product was used as an impact modifier in PVC. The tensile strength and hardness decreased with increasing the grafted natural product content, but the elongation at break and impact strength increase with increasing the grafted natural rubber content. The appropriate amounts of grafted natural rubber product used were 10 and 15 phr.

Chawalat [16] studied the flexural strength improvement of PP/EPDM. The composites prepared by mixing various amounts of PP, and EPDM, reinforced additives on two-roll mills and subjected the composites to compression molding to obtain the specimens for testing. X-ray fluorescence spectroscopy, differential scanning calorimeter (DSC), and SEM were used to study elements, melting temperature and dispersion of the composite, respectively. The addition of EPDM increased on the impact strength while the flexural strength, melt flow index and hardness decreased. The addition of talc gave specific improvement on flexural strength and hardness, while clay provided almost no improvement on properties.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1. Prevulcanized natural rubber latex (NR) : Revertex (Thailand) Co., Ltd.
2. Styrene monomer (St) : Siam Chemical Industry Co., Ltd.
3. Tert-butyl hydroperoxide (tert-BuHP) : Fluka
4. Tetraethylene pentamine (TEPA) : Fluka
5. Divinyl benzene (DVB) : Merck
6. Oleic acid : Fluka
7. Ammonia solution : Fluka
8. Sodium hydroxide : Merck
9. Sodium sulfate : Carlo Erba
10. Aluminium oxide : Fluka
11. Polypropylene (2511 TC) : Thai Petrochemical Industry (Public) Co., Ltd.
12. EPDM (JSR EP35) : Japan Synthetic Rubber Co., Ltd.
13. Antioxidant (Irganox 1076) : PI industry Co., Ltd.

3.2 Glasswares

1. 4-Necked bottom reactor 500 cm^3
2. Liebig condenser
3. Nitrogen gas tube
4. Other general laboratory glasswares

3.3 Instruments and Apparatus

1. Two-roll mills : Lab Tech. Engineering, CU
2. Compression molding : Lab Tech. Engineering, CU
3. Crushing machine : Lab Tech. Engineering, CU
4. Scanning Electron Microscope : JSM 35CF, STREC CU
5. Transmission Electron Microscope : JSM 200CX, STREC CU
6. Universal testing machine : Instron Corporation SerieIX, RRIT
7. Impact testing machine : Impact Radmana ITR2000, MTEC
8. Hardness testing machine : Zwich, RRIT
9. Tear strength testing machine : Instron, RRIT
10. Differential Scanning Calorimeter : Perkin Elmer DSC7, MTEC
11. Thermogravimetric Analyzer : Perkin Elmer TGA7, MTEC

3.4 Experimental Procedure

3.4.1 Purification of monomer

Styrene monomer was supplied by Siam Chemical Industry Co., Ltd. It was purified by removing the added inhibitor before use. It was washed twice with 10% aqueous sodium hydroxide in a separating funnel. The aqueous phase was drained off, and the monomer phase was washed with distilled deionized water until pH 7 was obtained. Then anhydrous sodium sulfate (100g/l) was added to absorb the remaining amount of water in the monomer phase. Finally, the dried monomer was passed through an activated aluminum oxide column. The purified styrene was stored in a brown capped bottle under nitrogen atmosphere and kept in a refrigerator at –5 °C.

3.4.2 Preparation of Natural Rubber-Polystyrene Composite

An emulsion polymerization process was used to prepare natural rubber-polystyrene composite. The preparation procedure of composite product is presented in flow diagram 1. The apparatus set up is shown in Figure 3.1.

Prevulcanized natural rubber latex was charged into a 500 cm^3 bottom reactor and diluted with distilled water to maintain total solid content at 50%. As a buffer, ammonium hydroxide was placed to give the pH of the latex above 8.5. The mixture was de-oxygenated by bubbling nitrogen gas at room temperature. Subsequently, the emulsifier-oleic acid, amine activator-TEPA, the crosslinking agent-DVB, and styrene monomer were mixed respectively and the temperature was increased to 50 – 80°C. After the period of 1 hr, in order to swell NR particle by styrene monomer, the initiator tert-BuHP was added. The bipolar redox initiating system tert-BuHP/TEPA was employed in the ratio 1/1. The reaction mixture was stirred at the constant temperature for 1 – 8 hours to finish the reaction. Any unreacted monomer retained in the product was finally removed by keeping the product in oven until it was thoroughly dry (70°C, 48 hours). To form a sheet for subsequent mechanical tests, the product was mixed by a two-roll mill at 110°C for 3 min. The product was united and then compressed sample to give a final opaque sheet-thickness of ca 3 mm.

The appropriate condition was investigated by varying the initiator concentration, crosslinking agent concentration, emulsifier concentration, reaction time and temperature, and ratio of natural rubber/ styrene monomer as shown Table 3.1

Table 3.1 The range of parameters investigated in the polymerization process.

Ingredient	Unit	Quantity
Initiator/activator (1/1)	phr	0.5, 1.0, 1.5, 2.0
Crosslinking agent	%wt of monomer	0, 0.25
Emulsifier	%wt of monomer	0.5, 1.0, 1.5, 2.0
Reaction temperature	°C	50, 60, 70, 80
Reaction time	Hours	1, 2, 6, 8
Ratio NR/St	-	80:20, 70:30, 60:40, 50:50

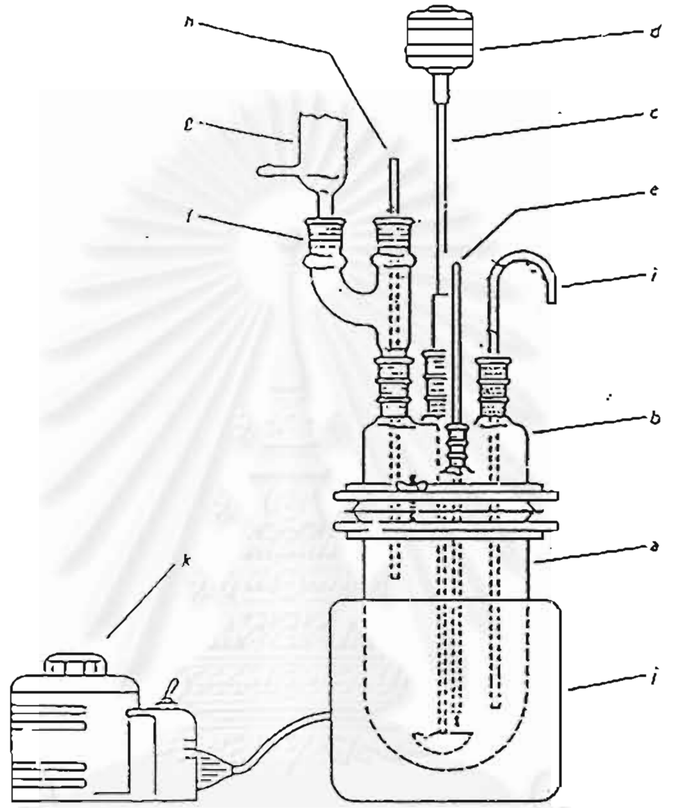


Figure 3.1 Apparatus for emulsion polymerization of NR/PS IPNs [31].

(a) reaction kettle bottom

(b) reaction kettle top

(c) stainless steel stirrer

(d) air motor

(e) thermometer

(f) adapter

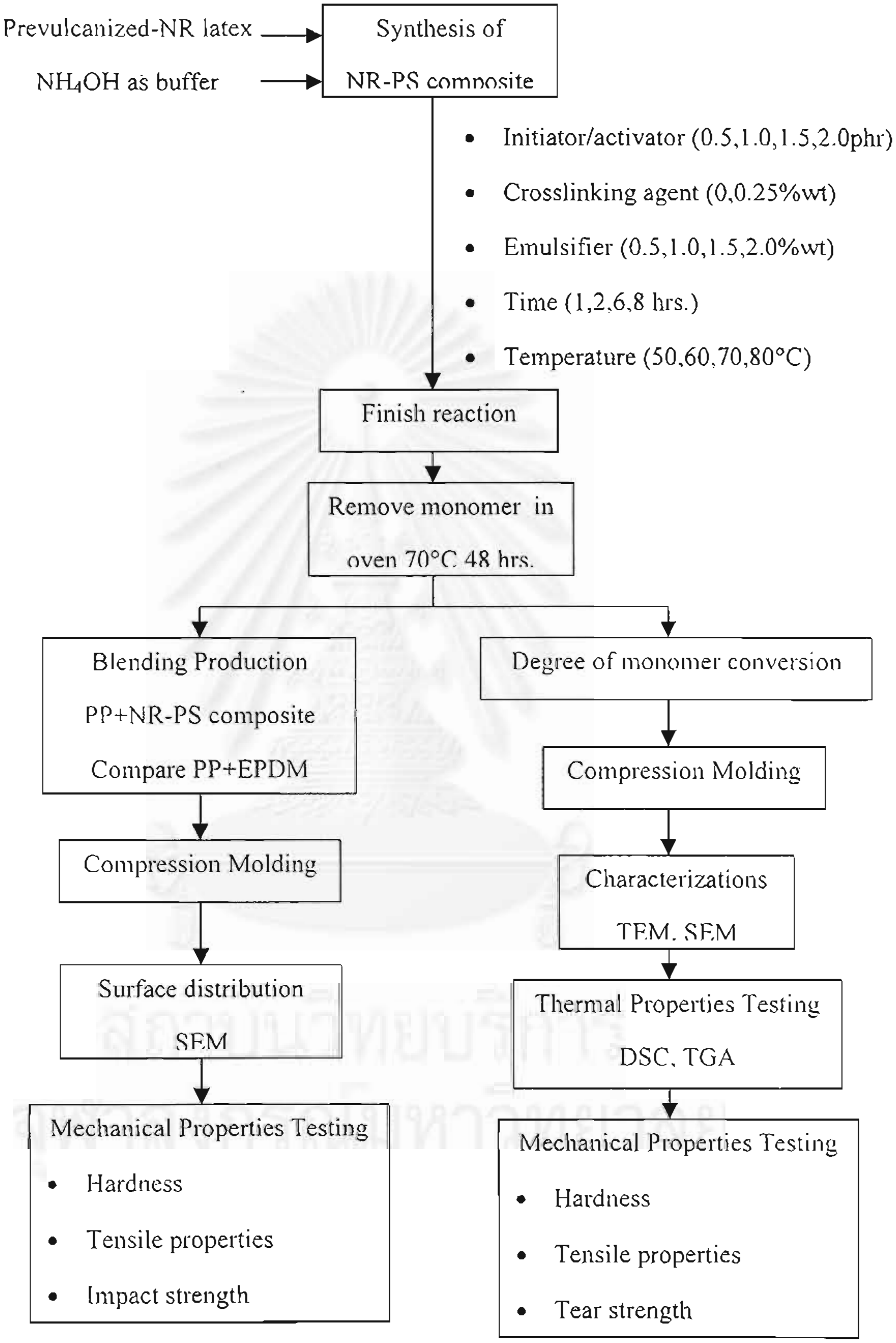
(g) condenser

(h) nitrogen-inlet tube

(i) sampling tube

(j) water bath

(k) variable transformer



Flow diagram 1 Experiment scheme of preparation of NR-PS composite

3.5 Characterization

3.5.1 Determination of the morphology of NR-PS composite

a) Transmission Electron Microscopy (TEM)

A JEM – 200 CX transmission electron microscopy was used in order to observe ultramicrotome sections of NR-PS composite which were prepared in the following way. First, a smooth surface of the NR-PS composite was dipped in osmium tetroxide (solution) for 48 hrs in order to stain the NR phase. The staining not only enhanced the contrast for the microscopic viewing of the blends but also hardened the rubber phase. In this way, ultramicrotome sections could be prepared without altering the particle morphology of the no longer soft natural rubber particles.

b) Scanning Electron Microscopy (SEM)

A JEM – 35 CF scanning electron microscope was used for the examination of NR-PS composites which were prepared by coating the gold vapor deposition before viewing.

3.5.2 Determination of Thermal Properties of the Composite Product

a) Differential Scanning Calorimetry (DSC)

A 10-20 mg sample of a dried sample was placed into an aluminum pan and measured between 50 and 150°C in a Perkin-Elmer DSC7 thermal analyzer. The heating and cooling rate was 10°C/min.

b) Thermogravimetric Analysis (TGA)

A Perkin Elmer TGA7 thermogravimetric analyzing system was used to follow the weight loss of a 10 mg sample between 50 and 800°C while the system was purged with ordinary air. The heating rate was 20°C/min.

3.6 Mechanical Testing

The ASTM and ISO test methods were used for investigating the mechanical properties of composite product as follows:

a) Hardness

(ASTM D2240: Standard test method for rubber property-Durometer Hardness)

For the assignment of the specimen for hardness testing, the test specimen was of at least 6 mm in thickness. The surface of the specimen was flat and over a sufficient area to permit the presser foot to contact the specimen. For materials having hardness values above 50 type D Durometer, the thickness of the specimen was of at least 3 mm and measurements should not be made closer than 6 mm to any edge.

According to the thickness assignment, the test specimens in this experiment were composed of plied pieces to obtain the necessary thickness. The type D Durometer was used in this experiment. The conditions in testing are shown as follows:

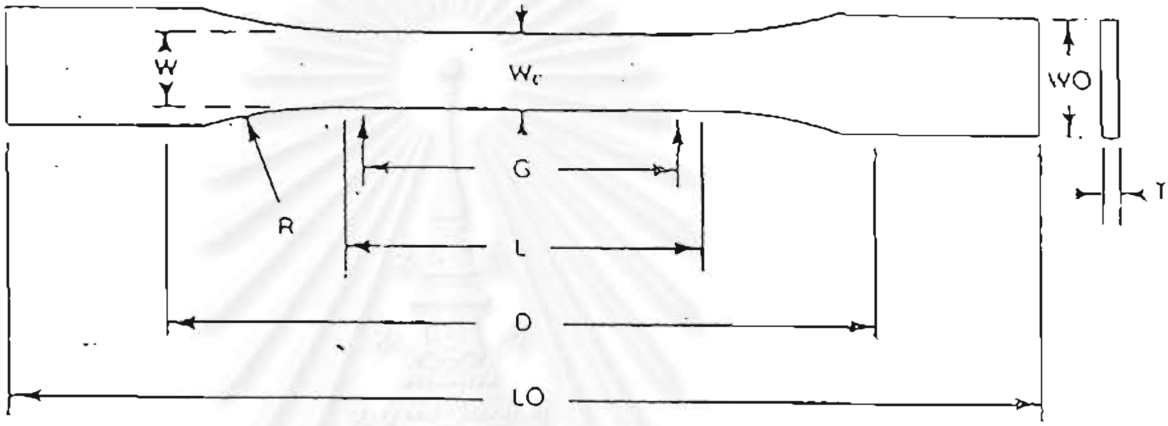
Temperature:	25°C
Relative humidity:	50%
Number of pieces plied:	2 pieces.

For all of the properties measured, at least five samples were tested to obtain a reliable average and standard deviation.

b) Tensile properties

(ASTM D638: Standard test method for tensile properties)

The tensile strength, the elongation and the modulus were determined. The test specimen dimension (type I) is shown in Figure 3.2.



W : 13 mm Wo : 19 mm G : 50 mm R : 76

L : 57 mm Lo : 165 mm D : 115 mm

Figure 3.2 Schematic of tensile test specimen (type I)

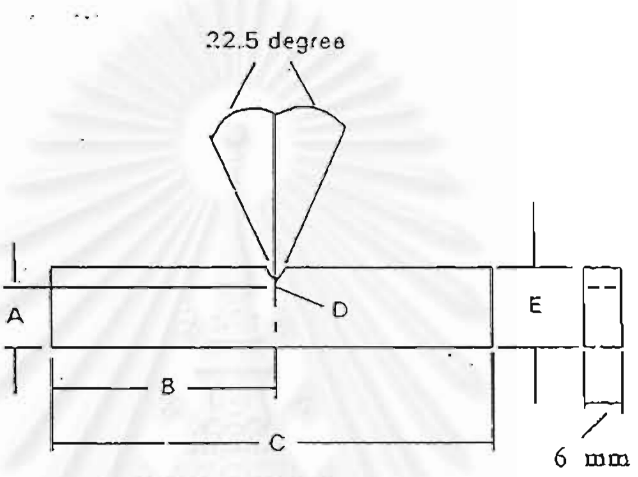
The tensile testing conditions were as follows:

Temperature:	23°C
Relative humidity:	50%
Speed of testing:	5 mm/min
Distance between grips:	115 mm
Gage length:	50 mm

c) Impact resistance

(ASTM D256: Standard test method for impact resistance)

The test specimens dimension for Cantilever Beam (Izod type) test is shown in Figure 3.3.



Unit : mm

A: 10.16 ± 0.05

B : 32.00 max, 31.50 min

C : 63.50 max, 63.30 min

D : 0.25 ± 0.05

E : 12.75 ± 0.15

Figure 3.3 Schematic of Izod type test specimen

The machine parameters and testing condition of the impact test are listed below:

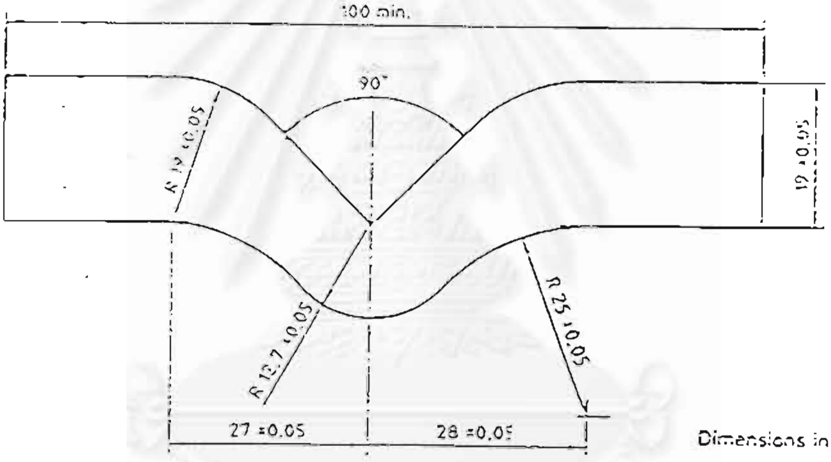
Temperature:	25°C
Relative humidity:	50%
Depth of specimen:	10.16 mm
Pendulum capacity:	21.6 J

d) Tear strength

(ISO 34: Rubber, vulcanized or thermoplastic-determination of tear strength)

(Part I: Trouser, angle and crescent lest pieces)

The value of tear strength obtained depended on the shape of the test specimen, speed of stretching and temperature of the test. In this experiment, the composite sheets were used in method B, procedure (a) that used an angle test specimen without nick. The test specimen was cut from composite sheets of uniform thickness. The dimension and the shape of the specimen are shown in Figure 3.4.



Dimensions in millimetres

Figure 3.4 Schematic of angle test specimen.

The tear testing conditions are shown as follows:

Temperature:	25°C
Relative humidity:	50%
Crosshead speed:	500 mm/min
Full scale load range:	5.0 kN

3.7 NR-PS IPNs product and PP blends

The isotactic polypropylene powder 100 phr, 5 to 20 phr NR-PS composite and 0.2 phr antioxidant were prepared by blending all of the components on a two-roll mills at 165°C for 5 min. The PP was first introduced for preheating for 2 minutes and followed by the composite product, and antioxidant respectively. Furthermore, EPDM was used to replace the composite product in order to compare the mechanical properties. A batch was mixed for at least 10 minutes after blending. Distance between the rolls (the roll nip) was adjusted to facilitate mixing.

The thin sheet from two-roll mills was grinded by crushing machine. The sheet was then pressed by compression molding at 200°C, 1,600 psi for 5 min; the sheet thickness was 3 mm. The sheet was cut into the standard specimens according the ASTM and ISO methods.

CHAPTER IV

RESULT AND DISCUSSION

The natural rubber-polystyrene interpenetrating polymer networks (IPNs) and semi-interpenetrating polymer networks (semi-IPNs) were prepared by using the emulsion polymerization. Many different parameters, which consist of initiator concentration, crosslinking agent concentration, emulsifier concentration, reaction temperature and reaction time, have been taken into account. The morphology of the resulting IPNs and semi-IPNs were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Various contents of the composite products were blended with isotactic PP. To give suitable properties, the mechanical properties of the blend were determined to find the optimum ratio of the composite product and PP.

4.1 Preparation of IPNs product

The present study, based on semi-IPNs (where only NR was crosslinked from prevulcanized-NR latex) and IPNs (where both NR and PS were crosslinked), was carried out to evaluate the effect of initiator concentration, emulsifier concentration, reaction temperature, reaction time, and monomer content on the conversion of styrene monomer. Styrene was added to carefully stabilize prevulcanized natural rubber latex and polymerized in situ. The bipolar redox system, tert-BuHP/TEPA , was used to promote a core-shell arrangement. The resulting materials were cast to yield solid sheet. The appropriate conditions were studied to yield high percent conversion.

4.1.1 The Effect of Initiator/Activator Concentration on Monomer Conversion

The effect of initiator concentrations on the degree of monomer conversion was studied by varying the initiator concentrations to 0.5, 1.0, 1.5, and 2.0 phr (parts per 100 part of rubber content). The bipolar redox initiating system was used in this experiment. This system consists of tert-BuHP and TEPA, which promotes a core-shell morphology. The ratio of tert-BuHP/TEPA was employed in 1/1. The details are shown in Table 4.1 and Figure 4.1.

The parameters of emulsion polymerization were obtained as follows:

• Rubber/styrene monomer	: 70:30
• Crosslinking agent	: 0.25 % wt of styrene monomer
• Emulsifier concentration	: 1 phr
• Reaction temperature	: 50°C
• Reaction time	: 6 hrs

The degree of monomer conversion is defined as the mass of polystyrene formed divided by the initial mass of monomer as shown in Appendix A.

In Figure 4.1, the degree of monomer conversion initially increased rapidly with the increasing amount of initiator concentration, and slowly increased at high concentration. First, the increase in the initiator concentration produced more radical sites, therefore the degree of monomer conversion could increase. At higher initiator concentrations, plenty of initiator radical is formed and radical recombination can occur to some extent to slightly increase all the reaction properties in terms of lower increasing conversion. The optimum initiator concentration of 1.5 phr was found.

Table 4.1 Effect of initiator concentration on the percent degree of monomer conversion: NR: PS = 70:30; crosslinking agent = 0.25% wt of monomer; emulsifier = 1 phr; temperature = 50°C; time = 6 hrs.

Initiator concentration (phr)	% Conversion average of styrene monomer to polystyrene
0.5	12.5
1.0	62.8
1.5	79.8
2.0	80.98

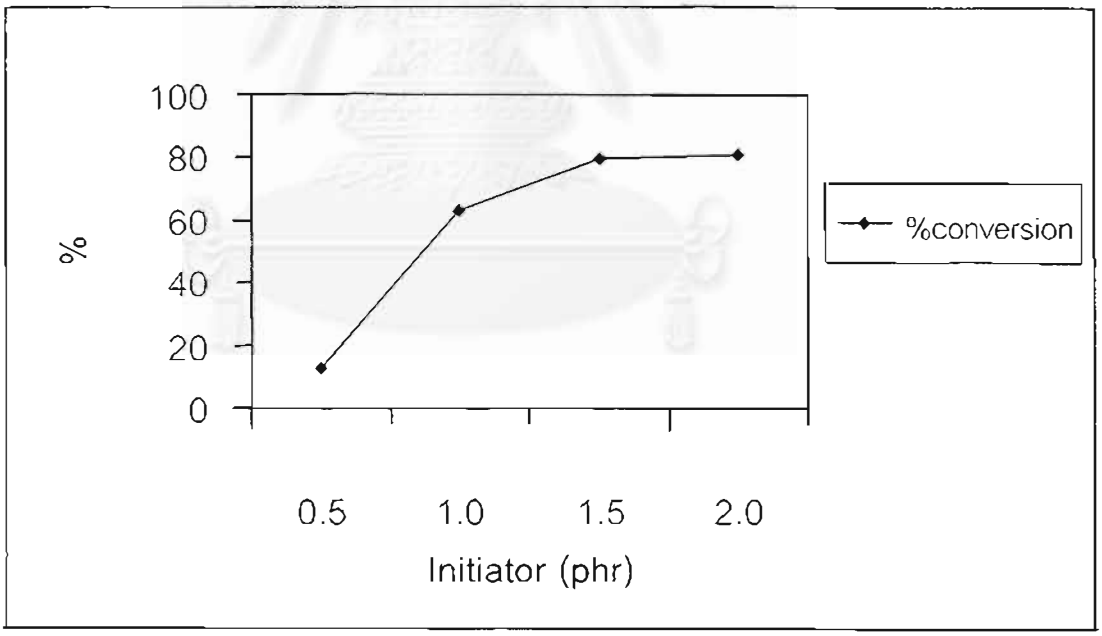


Figure 4.1 Effect of initiator concentration on the degree of monomer conversion.

4.1.2 The Effect of Emulsifier Concentration on Monomer Conversion

Anionic surfactants are the most commonly used surfactants in emulsion polymerization. In this experiment fatty acid, oleic acid, was used as emulsifiers. NH_4OH was added to stabilize the latex.

The effect of emulsifier concentration on the degree of monomer conversion was investigated by varying oleic acid concentration to 0.5, 1.0, 1.5, and 2.0 % wt of styrene monomer. The parameters were kept constant as follows:

• Rubber/styrene monomer	: 70:30
• Initiator/activator	: 1.5 phr
• Crosslinking agent	: 0.25 % wt of monomer
• Reaction temperature	: 50°C
• Reaction time	: 6 hrs.

Table 4.2 and Figure 4.2 summarize the effects of emulsifier concentration on degree of monomer conversion. The details of all data and calculation are shown in the Appendix A.

Figure 4.2 shows the effect of oleic acid concentration on the degree of monomer conversion. It can be seen that the degree of monomer conversion increases with an increase in the emulsifier concentration. At surfactant concentration above 1.0 % wt of monomer, the degree of monomer conversion increases only slightly. This is due to the fact that when the concentration of surfactant exceeds its critical micelle concentration (CMC), the excess surfactant molecules aggregate together to form small colloidal clusters referred to as micelles. The appropriate emulsifier concentration in this emulsion polymerization was found at 1.5% wt of monomer.

Table 4.2 Effect of emulsifier concentration on the degree of monomer conversion: NR/PS = 70:30; initiator = 1.5 phr; crosslinking agent = 0.25 % wt of monomer; temperature = 50°C; time = 6 hrs.

Emulsifier concentration (% wt of styrene monomer)	% conversion average of styrene monomer to polystyrene
0.5	58.6
1.0	65.9
1.5	76.3
2.0	80.8

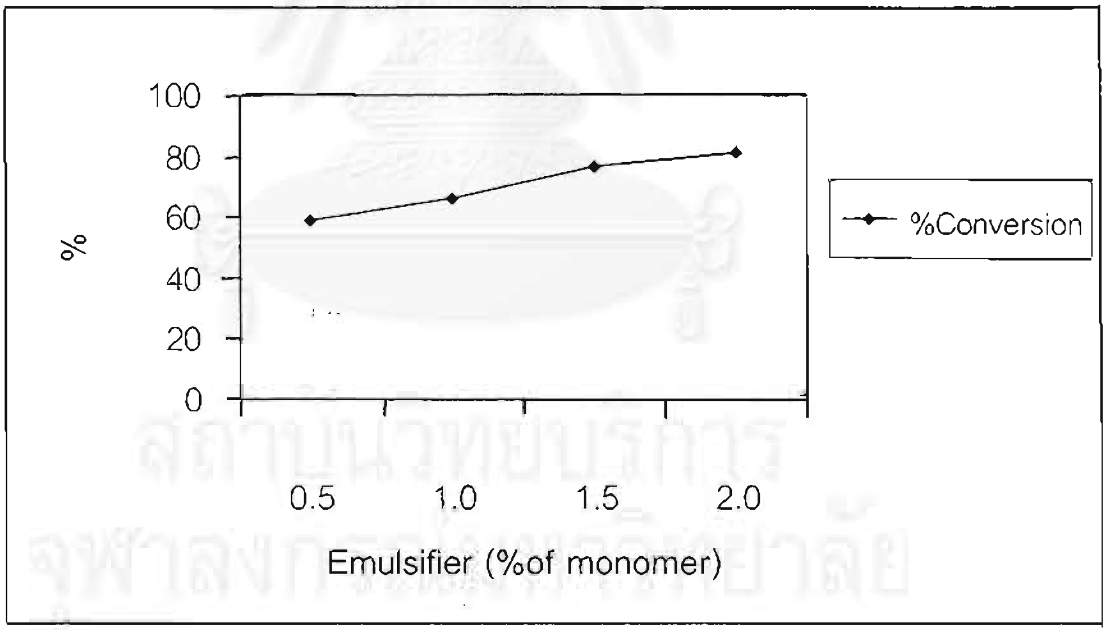


Figure 4.2 Effect of emulsifier concentration on the degree of monomer conversion

4.1.3 Effect of the Reaction Temperature on Monomer Conversion

The effect of the reaction temperature on the degree of monomer conversion was investigated by varying the reaction temperature to 50, 60, 70, and 80°C, which are shown in Table 4.3, and Figure 4.3.

Basic formulations for emulsion polymerization of IPNs were prepared as follows:

- Rubber/styrene monomer : 70:30
- Initiator/activator : 1.5 phr
- Crosslinking agent : 0.25 % wt of monomer
- Emulsifier concentration : 1.5 % wt of monomer
- Reaction time : 6 hrs.

The reaction temperature imposes a strong effect on the conversion of monomer, due to the reaction temperature which influences the reactivity ratio of styrene monomer in the aqueous phase. When the temperature increases, decomposition of the initiator increases, resulting in an increased number of free radicals and an increased rates of polymerization. At temperatures above 60°C, the degree of monomer conversion increases slightly. The appropriate temperature for this reaction is 60°C.

Table 4.3 Effect of reaction temperature on the degree of monomer conversion: NR/PS = 70:30, initiator = 1.5 phr, crosslinking agent = 0.25%wt of monomer, emulsifier = 1.5 %wt of monomer, time = 6 hrs.

Reaction temperature (°C)	% conversion average of styrene monomer to polystyrene
50	70.3
60	77.2
70	78.9
80	78.6

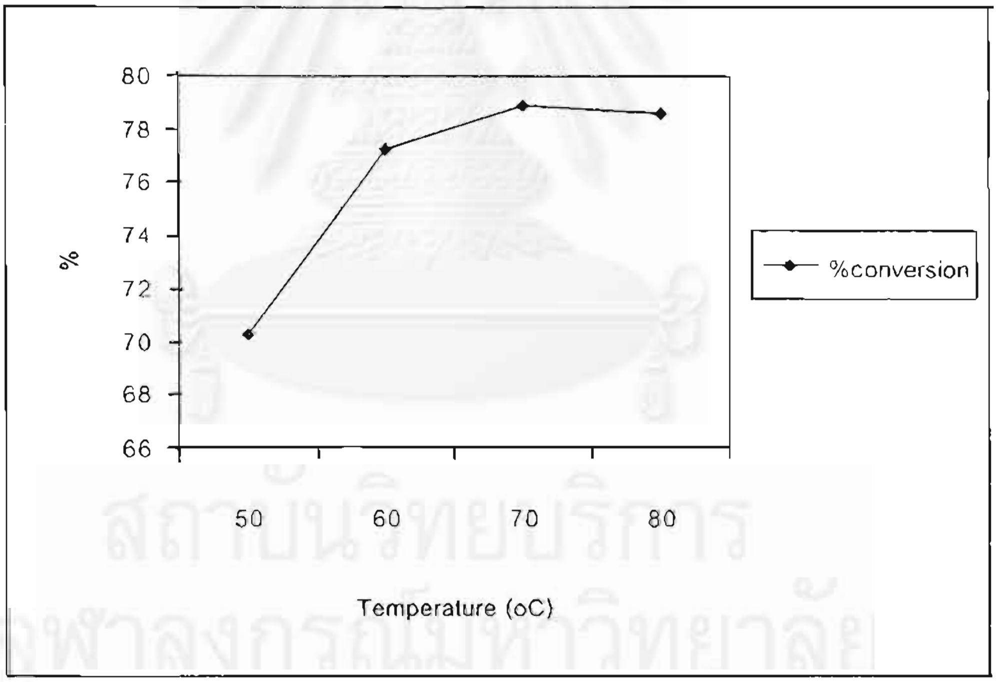


Figure 4.3 Effect of reaction temperature on degree of monomer conversion.

4.1.4 Effect of the Reaction Time on Monomer Conversion

The effect of the reaction time on the degree of monomer conversion was shown in Table 4.4 and Figure 4.4. The parameters of IPNs product were obtained as follows:

- Rubber/styrene monomer : 70:30
- Initiator/activator : 1.5 phr
- Crosslinking agent : 0.25 % wt of monomer
- Emulsifier concentration : 1.5 % wt of monomer
- Reaction temperature : 60 °C

This effects were investigated by varying the reaction time to 1, 2, 6, 8 hrs. In Figure 4.4, it can be seen that when the time is increased the degree of monomer conversion also increases. The reaction is completed within only 2 hrs. with the highest monomer conversion at 80.2 %.

Table 4.4 Effect of reaction time on degree of monomer conversion : NR/PS =70:30, initiator/activator = 1.5 phr, crosslinking agent = 0.25%wt of monomer, emulsifier = 1.5%wt of monomer, temperature 60°C.

Reaction Time (hr)	% conversion average of styrene monomer to polystyrene
1	58.3
2	80.2
6	80.5
8	81.3

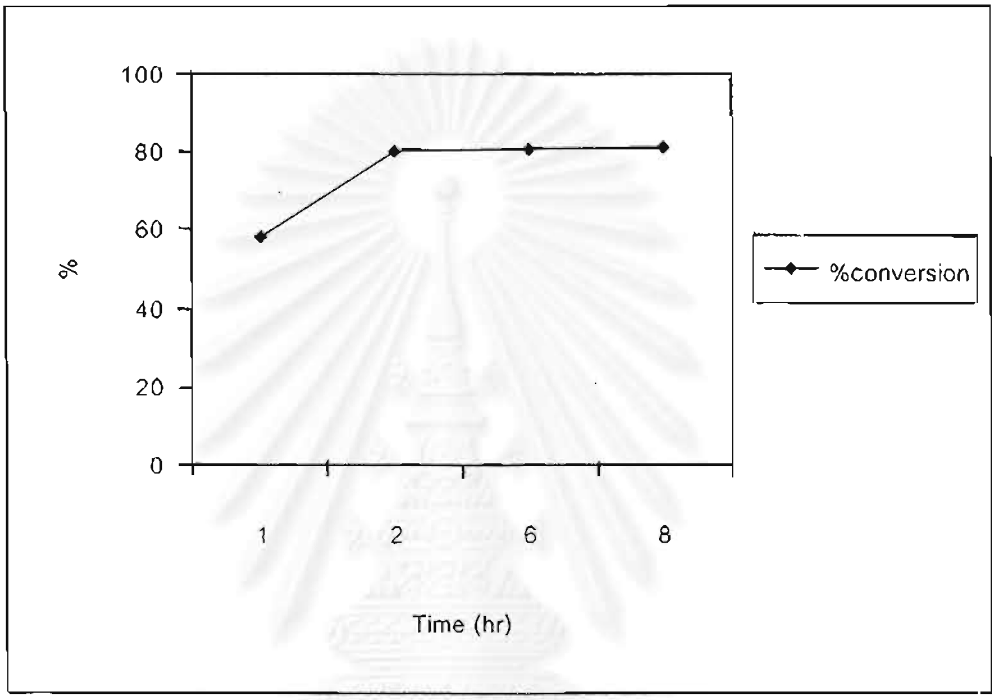


Figure 4.4 Effect of reaction time on degree of monomer conversion.

4.2 The Morphology of NR-PS Composite.

Core-Shell particle synthesis was prepared by batch emulsion polymerization. This method applied 1 hr swelling time to achieve a uniform distribution of monomers with the seed latex particles. The high solid content (50%) provided a large total surface area which facilitated the gathering of small particles and the stability of the latex. A core-shell arrangement of the polymer phase was assumed since the bipolar redox initiation system tert-BuHP/TEPA was used. Free radicals are produced at the particle/water or monomer droplet/ water interface since the peroxide is soluble in both the monomer and the NR particles whereas, the activator tetraethylene pentamine is water-soluble. Figure 4.5 is a TEM photograph of IPNs containing 40% crosslinked PS in the shell.

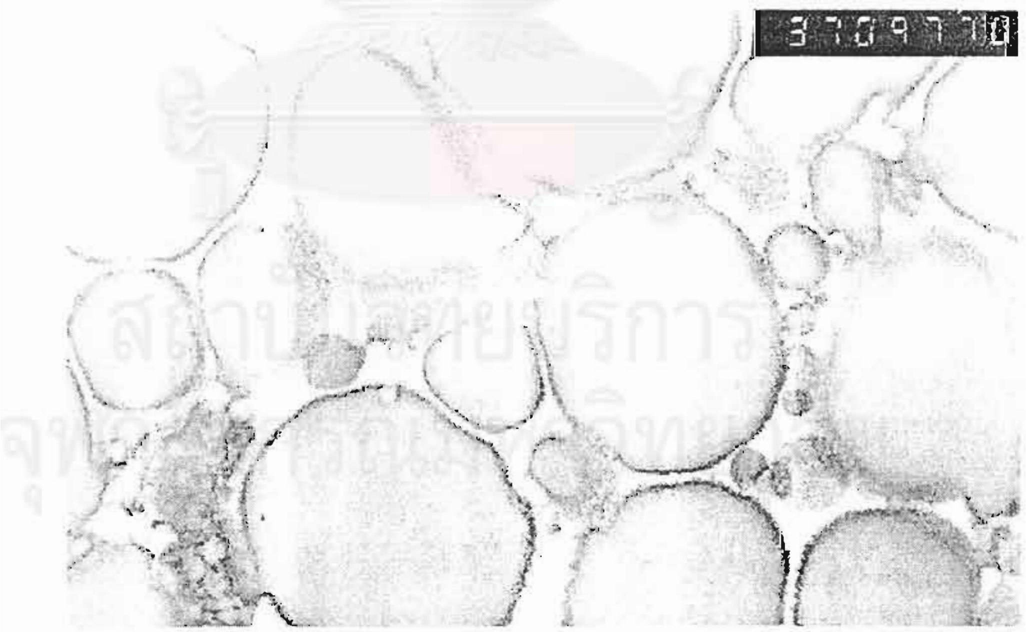


Figure 4.5 Transmission electron micrograph of an osmium tetroxide-strained ultramicrotome cut of IPNs containing 40% crosslinked PS in the shell.

4.2.1 Transmission Electron Microscopy (TEM)

TEM is used to observe ultramicrotome cuts of latex particles which have been incorporated into a PS matrix. Osmium tetroxide is used to stain the NR phase. From the photograph, the NR phase is darker than the PS phase.

TEM also presents the size of the rubber droplets. Rubber droplets used for impact modifier must be at least as large as the crack they are trying to stop. This puts the minimum size at several hundred angstroms, and a maximum size at about 3000-5000 angstroms.

4.2.1.1 Effect of monomer content on particle morphology

The increase in monomer content decreased the particle size of the NR phase. When the monomer content increases, more styrene monomer inserts in the NR phase. When there is increased styrene monomer, which polymerizes to polystyrene, the NR particle size decreases. Figure 4.6 shows the series ratios of NR:PS put in order from small to large particle sizes, including IPNs (a) 50:50, (b) 60:40, and (c) 70:30. The rubber droplet sizes are 2,600, 5,300, and 7,100 angstroms, respectively.

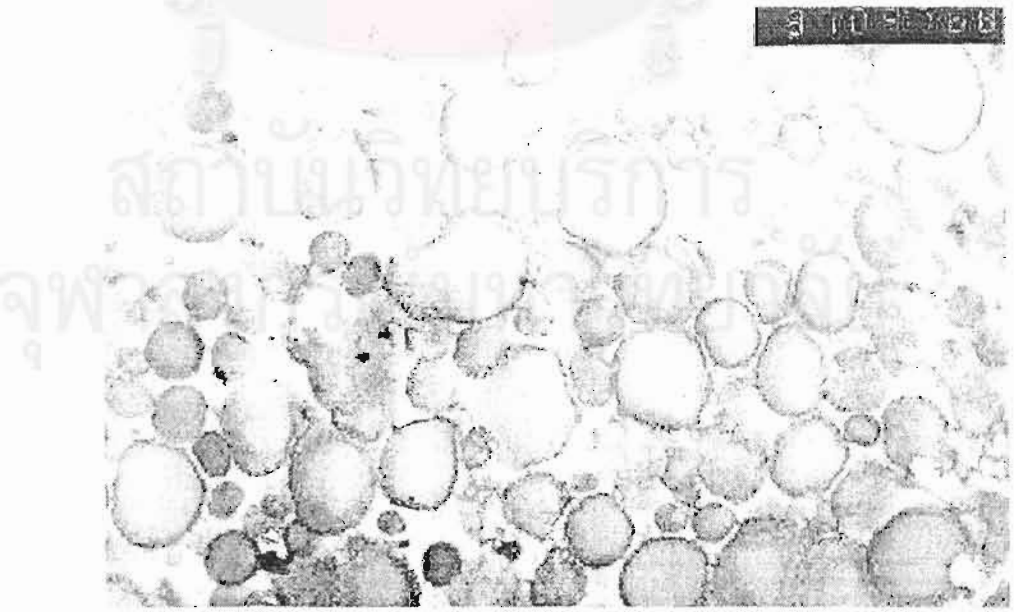


Figure 4.6 (a) TEM photomicrograph of NR:PS IPNs 50:50

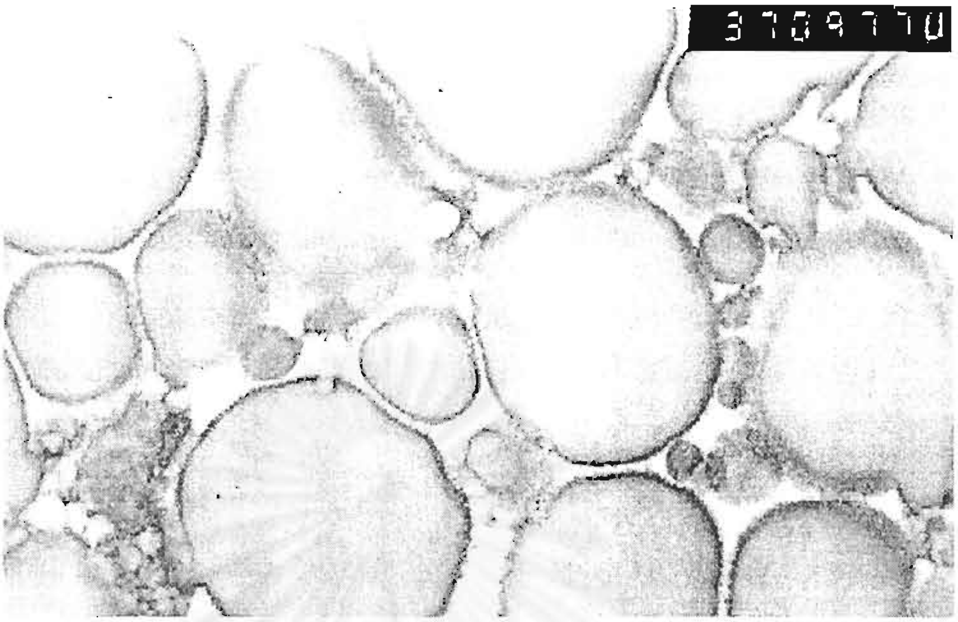


Figure 4.6 (b) TEM photomicrograph of NR:PS IPNs 60:40

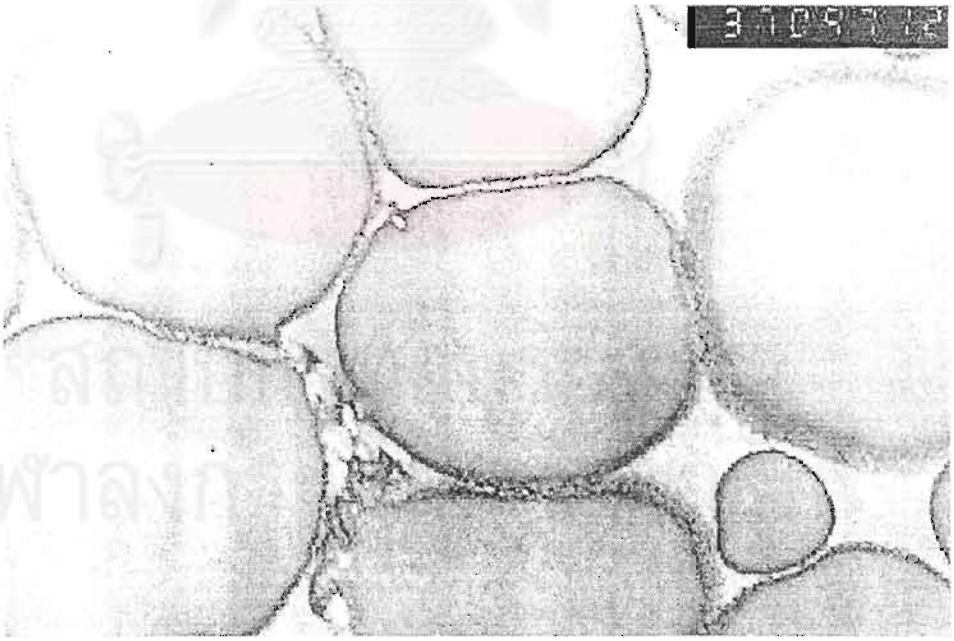


Figure 4.6 (c) TEM photomicrograph of NR:PS IPNs 70:30

4.2.1.2 Effects of Crosslinking Agent on Particle Morphology

Effects of crosslinking agent on particle morphology are presented in Figure 4.7. Figure 4.7 presents transmission electron micrograph of the osmium tetroxide-stanined ultramicrotome cut of an IPN and semi-IPNs. A_1, B_1, C_1 are semi-IPNs of NR:PS = 50:50, 60:40, and 70:30, respectively. A_2, B_2, C_2 are IPNs of NR:PS = 50:50, 60:40, and 70:30, respectively.

It can be seen that the particle size of NR decreases with increasing crosslinking agent. The increase in crosslinking agents of PS caused induced molecules of PS to become crosslinked. For this reason, the NR particle size decreased.

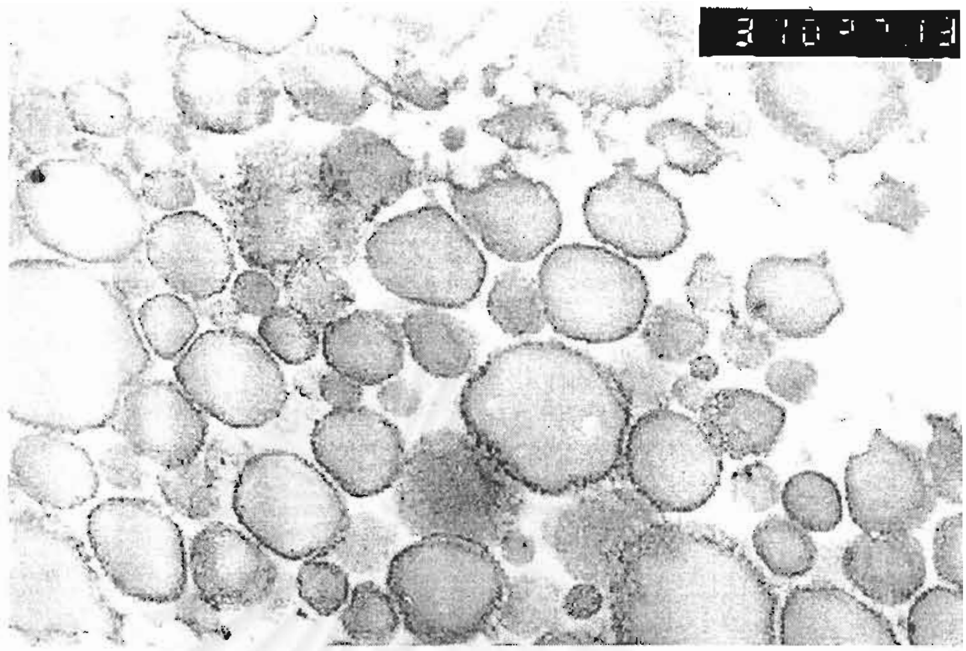


Figure 4.7 (A$_1$) Semi-IPNs of NR:PS = 50:50.

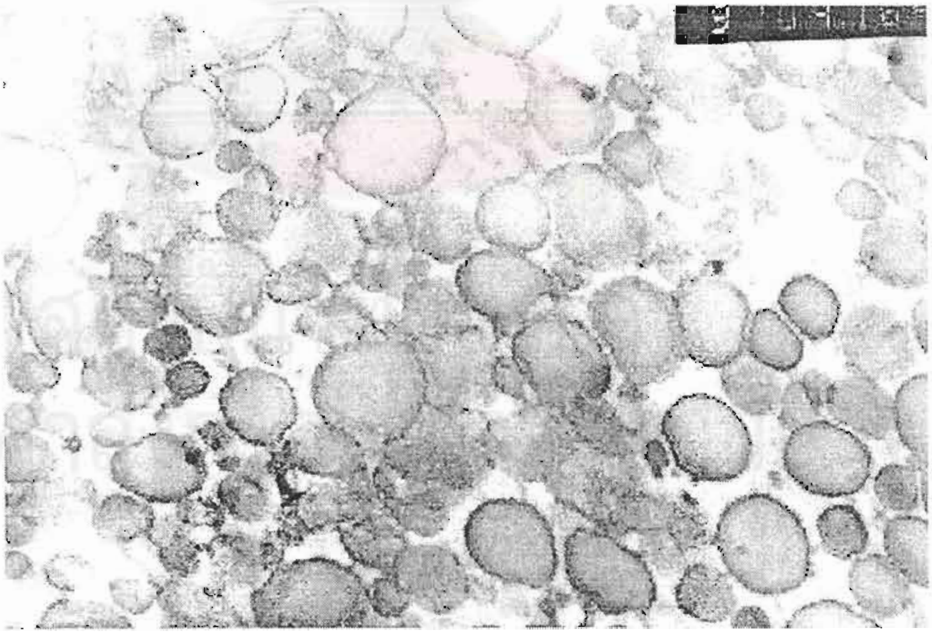


Figure 4.7 (A$_2$) IPNs of NR:PS = 50:50.

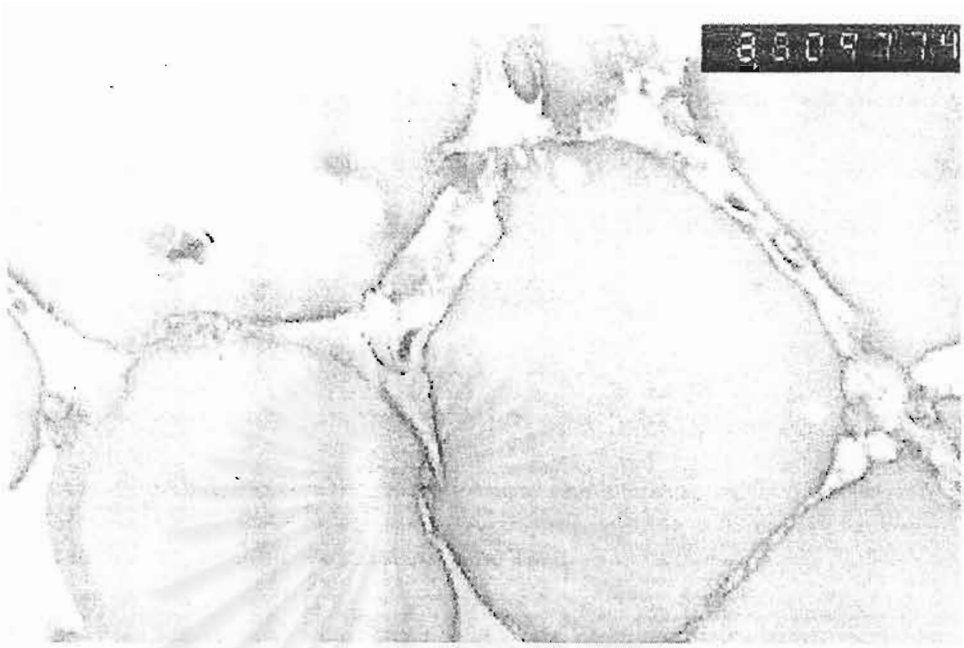


Figure 4.7 (C_1) Semi-IPNs of NR:PS = 70:30.

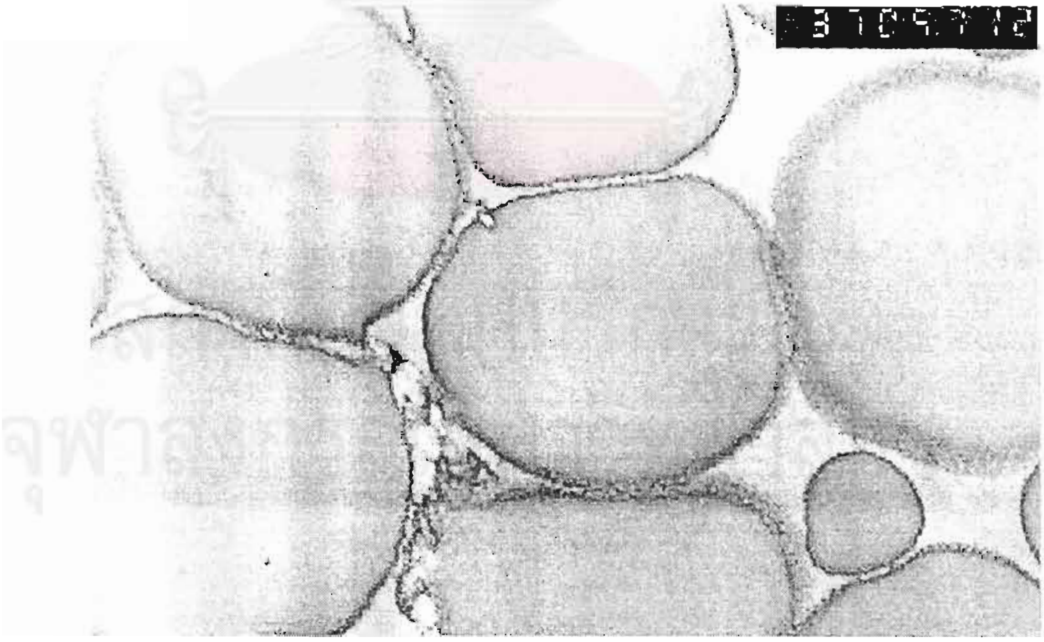


Figure 4.7 (C_2) IPNs of NR:PS = 70:30.

4.2.2 Scanning Electron Microscopy (SEM)

The scanning electron microscope was employed to investigate the particle surface and phase distribution of specimen. In Figures 4.8, 4.9, 4.10, 4.11, and 4.12 the phase distribution of IPNs of NR:PS = 60:40, 70:30 ,80:20 and semi-IPNs of NR:PS = 60:40 ,and 70:30 are shown respectively.

At 5,000 x magnification, the SEM electron micrographs of IPNs, semi-IPNs products show the distribution of PS and NR. The smooth surface as well as the PS particles distribution of the specimens can be seen.

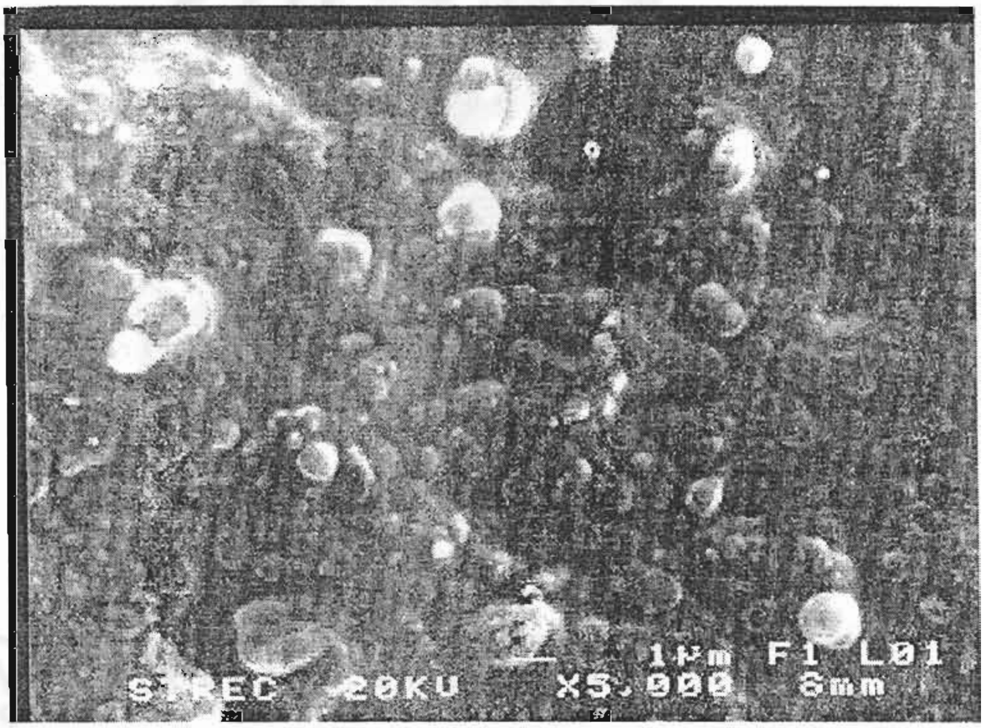


Figure 4.8 SEM photomicrograph of NR/PS IPNs 60:40.

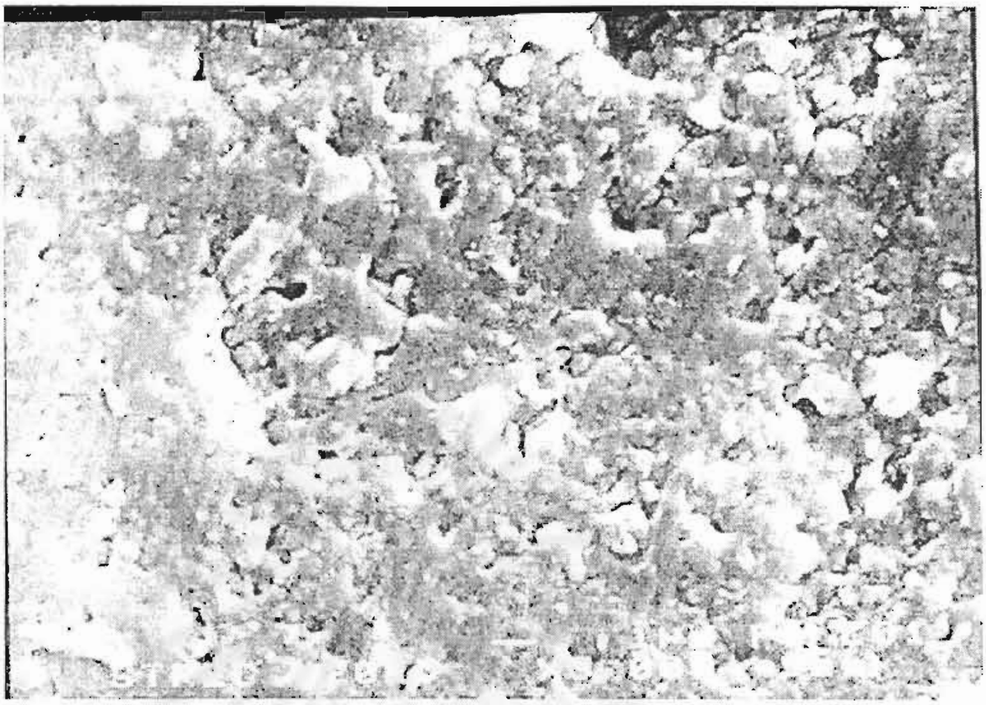


Figure 4.9 SEM photomicrograph of NR/PS IPNs 70:30.

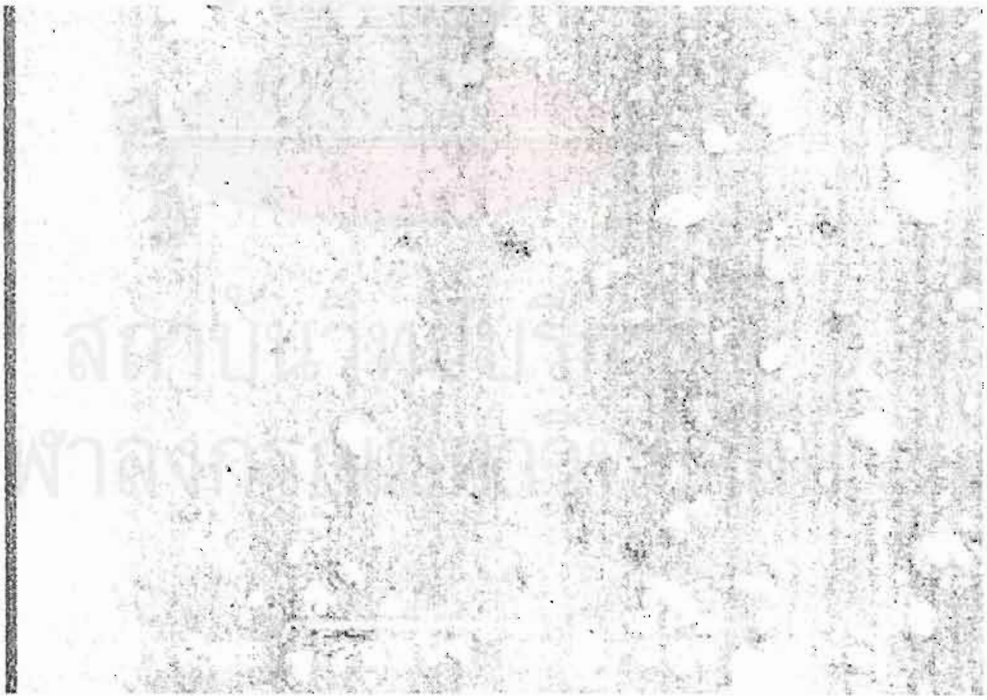


Figure 4.10 SEM photomicrograph of NR/PS IPNs 80:20.

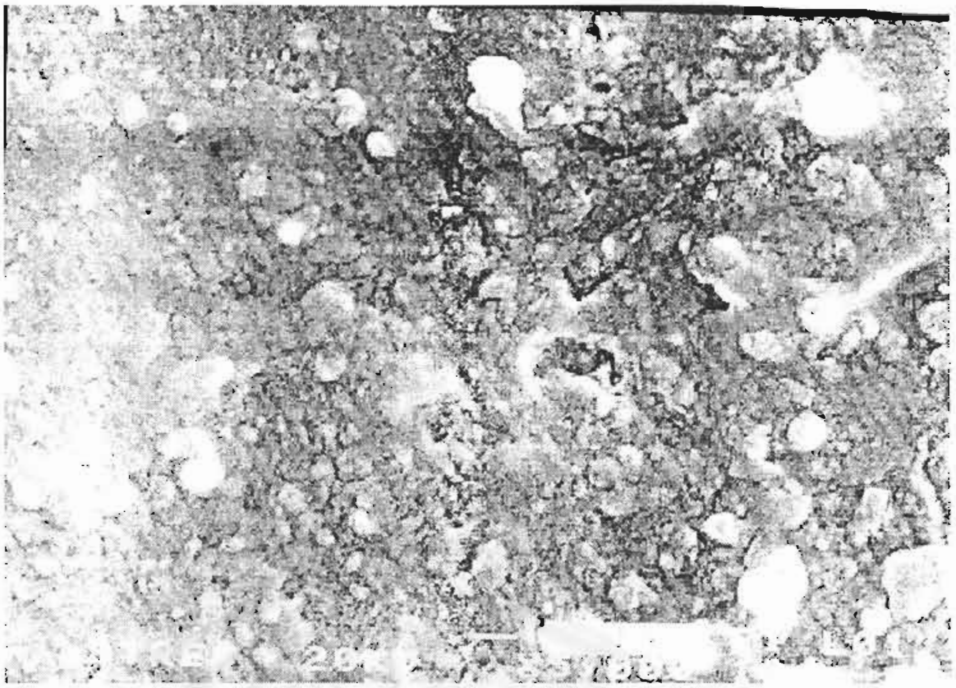


Figure 4.11 SEM photomicrograph of NR/PS semi-IPNs 60:40.

Figure 4.12 SEM photomicrograph of NR/PS semi-IPNs 70:30

4.3 Thermal Properties of IPNs Product

In the investigations, thermal properties were analyzed by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). DSC was used to obtain the glass transition temperature (Tg) °C and used for the evaluation of the miscibility between components of polymer blends. TGA analyzes thermal stability of IPNs products.

4.3.1 Differential Scanning Calorimetry

In the absence of miscibility, a composite of two polymers exhibits two distinct glass transitions of the pure components. The glass transitions (Tg) of the non -crosslinked NR latex was –63°C. Two comprehensive studies concerning the glass transition temperature of NR reported –71°C [32] and –67°C [33] as the true of Tg. These differences are due to different sample preparation, pretreatment, and the correction methods used. However, the main objective was to measure the glass transition temperature of the secondary polymers within the NR particles. The composition and the glass transition temperatures of composite NR/PS are shown in Table 4.5. DSC thermograms of these composite products are shown in Appendix B

Table 4.5 Glass transition temperature (Tg) of composite NR/PS

Component NR/PS	Tg (°C) of PS
IPNs 50:50	98.242
IPNs 60:40	98.861
IPNs 70:30	98.458
Semi-IPNs 60:40	97.966

From DSC thermogram, increasing the amount of the secondary polymers in the latex particles improved the resolution of the DSC measurements. The determined value of glass transition temperatures of·PS (98°C) closely coincide with pure PS. The literature reported 90°C for the Tg of PS. The measured high Tg for the PS phase can be explained by a relatively high molecular weight of the PS chains. The limiting glass transition temperature for PS is 100°C at very high molecular weights.

4.3.2 Thermogravimetric Analysis

Thermogravimetric analysis measurement changes in mass and helps determine the thermal stability and the decomposition curves. These composite products are used to increase their impact resistance. They must be stable at processing temperatures of 200 or 270°C for about 3-5 min depending on the toughened polymer matrix. Assuming the worst possible case, dried NR particles were exposed to a flow of ordinary air and heated at a constant rate 20°C/min until 800°C to analyze their degradation behavior at elevated temperatures. All of the decomposition curves are shown in Appendix C.

Figure 4.13 shows the comparison of the degradation behavior by derivative weight % of pure NR and IPNs of NR/PS = 60:40. Peak of IPNs 60:40 presents 2 peaks that mean two phase polymers. It can be seen that IPNs 60:40 is almost equal in thermal degradation to pure NR. The temperature for the maximum rate of decomposition (T_{max}) could be shifted from 399.8°C for pure NR to 402.6°C in IPNs 60:40. Of course, T_{max} depends on the heating rate, e.g., a slower heating rate of 10° C/min decreases T_{max} to 365°C for pure NR, a faster heating rate of 30°C/min increases T_{max} to 412°C.

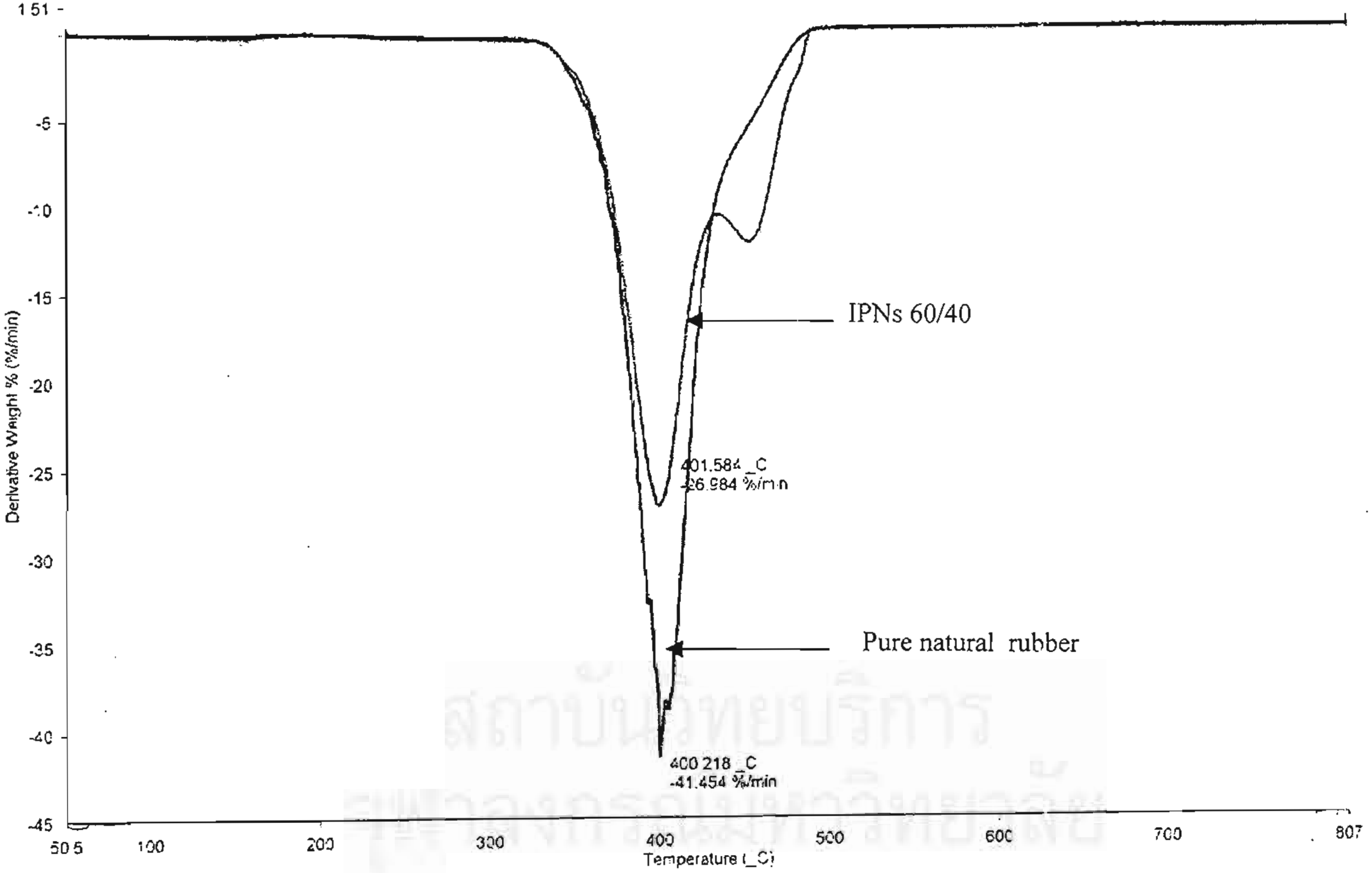


Figure 4.13 Comparison of the degradation of behavior of pure NR and NR/PS IPNs 60:40.

4.4 Mechanical Properties of IPNs product

Mechanical properties of composite NR/PS were investigated to evaluate the values of tensile properties, hardness and tear strength as shown in Table 4.6. The details of all data and calculations are shown in Appendix D.

Table 4.6 Effect of PS content on the mechanical properties of IPNs and semi-IPNs products.

Properties	50/50		60/40		70/30		80/20	
	IPNs	Semi-	IPNs	Semi-	IPNs	Semi-	IPNs	Semi-
Tensile strength (MPa)	13.13	12.02	12.85	11.40	10.98	10.01	9.23	8.87
Elongation at Break (%)	409.0	468.9	628.9	660.8	687.5	759.0	764.9	799.0
Modulus (MPa)	6.775	6.355	5.820	5.670	4.988	4.755	3.796	3.309
Hardness (Shore D)	80.94	80.52	77.70	75.50	70.80	69.30	52.60	52.30
Tear strength (N/mm)	47.45	45.45	45.21	43.12	42.50	40.78	38.07	36.60

4.4.1 Tensile Properties

The effect of PS content on tensile properties of IPNs product is shown in Figures 4.14a, 4.14b, and 4.14c. In Figures 4.14a and 4.14c, the tensile strength (TS) and modulus increase with increasing PS content. Properties, like TS and modulus for both semi- and IPNs, exhibited increasing trends because PS is characterized by quite high mechanical strength and plastomer can reinforce rubber phase.

In Figure 4.14b, the elongation at break decreases with increasing PS contents. It can be seen that the PS is a naturally rigid, glassy thermoplastic (low percent strain), therefore the rubber component in NR/PS composite improves the elongation property of the product.

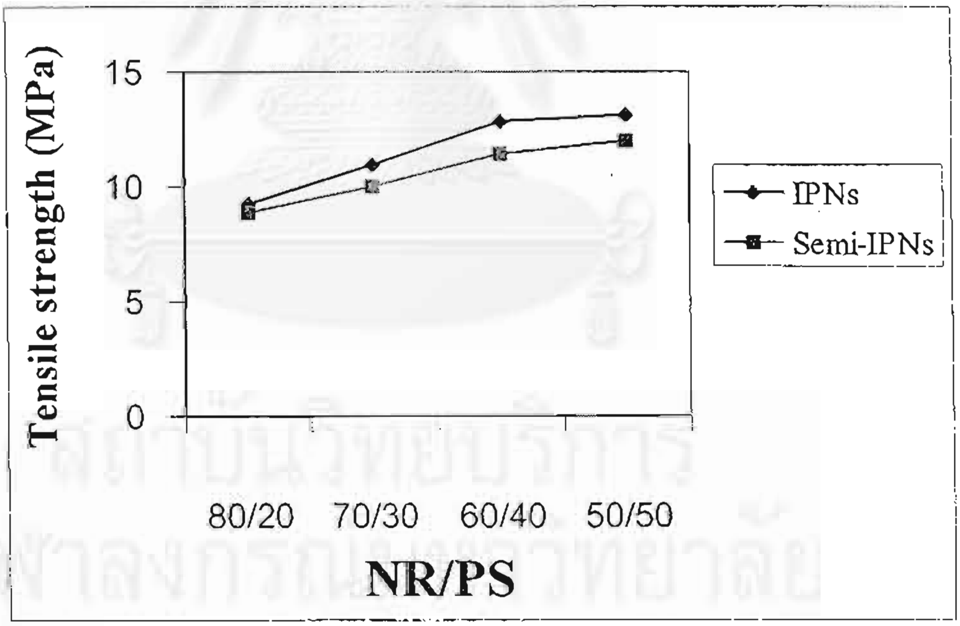


Figure 4.14a The tensile strength of semi- and IPNs of NR/PS composite.

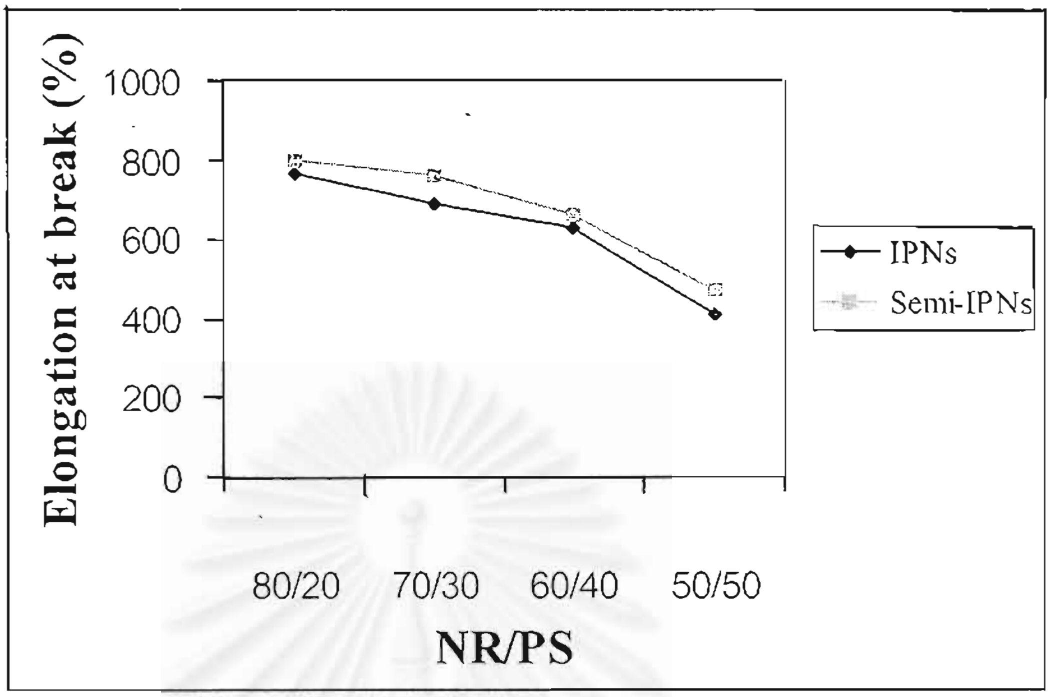


Figure 4.14b The elongation at break of semi- and IPNs of NR/PS composite.

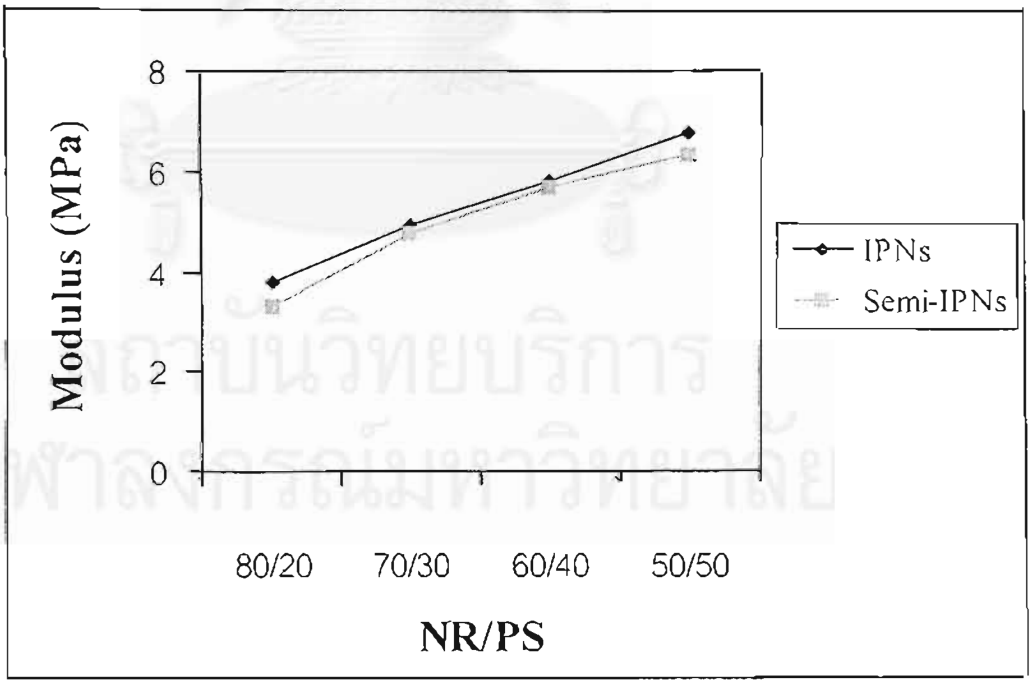


Figure 4.14c The modulus of semi- and IPNs of NR/PS composite.

4.4.2 Hardness

The hardness of NR/PS composite products are shown in Figure 4.15. The hardness of composites increased with increasing PS content. This can be explained by the PS component in NR/PS composite which had more plastic property. Consequently, the blends were more rigid.

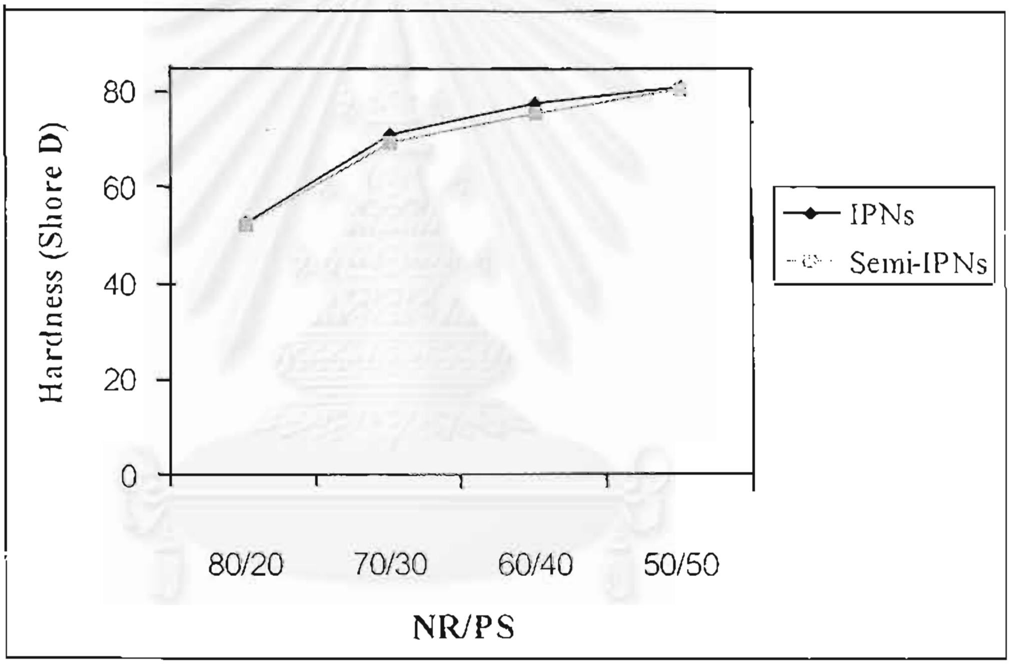


Figure 4.15 The hardness of semi- and IPNs of NR/PS composite.

4.4.3 Tear strength

The effect of PS content on tear strength of NR/PS composite is presented in Figure 4.16. Analysis of tear strength revealed that incorporation of PS resulted in improvement. As the PS content increased, the tear strength also increased, indicating that the PS is capable of imparting substantial reinforcement in property.

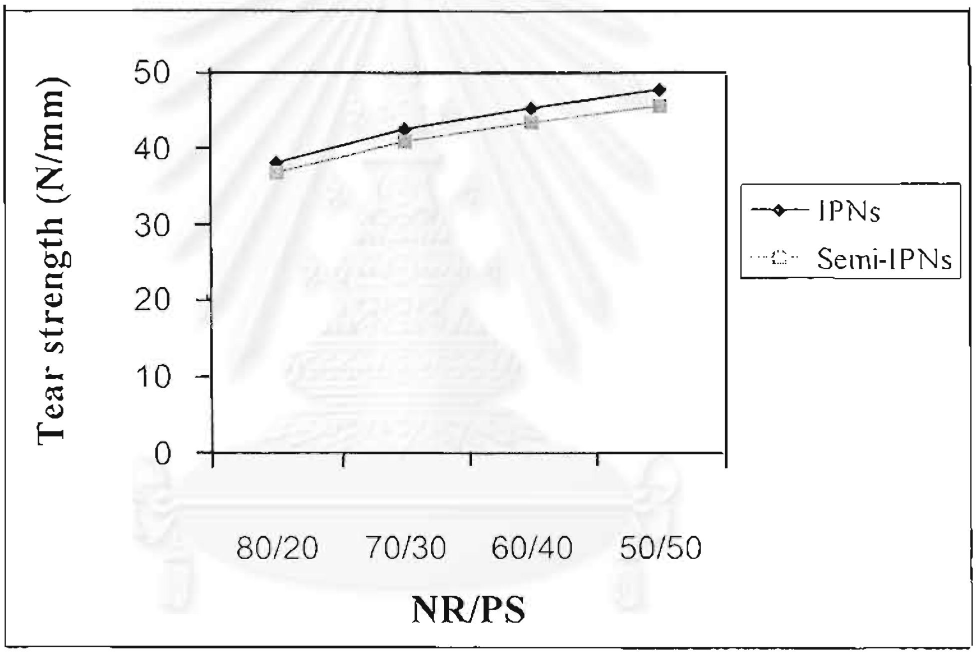


Figure 4.16 The tear strength of semi- and IPNs of NR/PS composite.

4.4.4 Comparison of the Mechanical Property with EPDM

NR/PS composite products of this research are used for impact modifier for PP. A popular impact modifier used with PP is EPDM. So it is necessary to compare NR/PS composite products, which improved the NR properties by addition with PS, to EPDM. From the comparison of all products, including semi- and IPNs NR/PS = 50:50, 60:40, 70:30, and 80:20, it was observed that the IPNs products have better mechanical properties than semi-IPNs. This is due to crosslinking agent, which induced better miscibility and finer morphology. Comparisons of IPNs products with EPDM found that IPNs products were chosen to blend with PP are NR/PS ratios = 50:50, 60:40, and 70:30. In Table 4.7 the mechanical properties comparisons of selected-IPNs products and EPDM are presented.

Table 4.7 The mechanical properties comparisons of selected-IPNs products and EPDM.

Mechanical Properties	EPDM	IPNs 50:50	IPNs 60:40	IPNs 70:30
Tensile strength	10.8	13.13	12.85	10.98
Elongation	280	409	659	668.7
Modulus 200%	6.6-9.5	6.77	5.82	4.92

4.5 Blending of IPNs products and PP

4.5.1 Properties of PP and IPNs products

An isotactic homopolymer of PP (2511TC) was used. It was supplied by Thai Petrochemical Industry Public Co., Ltd. (TPI). Typical data of PP (2511TC) are shown in Table 4.8.

Table 4.8 Typical data of PP grade 2511 TC

Typical Data	Unit	Value	Test Method
Property			
MFI 2.16 kg/230°C	g/10 min	45	ASTM D1238
Tensile Strength at Yield	N/mm^2	21	ASTM D638
Charpy Impact Strength At-20°C	mJ/mm^2	5.5	DIN 53453
Shear Modulus	N/mm^2	430	DIN 53457
Ball Indentation Hardness	N/mm^2	53	DIN 53456
Heat Distortion Temp.			
at 0.45 N/mm^2	°C	90	ASTM D648

Source : Thai Petrochemical Industry Public Co., Ltd.

IPNs products were prepared by emulsion polymerization for 2 hours at 60°C. The basic formulation was as follows:

- Initiator/activator(1/1) concentration : 1.5 phr
- Crosslinking agent concentration : 0.25% wt of monomer
- Emulsifier concentration : 1.5 % wt of monomer
- NR/PS content : 50/50, 60/40, 70/30

The properties of NR/PS composite are shown in Table 4.7. The PP and 10, 15, 20, and 25 phr of IPNs products (50/50, 60/40, 70/30) were prepared. The mechanical properties were investigated. The properties of PP and EPDM blends were compared.

4.5.2 Mechanical Properties of PP Blended with IPNs products

The effects of the composition of PP/IPNs product blends and PP/EPDM blends on the mechanical properties were investigated. The values of tensile properties, hardness, and impact strength are shown in Tables 4.9, 4.10, and 4.11, respectively.

Table 4.9 Effect of EPDM and IPNs products content on the tensile strength (MPa) of PP/rubber blends.

PP/Rubber	EPDM	70/30	60/40	50/50
100/0	15.00	15.00	15.00	15.00
90/10	14.00	14.16	18.03	18.85
85/15	12.61	12.98	13.36	15.74
80/20	11.12	12.54	11.72	13.48
75/25	10.25	10.33	10.68	12.25

Table 4.10 Effect of EPDM and IPNs products content on the hardness (Shore D) of PP/rubber blends.

PP/Rubber	EPDM	70/30	60/40	50/50
100/0	60.8	60.8	60.8	60.8
90/10	54.0	50.8	54.3	60.9
85/15	49.3	50.2	52.6	59.7
80/20	46.0	48.6	50.9	56.3
75/25	45.4	44.9	50.3	55.2

Table 4.11 Effect of EPDM and IPNs products content on the impact strength (kJ/m^2) of PP/rubber blends.

PP/ Rubber	EPDM	70/30	60/40	50/50
100/0	205.8	205.8	205.8	205.8
90/10	630.4	383.4	428.8	395.8
85/15	664.0	409.6	436.4	417.0
80/20	711.2	419.6	444.0	429.8
75/25	715.6	438.6	472.4	450.2

1. Tensile Strength

The effect of impact modifier contents, IPNs products and EPDM on the tensile strength of PP blends are shown in Figure 4.17. In Figure 4.17, the tensile strength decreases slightly with increasing impact modifier content. This can be explained by the high toughness which is obtained by the addition of an amorphous rubber. But, the stiffness and strength of the PP are degraded. The tensile strength increases with increasing PS in IPNs products due to the fact that PS has high tensile strength. Thus the blends products have higher tensile strength.

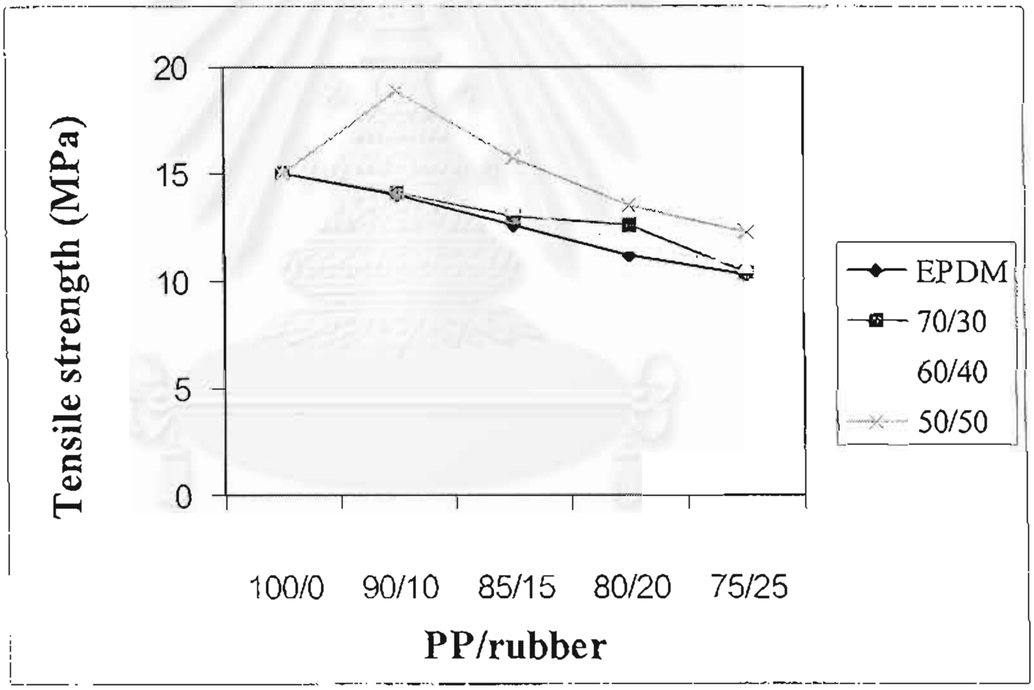


Figure 4.17 The tensile strength of PP/rubber blends.

2. Hardness

The hardness of PP/rubber blends are presented in Figure 4.18. The hardness of blend decreased only slightly with increasing rubber content. This can be explained by the fact that the rubber components in blend products are more elastic. Consequently the blends deformed easily.

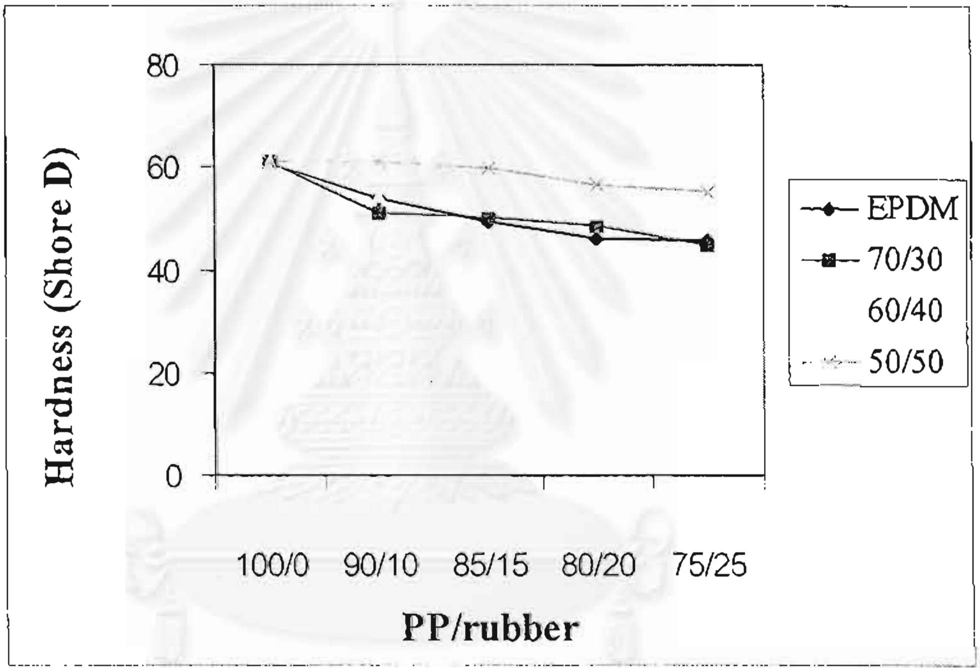


Figure 4.18 The hardness of PP/rubber blends.

3. Impact Strength

Figure 4.19 shows the effect of impact modifier content on the impact strength of PP/rubber blends. The impact strength increases with increasing rubber phase. At 25 phr impact modifier (EPDM, and IPNs 60:40), maximum values of 715.6 and 472.4 kJ/m^2 were reached, respectively. Comparison between IPNs products and EPDM impact modifier, showed that impact strength of PP/EPDM are higher than PP/IPNs product blends.

The impact resistance of glassy plastics is increased by the addition of small quantities of rubber in the form of a polymer blend. The rubber promotes crazing in the material, which absorbs the energy locally. The effect of a large number of impact modifiers content is to dissipate a large amount of energy. This makes crack propagation more difficult, leading to the increased impact strength.

The impact strength, considered from IPNs product, increases with increasing PS content 30-40%, but at PS content 50% impact strength decreases. At low PS content, it can well mix with PP. At high PS content the impact strength decreases because the PS is a brittle plastic. When the PS content is more than 40%, the impact strength decreases. Impact modifier from IPNs products that appropriate for PP blends is IPNs of NR/PS = 60:40. The appropriate impact modifier contents used are in the range of 10-15 phr. For 15 phr of IPNs 60:40 and PP, the mechanical properties are as follows:

• Tensile strength (MPa)	13.36
• Hardness (Shore D)	52.6
• Impact strength (kJ/m^2)	436.4

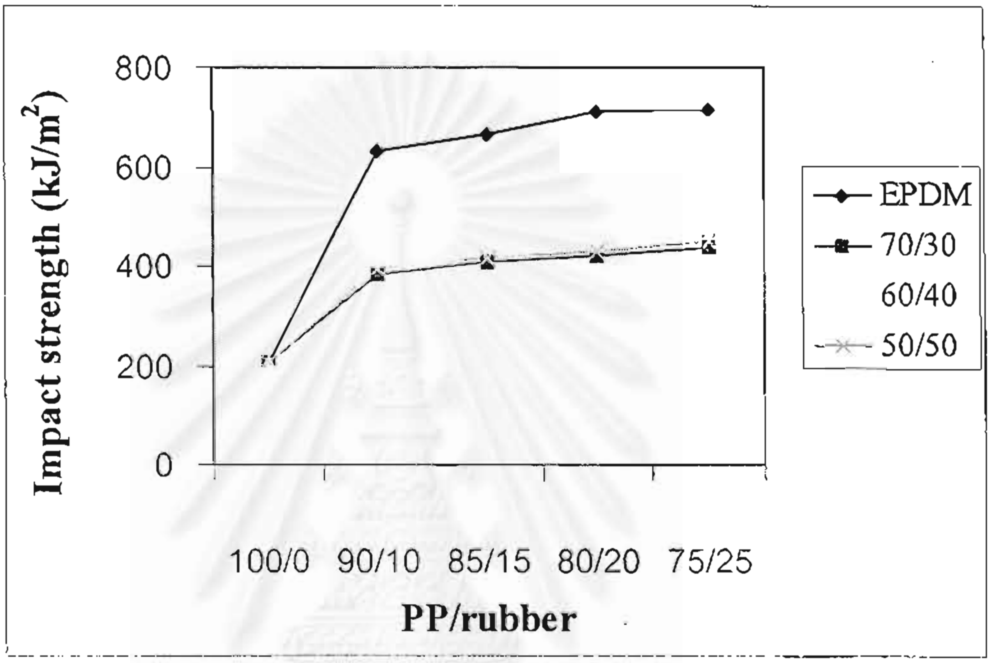


Figure 4.19 The impact strength of PP/rubber blends.

4.5.3 Scanning Electron Microscopy (SEM)

The scanning electron microscopy was used to analyze the distribution of polymer blend on surface of the specimen. Figures 4.20 and 4.21 show the surface of PP/EPDM blend and PP/IPNs 60:40 blend at 15 phr of EPDM and IPNs products.

In Figure 4.20, at 5,000 x magnification, the SEM micrograph of the PP/EPDM blend at EPDM 15 phr shows the distribution of EPDM particle in PP matrix. The EPDM particles distribution of PP/EPDM blend can be seen quite well.

In Figure 4.21, at 5,000 x magnification, the SEM micrograph of the PP/IPNs product blend at IPNs product is 15 phr. This figure shows the distribution of IPNs in the PP matrix. It can be seen that the smooth surface of PP/IPNs product blend seems to be a bulk IPNs product distribution in the PP matrix.

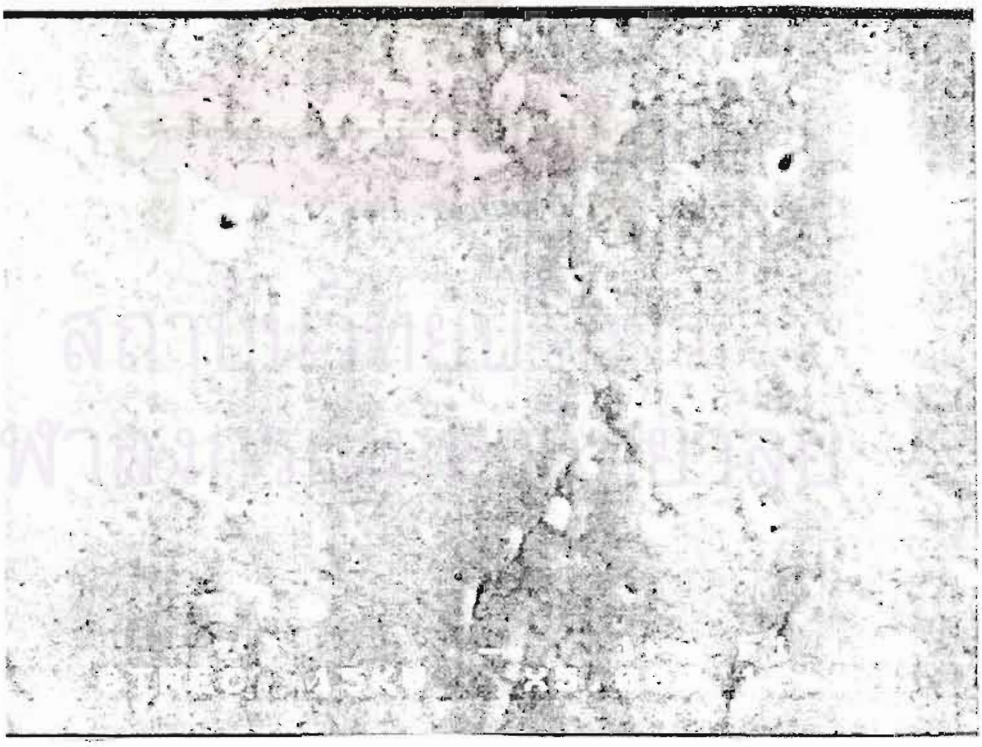


Figure 4.20 SEM photomicrograph of surface of PP/EPDM blend.

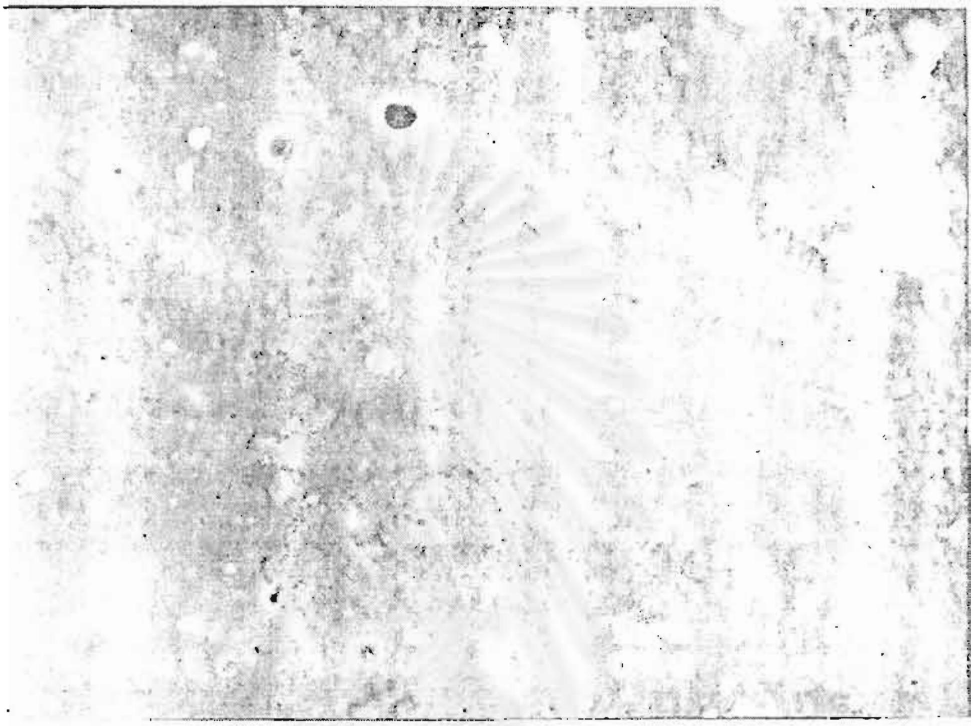


Figure 21 SEM photomicrograph of surface of PP/IPNs product blend.

CHAPTER V

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

5.1.1 The Preparation of IPNs products

The IPNs of natural rubber and polystyrene were prepared by core-shell emulsion polymerization. A prevulcanized natural rubber latex was coated with a shell of polystyrene. The bipolar redox initiating system tert-butyl hydroperoxide / tetraethylene pentamine promoted a core-shell arrangement. The optimum condition of IPNs was found. IPNs products were characterized.

In this work, the IPNs of natural rubber and polystyrene formed the completed core-shell. The appropriate conditions were an initiator concentration 1.5 phr, crosslinking agent concentration 0.25% wt of monomer, emulsifier concentration 1.5%wt of monomer, and reaction temperature of 60°C for 2 hours. The maximum degree of monomer conversion was 80.02%. TEM, in combination with different stain methods, was used to observe the morphology of IPNs products, and indicated that natural rubber acts as a core and polystyrene as a shell. DSC and TGA confirmed a two phase particle morphology.

Full IPNs were characterized by higher tensile strength, modulus and tear strength than the corresponding semi-IPNs, while the latter exhibited higher elongation. Crosslinking of the plastomer component induced better miscibility and finer morphology.

It can be concluded that effective IPNs have a wide rage of mechanical properties. The usage of these products depends on the content of NR and PS. These IPNs products can be used for shoe soles, rubber floor tiles, car floor rubbers, etc.

5.1.2 The Product of PP/IPNs product Blends

The IPNs products could be used as an impact modifier for PP to form PP/IPNs of NR/PS by mechanical blending and compression molding. The good mechanical properties of blend were obtained at 10 and 15 phr of the IPNs products.

5.2 Suggestion

1) The presence of nonrubber, contaminants such as, protein, etc., could effect the polymerization of styrene monomer to polystyrene. These contaminants, which may act as catalyst inhibitors can stop the roles of free radicals. Therefore, the elimination of nonrubber contaminants such as proteins from natural rubber before the polymerization process, should be further studied.

2) The effect of different processing methods.

3) The blend of composite products with other thermoplastic.

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APPENDICES

APPENDIX A

Calculation of Monomers Conversion

The monomer conversion is defined as the mass of styrene formed divided by the initial mass of monomer. The definition of conversion of monomers is

$$\text{Conversion} = \frac{\text{Styrene formed}}{\text{Initial mass of monomers in sample}}$$

Table A Effect of initiator concentration, emulsifier concentration, reaction temperature, and reaction time on the monomer conversion.

Experiment	Analyze No.	%Monomer Conversion	Average
Initiator Concentration			
1. 0.5 phr	1	11.8	12.5
	2	15.3	
	3	10.40	
2. 1.0 phr	1	63.0	62.8
	2	59.8	
	3	65.6	
3. 1.5 phr	1	78.8	79.8
	2	79.3	
	3	81.3	
4. 2.0 phr	1	76.4	80.9
	2	81.0	
	3	85.4	
Emulsifier concentration			
1. 0.5 %wt	1	53.7	58.6
	2	58.2	
	3	63.9	
2. 1.0 %wt	1	65.2	65.87
	2	67.8	
	3	64.6	
3. 1.5 %wt	1	69.8	76.3
	2	78.8	
	3	80.3	

Table A (Continued)

Experiment	Analyze No.	%Monomer Conversion	Average
4. 2.0%wt	1	80.9	80.8
	2	79.2	
	3	82.3	
Reaction temperature(°C)			
1. 50	1	69.8	70.3
	2	65.6	
	3	75.5	
2. 60	1	70.8	77.2
	2	79.1	
	3	81.7	
3. 70	1	80.78	78.9
	2	79.55	
	3	76.57	
4. 80	1	79.2	78.9
	2	78.95	
	3	77.65	
Reaction time (hr)			
1. 1	1	56.9	58.3
	2	59.3	
	3	58.7	
2. 2	1	81.5	80.2
	2	79.2	
	3	79.9	

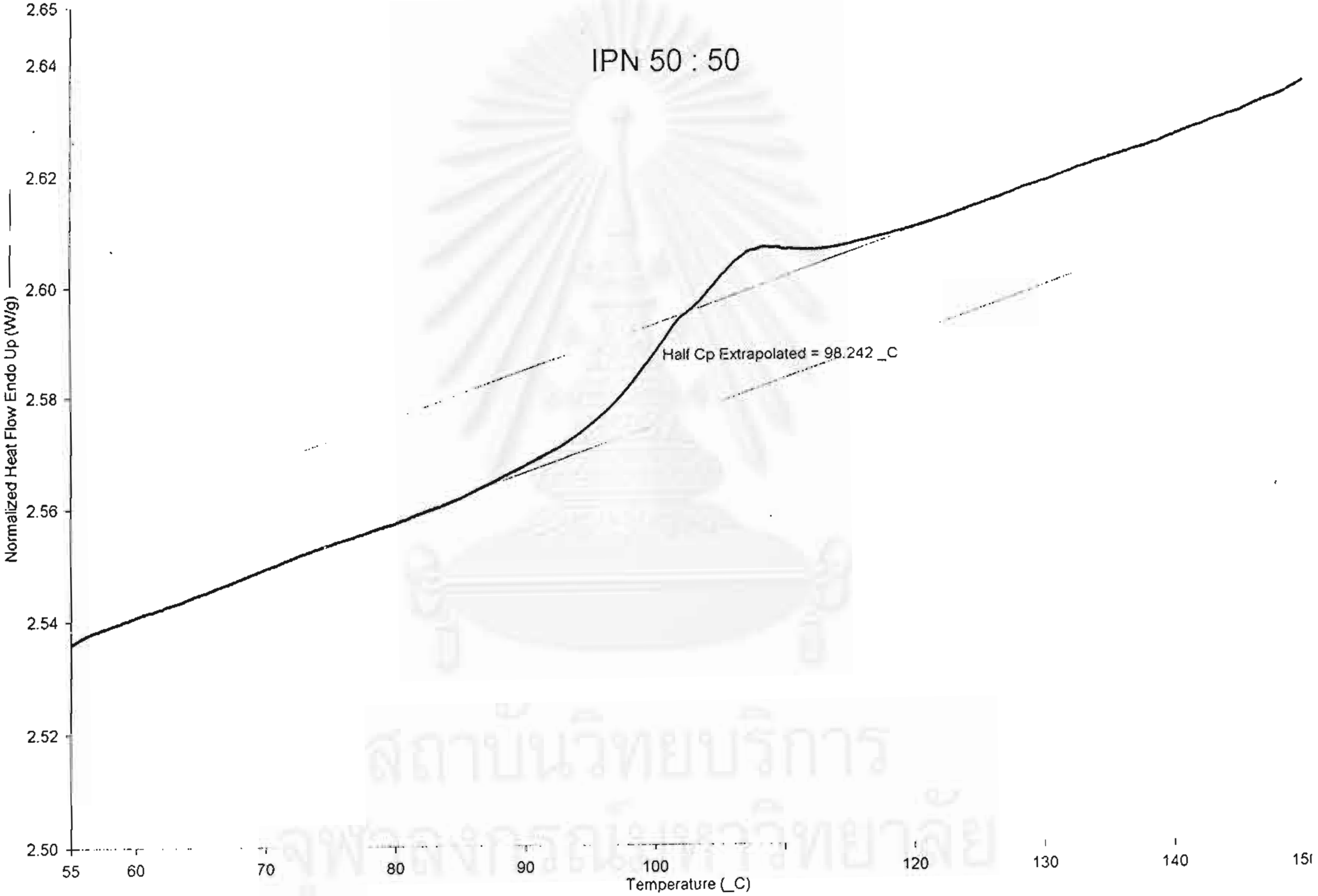
Table A (continued)

Experiment	Analyze No.	%Monomer Conversion	Average
3. 6	1	79.8	80.5
	2	80.3	
	3	81.4	
4. 8	1	81.5	81.3
	2	80.3	
	3	82.1	

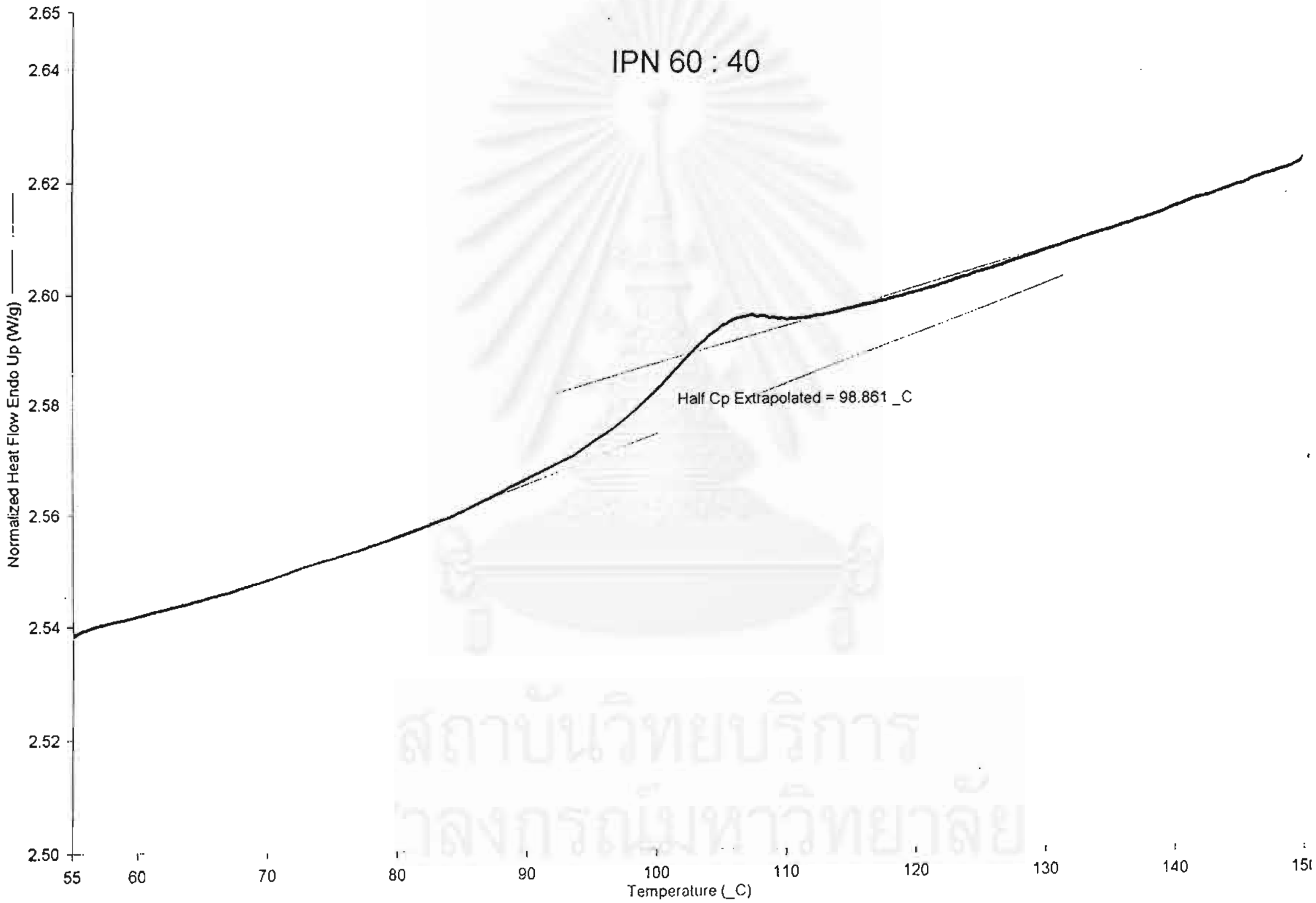
APPENDIX B

In this research the DSC method was chosen for determination of glass transition temperature. The details are as follows:

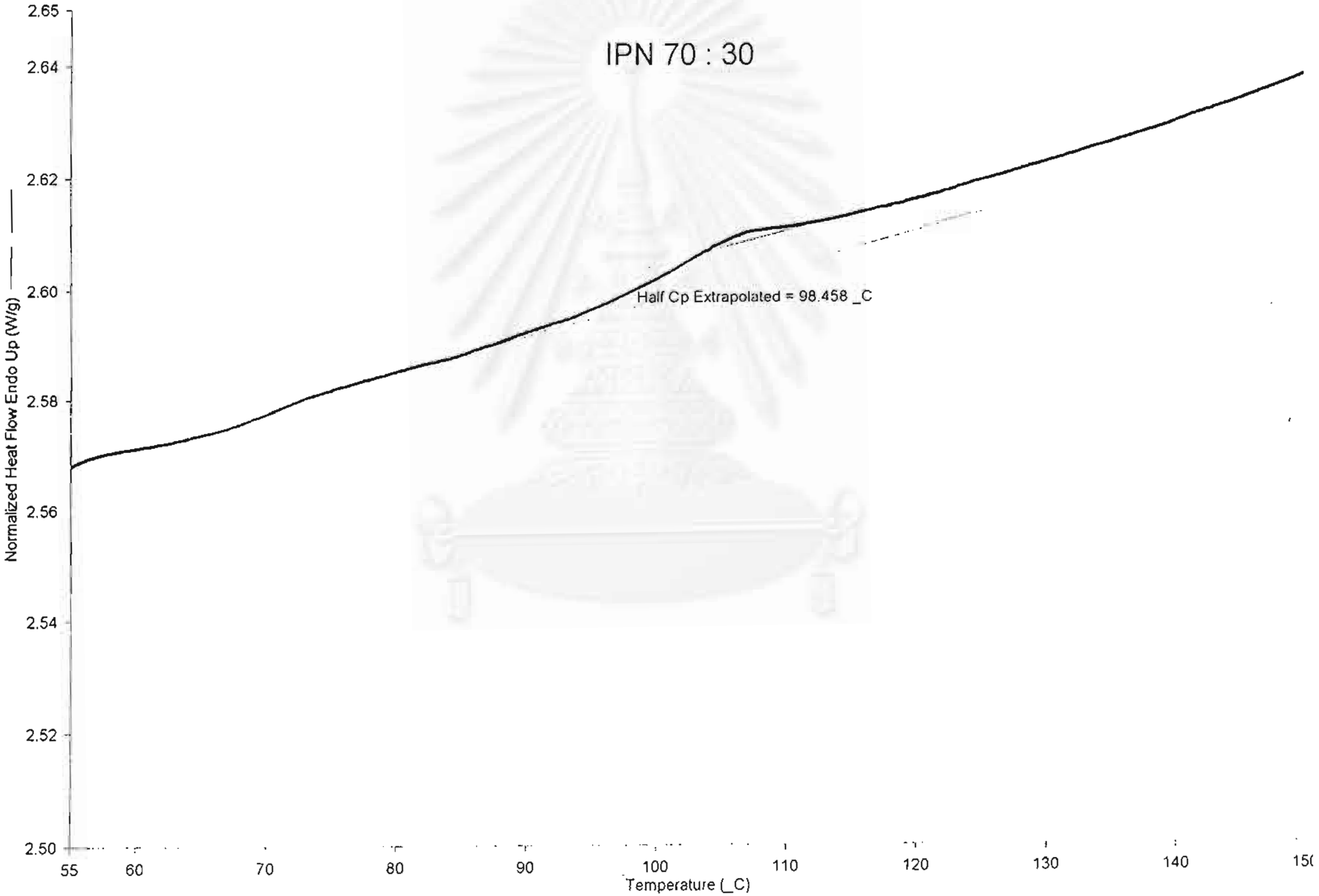
Sample weight: 10-20 mg
Container: aluminum pan
Temperature: 50 – 150°C



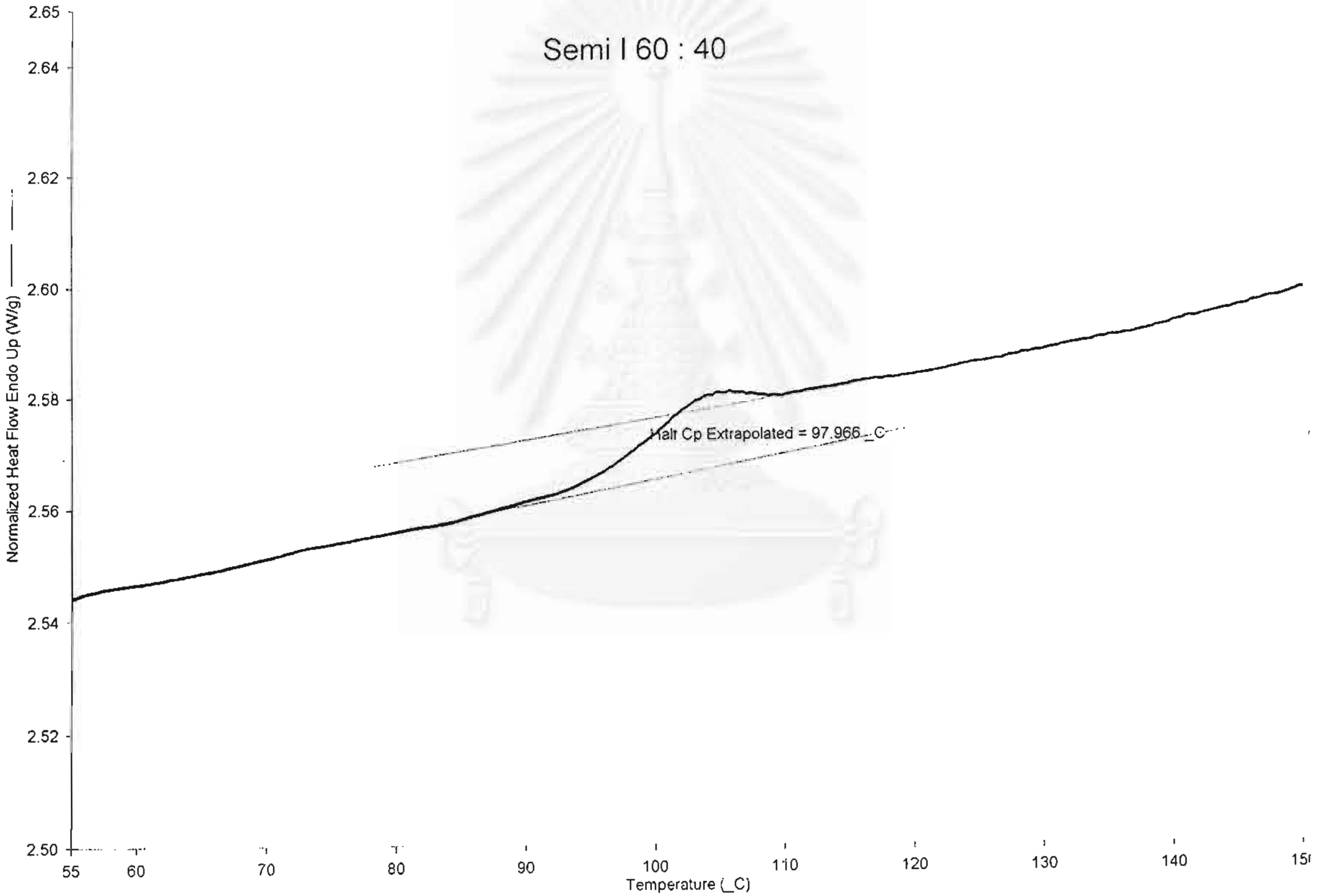
FigureB1 DSC thermograph of NR/PS IPNs 50/50



FigureB2 DSC thermograph of NR/PS IPNs 60/40



FigureB3 DSC thermograph of NR/PS iPNs 70/30



FigureB4 DSC thermograph of NR/PS semi-IPNs 60/40

APPENDIX C

This experiment was analyzed thermal degradation properties from thermogravimetric Analysis (TGA). The test conditions are as follows:

Sample Weight: 10 mg
Container: Platinum pan
Temperature: 50-800°C
Heating-Cooling rate: 20°C/min
Purged-gas: original air 30/15

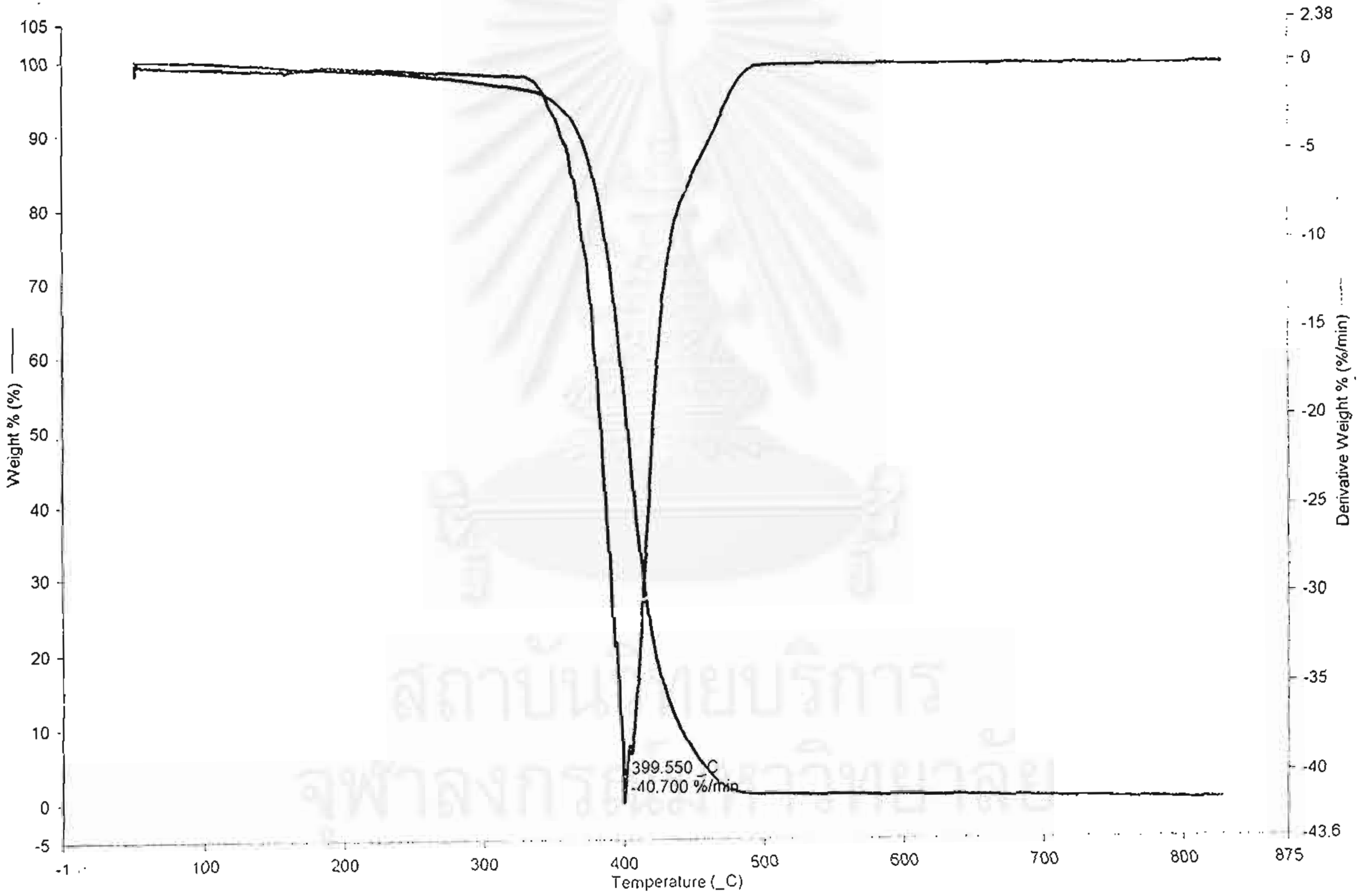


Figure C1 TGA decomposition curve of pure NR

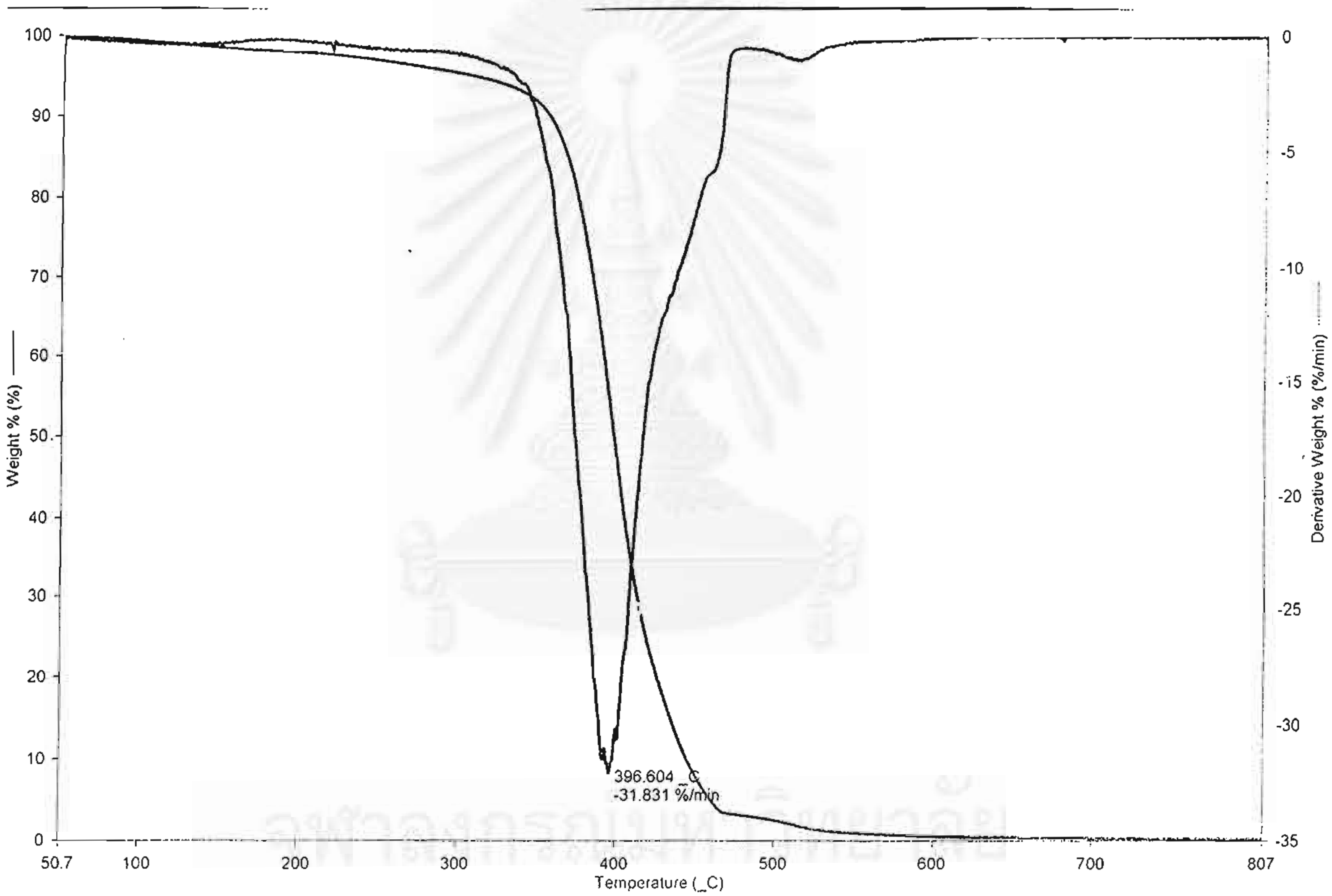


Figure C2 TGA decomposition curve of IPNs 80/20

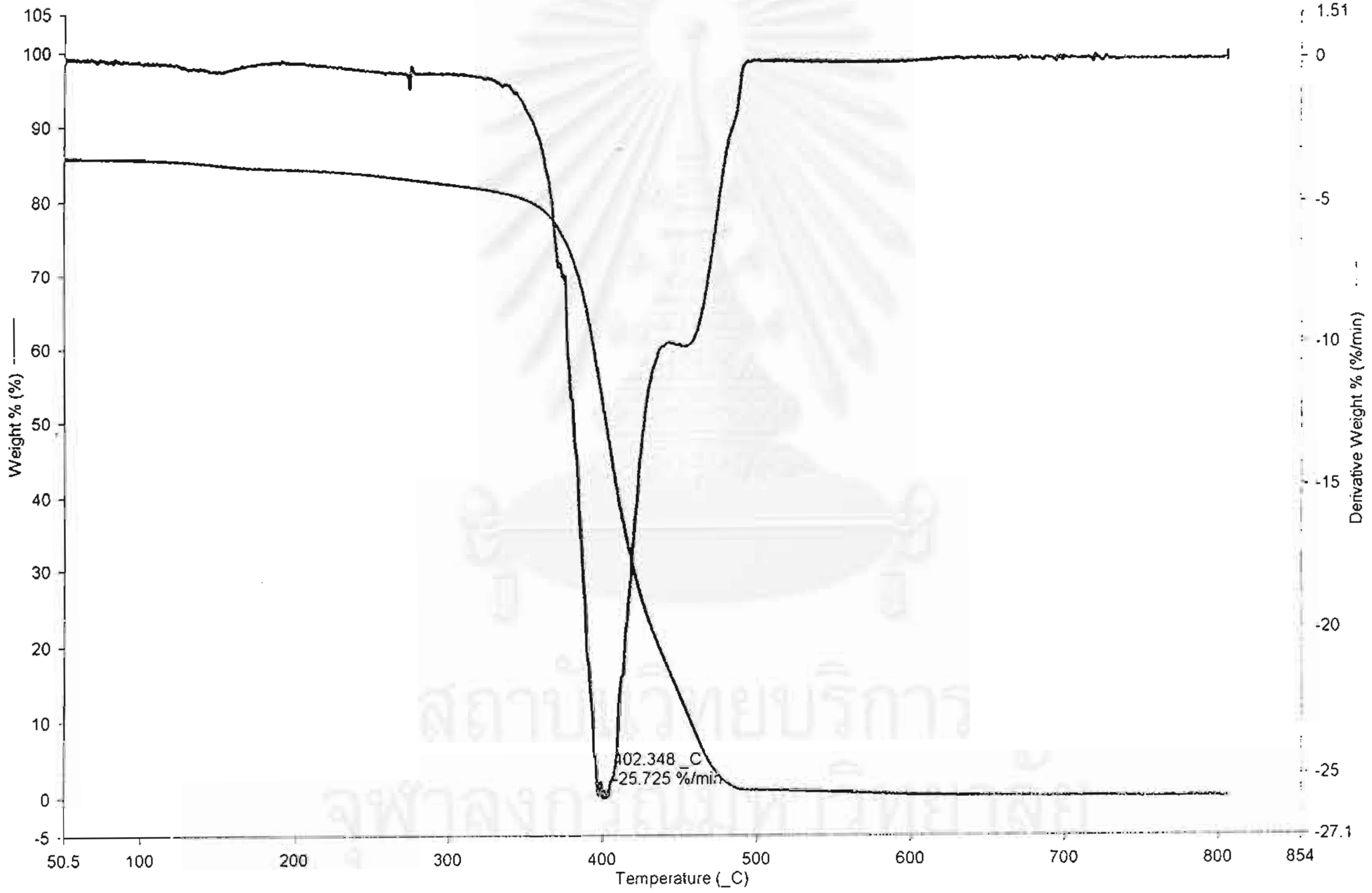


Figure C3 TGA decomposition curve of IPNs 70/30

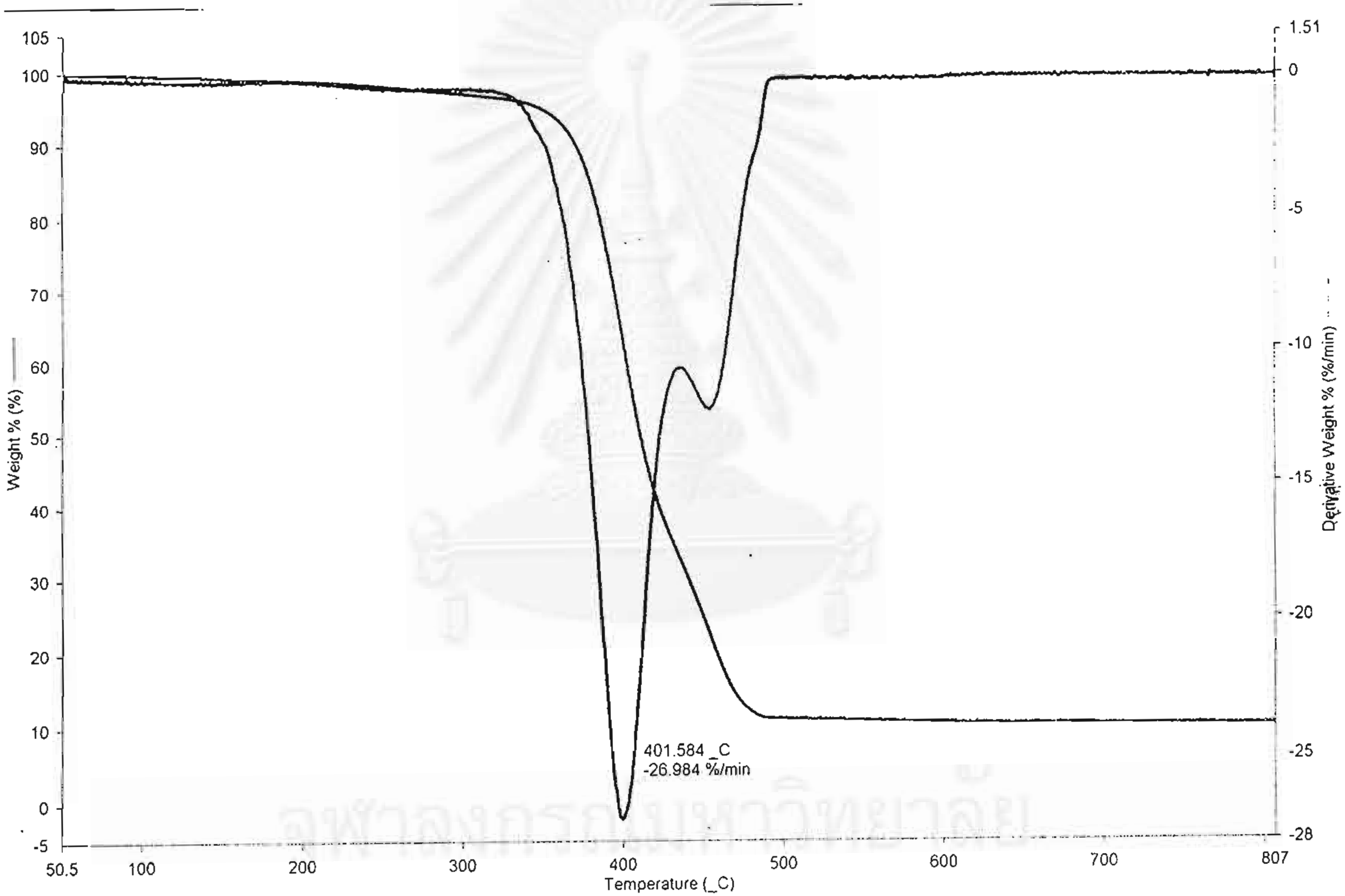


Figure C4 TGA decomposition curve of IPNs 60/40

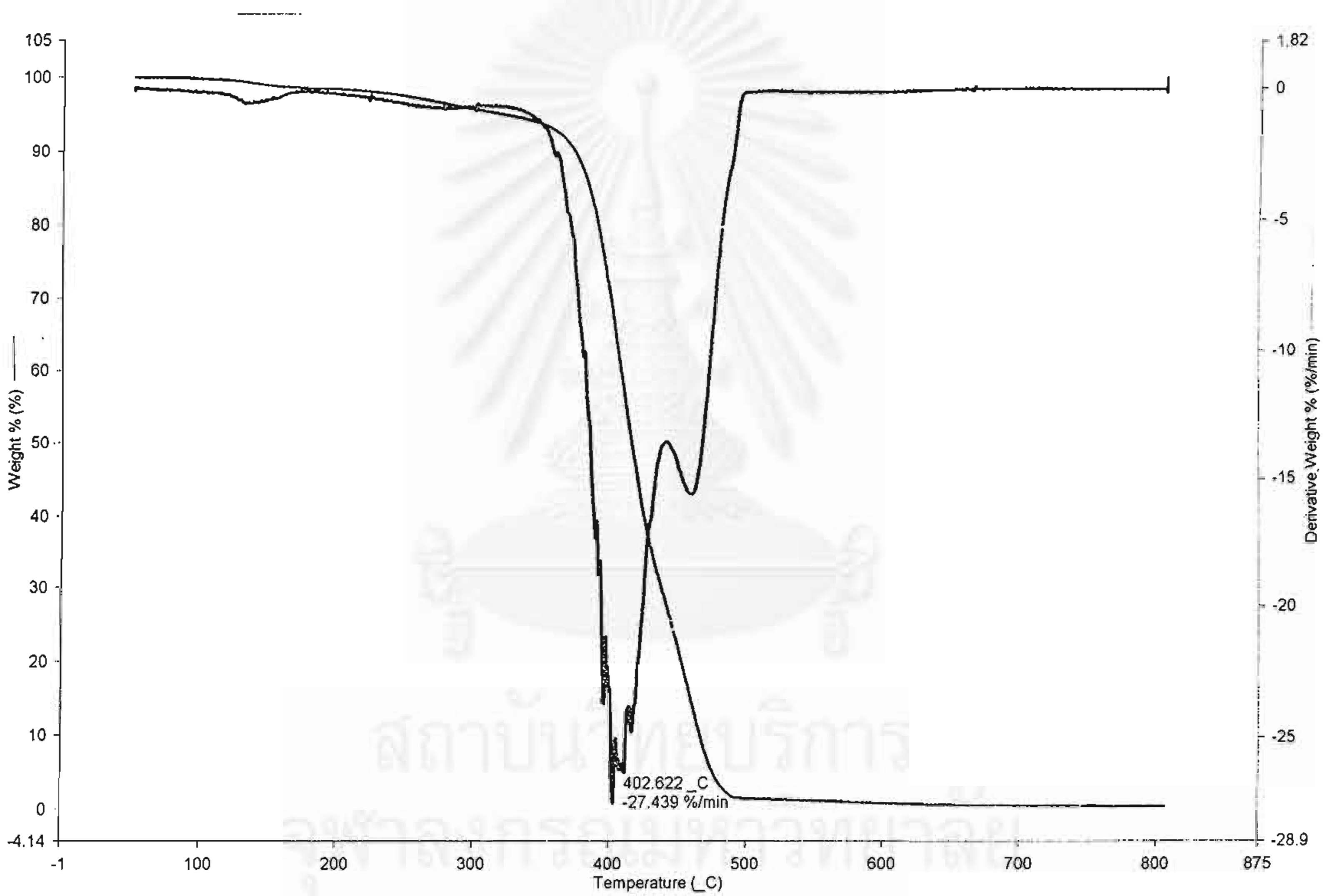


Figure C5 TGA decomposition curve of semi-IPNs 60:40

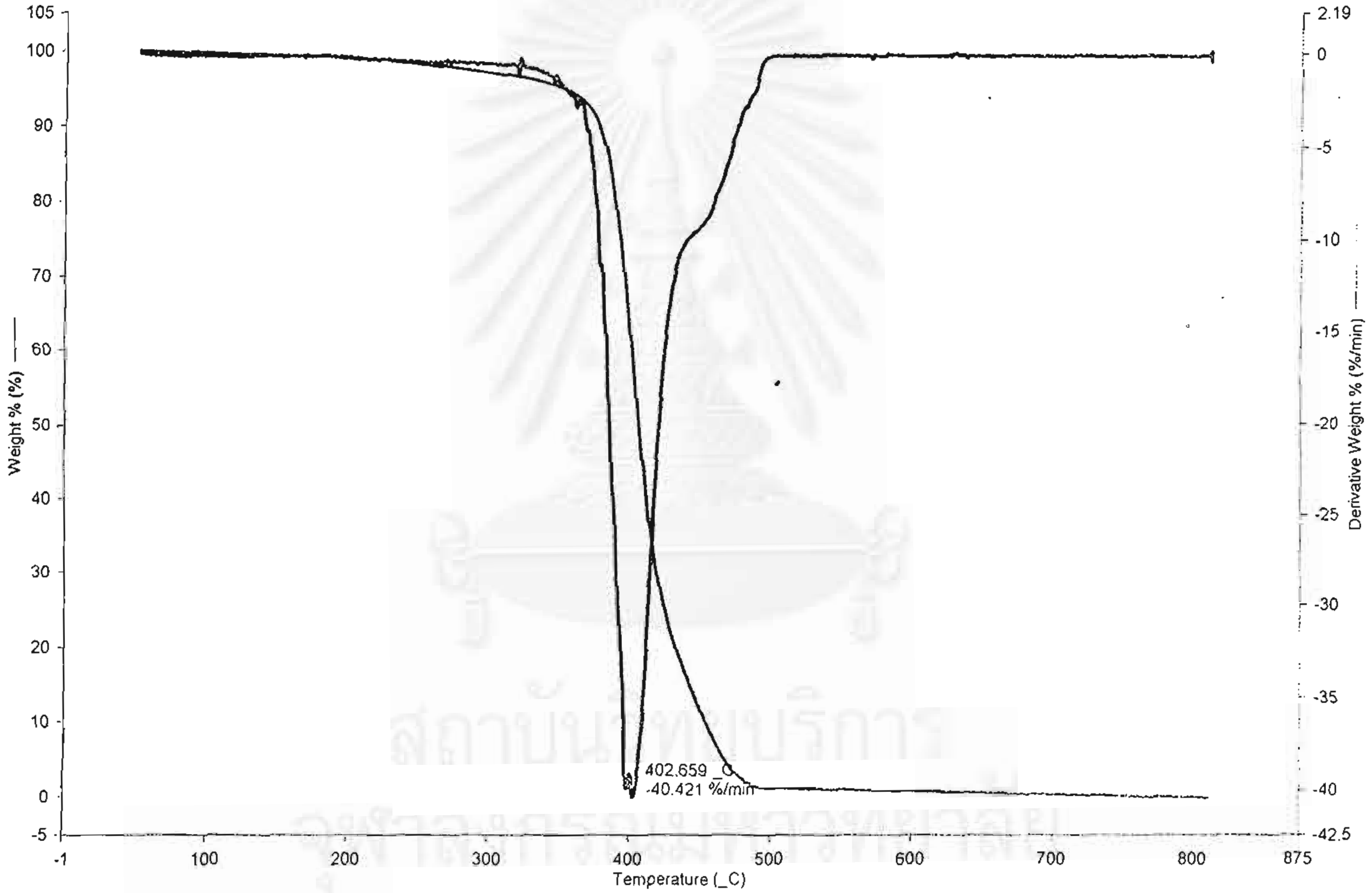


Figure C6 TGA decomposition curve of semi-IPNs 70/30

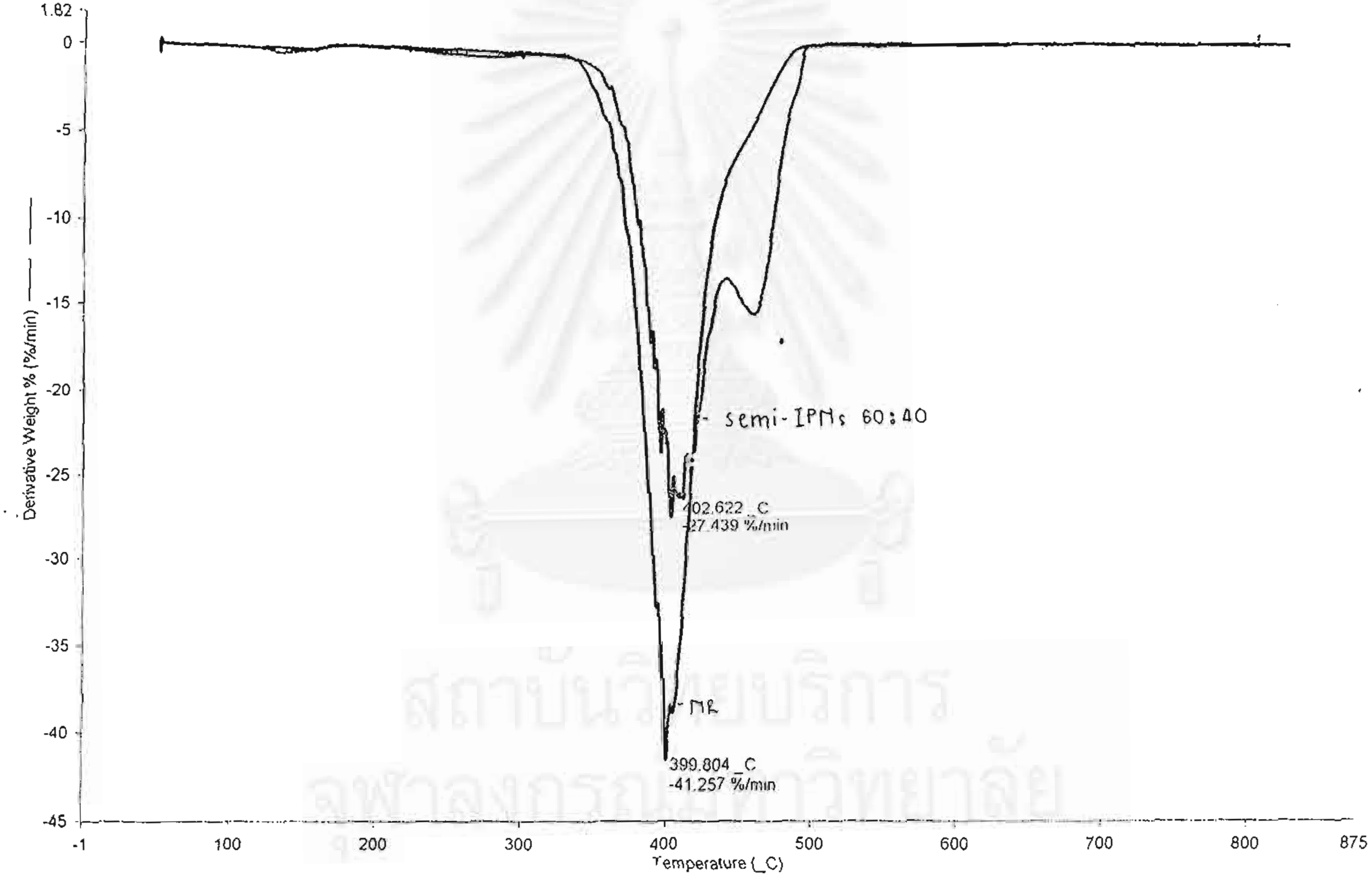


Figure C7 TGA decomposition curve of NR/PS semi-IPNs 60/40 compare with pure NR

APPENDIX D

Statistic of Mechanical Properties Data

The sampling distributions of mechanical properties data were calculated by standard deviation (SD).

$$SD = \frac{\Sigma (x_i - x_a)^2}{n-1}$$

Where n is the number of sample.

x_i is the sample.

x_a is the sample mean.

Table D1.1 Tensile strength of IPNs products

NR/PS	50/50		60/40		70/30		80/20	
	IPNs	semi-	IPNs	semi-	IPNs	semi-	IPNs	semi-
Tensile strength (MPa)	13.23	12.19	12.78	11.33	11.26	9.89	9.18	8.85
	13.05	11.52	12.95	11.26	10.89	9.96	9.02	8.76
	12.98	12.07	13.03	11.58	10.56	10.09	9.58	8.98
	13.33	12.03	12.53	11.49	11.07	10.12	9.42	9.03
	13.06	11.89	12.96	11.34	11.12	9.99	8.95	8.73
Mean	13.13	12.02	12.85	11.40	10.98	10.01	9.23	8.87
SD	0.14	0.26	0.20	0.13	0.27	0.09	0.27	0.13

Table D1.2 Elongation at break of IPNs products

NR/PS	50/50		60/40		70/30		80/20	
	IPNs	semi-	IPNs	semi-	IPNs	semi-	IPNs	semi-
Elongation at	410.0	473.8	632.8	658.0	688.7	757.3	762.5	801.7
Break (%)	415.3	463.7	638.7	658.0	686.0	759.9	463.0	798.7
	407.8	467.2	627.3	659.8	698.0	763.8	766.8	792.6
	406.3	465.4	625.2	663.7	684.4	761.6	765.3	799.0
	405.6	474.0	620.5	654.5	680.4	752.4	766.9	803.0
Mean	409.0	468.9	628.9	660.8	687.5	759.0	764.9	799.0
SD	3.90	4.80	7.04	5.21	6.59	4.39	2.07	4.01

Table D1.3 Modulus of IPNs products

NR/PS	50/50		60/40		70/30		80/20	
	IPNs	semi-	IPNs	semi-	IPNs	semi-	IPNs	semi-
Modulus	6.083	6.378	5.872	5.660	4.895	4.725	3.805	3.310
(MPa)	6.765	6.352	5.830	5.715	4.933	4.728	3.772	3.325
	6.783	6.349	5.792	5.650	4.950	4.739	3.790	3.295
	6.750	6.298	5.809	5.666	4.912	4.876	3.787	3.301
	6.774	6.399	5.797	5.659	4.910	4.705	3.826	3.314
Mean	6.775	6.355	5.820	5.670	4.920	4.755	6.796	3.309
SD	0.02	0.04	0.03	0.02	0.02	0.07	0.02	0.02

Table D2 Hardness of IPNs products

NR/PS	50/50		60/40		70/30		80/20	
	IPNs	semi-	IPNs	semi-	IPNs	semi-	IPNs	semi-
Hardness	80.83	80.64	77.89	75.54	70.98	69.43	52.78	52.43
(Shore D)	80.98	80.27	77.50	75.83	70.95	69.47	52.32	52.21
	80.93	80.35	77.08	75.76	70.38	69.03	52.49	52.11
	80.75	80.58	77.20	75.22	70.71	69.26	52.59	52.98
	81.21	80.76	78.83	75.15	70.98	69.31	52.82	51.77
Mean	80.94	80.52	77.70	75.50	70.80	69.30	52.60	52.30
SD	0.18	0.20	0.70	0.31	0.26	0.17	0.21	0.45

Table D3 Tear strength of IPNs products

NR/PS	50/50		60/40		70/30		80/20	
	IPNs	semi-	IPNs	semi-	IPNs	semi-	IPNs	semi-
Tear strength	47.78	45.32	45.32	43.57	42.21	40.88	38.26	36.57
(N/mm)	47.52	45.47	45.25	43.05	42.38	40.76	37.95	36.87
	47.38	45.59	45.18	43.08	42.79	40.56	38.07	36.38
	47.25	45.68	45.03	42.92	42.58	40.98	38.11	36.40
	47.32	45.19	45.27	42.98	42.54	40.72	37.96	36.78
Mean	47.45	45.45	45.21	43.12	42.50	40.78	38.07	36.60
SD	0.21	0.20	0.11	0.26	0.22	0.15	0.13	0.22

Table D4 Tensile strength (MPa) of PP blended with IPNs products and EPDM

Tensile strength (MPa)	EPDM	70/30	60/40	50/50
Rubber content (phr)				
10	13.53	14.51	17.84	18.57
	14.08	15.61	18.38	19.10
	14.51	14.02	18.11	18.39
	13.87	12.15	17.95	18.85
	14.01	14.96	17.87	19.34
Mean	14.00	14.16	18.03	18.85
SD	0.41	1.21	0.22	0.38
15	12.18	13.20	13.54	15.38
	12.76	12.88	14.23	15.98
	12.17	13.71	12.30	15.53
	13.12	13.00	12.68	15.87
	12.83	12.11	14.00	15.94
Mean	12.61	12.98	13.36	15.74
SD	0.42	0.67	0.85	0.27
20	10.58	12.11	13.12	12.96
	11.35	12.58	10.26	13.38
	11.59	11.52	11.48	13.95
	10.99	13.49	11.04	13.50
	11.09	13.02	12.70	13.61
Mean	11.12	12.52	11.72	13.48
SD	0.38	0.77	1.18	0.36

Table D4 (continued)

Tensile strength (MPa)	EPDM	70/30	60/40	50/50
Rubber content (phr)				
20	10.26	11.92	11.52	12.30
	10.19	10.34	12.20	12.83
	10.52	9.32	8.48	11.97
	10.23	9.80	10.47	12.55
	10.06	10.27	10.73	11.60
Mean	10.25	10.33	10.68	12.25
SD	0.17	1.13	1.40	0.48

Table D5 Hardness of PP blended with IPNs products and EPDM

Hardness (N)	EPDM	70/30	60/40	50/50
Rubber content (phr)				
10	53.3	50.8	54.3	59.8
	52.4	43.6	55.2	60.5
	54.0	53.4	52.5	61.8
	54.3	46.6	55.3	60.3
	54.6	55.3	52.0	62.1
Mean	54.0	50.8	54.3	60.9
SD	0.88	4.82	1.53	1.0

Table D5 (continued)

Hardness (N)	EPDM	70/30	60/40	50/50
Rubber content (phr)				
15	47.0	48.3	50.8	58.6
	49.5	49.5	53.2	59.9
	48.3	53.4	52.6	60.1
	49.3	51.4	54.7	59.9
	49.7	50.2	52.6	60.0
Mean	49.3	50.2	52.6	59.7
SD	1.12	1.94	1.40	0.62
20	46.7	48.5	51.1	57.2
	44.7	51.6	43.8	56.0
	44.6	53.0	47.0	56.5
	46.0	46.2	51.0	55.9
	48.6	48.6	50.9	55.9
Mean	46.0	48.2	50.9	56.3
SD	1.64	2.70	3.27	0.56
25	45.4	41.2	53.8	55.5
	48.5	47.6	49.7	54.8
	45.5	45.2	45.6	55.7
	44.7	36.6	51.0	53.9
	40.5	44.9	50.3	56.1
Mean	45.4	44.9	50.3	55.2
SD	2.87	4.29	2.96	0.87

Table D6 Impact strength of PP blended with IPNs products and EPDM

Impact strength (kJ/m^2)	EPDM	70/30	60/40	50/50
Rubber content (phr)				
10	625	389	432	405
	638	385	424	397
	625	375	435	389
	632	687	420	398
	632	381	433	390
Mean	630.4	383.4	428.8	395.8
SD	5.50	5.55	6.46	6.53
15	661	398	447	412
	668	418	428	420
	669	405	440	418
	659	408	436	428
	663	419	431	407
Mean	664.0	409.6	436.4	417.0
SD	4.36	8.90	7.50	8.00
20	710	426	445	434
	715	406	435	425
	709	428	446	427
	718	415	446	433
	704	423	448	430
Mean	711.2	419.6	444.0	429.8
SD	5.45	9.07	5.15	3.83

Table D6 (continued)

Impact strength(kJ/m^2)	EPDM	70/30	60/40	50/50
Rubber content (phr)				
25	723	448	482	449
	706	443	478	445
	718	433	470	447
	711	438	478	458
	720	431	454	452
Mean	715.6	438.6	472.4	450.2
SD	6.95	7.02	11.17	5.07

APPENDIX E

This section presents product specification of main raw material chemicals, including PP (2511 TC), EPDM (EP35), antioxidant Irganox 1076, and Prevulcanize NR latex MR grade.

Table E1 Typical data of polypropylene grade 2511 TC

Typical Data	Unit	Value	Test Method
Property			
MFI 2.16 kg/230°C	g/10 min	45	ASTM 1238
Tensile Strength at Yield	N/mm^2	21	ASTM D638
Charpy Impact Strength			
At –20°C	mJ/mm^2	5.5	DIN 53453
Shear Modulus	N/mm^2	430	DIN 53457
Ball Indentation Hardness	N/mm^2	53	DIN 53456
Heat Distortion Temp.			
At 0.45 N/mm^2	°C	90	ASTM D648

Table E2 Product specification of EPDM grade EP 35

Item	Unit	Value	Test Method
Volatile Matter	%	0.75 max.	JIS K6383
Ash	%	0.20 max.	JSR AE102
Iodine Value	I_2/EPDM 100g	22-30	JSR AE104
Propylene Content	wt %	39-47	JSR AE103
Mooney Viscosity	ML_{1+4}(100°C)	75-91	JSR D6300
Tensile Strength	MPa	10.8 min	JIS K6301
Elongation	%	280 min	JIS K6301
200% Modulus	MPa	6.6-9.5	JIS K6301

Table E3 Typical physical properties of antioxidant (Irganox 1076)

Properties	Unit	Powder	Pellets
Appearance		white to cremecolored powder	yellow-brown pellets
Melting Point On set (Capillary method)	°C	105 min.	105 min.
Volatile (10g/ 2h/ 100°C)	%	1.0 max.	1.0 max.
Ash Content (5g/800°C)	%	0.5 max.	0.5 max.
Sieve residue (>63µ)	%	4.0 max.	-

Table E4 Specification of prevulcanized NR latex (MR grade)

Test Parameter	Unit	MR spec.
Total solids content	%	60.0-61.0
Ammonia content	% on latex wt.	0.60-0.70
pH Value	-	10-12
KOH No.	-	0.70 max.
VFA No.	-	0.50 max.
MST	sec (55% TSC)	750 min
Viscosity at 28°C		
Ford cup #3 (406)	sec	40 max.
LVT B/F (Eli) (SPI) 1/60 rpm.	cps	150 max.
Coagulum, ppm/%		
80#	ppm	<100/<0.01
320#	ppm	<500/<0.05
Chloroform No.	-	3 – 3+
Toluene swelling	%	80-90
Petri dish cast film		
(1.0– 1.5 mm. Thick)		
Colour	-	yellow
Clarity	-	clear
Balloon speck	-	trace

VITA

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