การสังเคราะห์พอลิสไตรีนทนแรงกระแทกสูงดัดแปรด้วยยางธรรมชาติผ่านพอลิเมอไรเซชันแบบแขวนลอย

นางสาวตติยา กิตติวัฒนะกุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

SYNTHESIS OF HIGH IMPACT POLYSTYRENE MODIFIED BY NATURAL RUBBER VIA SUSPENSION POLYMERIZATION

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2014

Thesis Title	SYNTHESIS OF HIGH IMPACT POLYSTYRENE MODIFIED BY NATURAL RUBBER VIA SUSPENSION POLYMERIZATION
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ตติยา กิตติวัฒนะกุล : การสังเคราะห์พอลิสไตรีนทนแรงกระแทกสูงดัดแปรด้วยยางธรรมชาติผ่านพอลิเมอไรเซชันแบบแขวนลอย (SYNTHESIS OF HIGH IMPACT POLYSTYRENE MODIFIED BY NATURAL RUBBER VIA SUSPENSION POLYMERIZATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: นพิดา หิญชีระนันทน์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ภัทรพรรณ ประศาสน์สารกิจ, 109 หน้า.

เป็นที่รู้กันดีว่าพอลิสไตรีนเป็นพลาสติกที่มีความเปราะจึงส่งผลให้มีสมบัติเชิงกลที่ต่ำ จากปัญหานี้จึงกลายเป็นข้อจำกัดในการนำไปใช้ในอุตสาหกรรมต่างๆ การเติมอิลาสโตเมอร์หรือสารพวกยางก็เป็นอีกวิธีหนึ่งในการเพิ่มสมบัติเชิงกลของพอลิสไตรีน ซึ่งรู้จักกันในชื่อ พอลิสไตรีนทนแรงกระแทกสูง ดังนั้นจุดประสงค์ของงานวิจัยนี้คือการสังเคราะห์กรีนพอลิสไตรีนโดยใช้ยางธรรมชาติเป็นสารเสริมแรง และการศึกษาหาตัวแปรและความสัมพันธ์ระหว่างตัวแปรที่มีผลอย่างมีนัยสำคัญในกระบวนการสังเคราะห์กรีนพอลิสไตรีนทนแรงกระแทกสูง โดยกรีนพอลิสไตรีนทนแรงกระแทกสูงจะถูกเตรียมผ่านกระบวนการพอลิเมอไรเซชันแบบแขวนลอยโดยใช้เบนโซอิลเปอร์ออกไซด์และพอลิไวนิลแอลกอฮอล์เป็นตัวริเริ่มปฏิกิริยาและสารช่วยในการแขวนลอย ตามลำดับ ตัวแปรของกระบวนการสังเคราะห์กรีนพอลิสไตรีนทนแรงกระแทกสูง ได้แก่ ความเข้มข้นของเบนโซอิลเปอร์ออกไซด์ ปริมาณของยางธรรมชาติ ความเข้มข้นของพอลิไวนิลแอลกอฮอล์ อัตราการปั่น รวมไปถึงระยะเวลาการเกิดปฏิกิริยาต่อค่าการเปลี่ยนแปลงของสไตรีน ขนาดเม็ดของกรีนพอลิสไตรีน ความทนต่อแรงดึงและความทนต่อแรงกระแทก ความเข็มข้นที่เหมาะสมของเบนโซอิลเปอร์ออกไซด์คือ 0.6% โดยน้ำหนักของสไตรีน ที่จะขึ้นรูปแผ่นได้ดี เรียบ โดยไม่มีรอยแตก จากผลการทดลองแบบ 2^3 แฟกทอเรียลพบว่าค่าการเปลี่ยนแปลงของสไตรีนไม่ขึ้นกับอัตราการปั่น ในขณะที่ค่าการเปลี่ยนแปลงของสไตรีนขึ้นกับปริมาณของยางธรรมชาติและความเข้มข้นของพอลิไวนิลแอลกอฮอล์ อย่างไรก็ตาม ตัวแปรที่ศึกษาทุกตัวส่งผลกระทบต่อสัดส่วนโดยน้ำหนักของเม็ดกรีนพอลิสไตรีนที่มีขนาดน้อยกว่า 1.18 มิลลิเมตร ในส่วนของสมบัติเชิงกล พบว่าตัวแปรที่ศึกษาที่มีผลอย่างมีนัยสำคัญต่อความทนต่อแรงดึงและความทนต่อแรงกระแทกโดยเรียงจากมากไปหาน้อย ปริมาณของยางธรรมชาติ > อัตราการปั่น > ความเข้มข้นของพอลิไวนิลแอลกอฮอล์ ปริมาณยางธรรมชาติส่งผลกระทบอย่างมากต่อขนาดของเม็ดและสมบัติเชิงกลของกรีนพอลิสไตรีนทนแรงกระแทกสูง สภาวะที่เหมาะสมที่ให้ค่าทนต่อแรงดึงสูงที่สุด (21.2 เมกะปาสคาล) และค่าทนต่อแรงกระแทกสูงที่สุด (13.5 จูล/เมตร) สูงที่สุดคือ ยางธรรมชาติเข้มข้น 4% โดยน้ำหนักของสไตรีน พอลิไวนิลแอลกอฮอล์เข้มข้น 2.0% โดยน้ำหนักต่อปริมาตรของน้ำปราศจากไอออน อัตราการปั่น 400 รอบ/นาที ที่ 90 องศาเซลเซียสนาน 6 ชั่วโมง นอกจากนี้การเพิ่มปริมาณยางธรรมชาติลงในพอลิสไตรีนยังช่วยทำให้กรีนพอลิสไตรีนทนความร้อนได้ดีขึ้นอีกด้วย

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....
ปีการศึกษา 2557 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
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5471975323 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: NATURAL RUBBER / SUSPENSION / POLYSTYRENE

TATIYA KITTIWATTANAKUL: SYNTHESIS OF HIGH IMPACT POLYSTYRENE MODIFIED BY NATURAL RUBBER VIA SUSPENSION POLYMERIZATION. ADVISOR: ASST. PROF. NAPIDA HINCHIRANAN, Ph.D., CO-ADVISOR: PROF. PATTARAPAN PRASASSARAKICH, Ph.D., 109 pp.

Polystyrene (PS) has been well known that it is brittle resulting its low mechanical properties. These drawbacks have limited its industrial applications. The addition of elastomer is one method to improve the mechanical properties called as “High Impact Polystyrene (HIPS)”. Therefore, the aim of this research was to produce green HIPS by using natural rubber (NR) as a modifier and to investigate the significant factors and their interaction on production of green HIPS. The green HIPS was prepared via suspension polymerization by using benzoyl peroxide (BPO) and poly(vinyl alcohol) (PVA) as an initiator and stabilizer, respectively. The studied parameters of the production of HIPS were BPO, NR, and PVA concentrations and agitation rate including reaction time on %Styrene (ST) conversion, green HIPS bead size, tensile and impact strength. The optimum BPO concentration was 0.6 wt% based on ST content that produced fine smooth sheet without cracking. From the 2^3 factorial design experiment result, it was observed that %ST conversion did not depend on agitation rate while this depended on NR content and PVA concentration. In addition, all studied parameters effected on the mass fraction of green HIPS bead with the size of <1.18 mm. For mechanical properties, it was observed that the significance of reaction parameters on tensile strength and impact strength of green HIPS (most to least significant) was NR content > agitation rate > PVA concentration. The NR content strongly affectd bead size and mechanical properties of green HIPS. The optimum condition that gave the highest tensile (21.2 MPa) and impact strength (13.5 J/m) was 4 wt% NR based on ST monomer, 2.0 % (w/v) PVA based on DI water volume and 400 rpm agitation rate at 90°C for 6 h. In addition, the incorporation of NR into PS matrix also improved the thermal stability of the synthesized green HIPS.

Field of Study:	Petrochemistry and Polymer Science	Student's Signature ....
		Advisor's Signature ....
Academic Year:	2014	Co-Advisor's Signature ....

ACKNOWLEDGEMENTS

The author would like to express her greatest gratitude to her advisor, Assistant Professor Napida Hinchiranan and co-advisor, Professor Pattarapan Prasassarakich, Ph.D., for their encouraging guidance, supervision and helpful suggestion during the course of this research. In addition, the author wishes to thank Professor Tharapong Vitidsant, Associate Professor Wimonrat Trakarnpruk and Assistant Professor Suwadee Kongparakul, Ph.D., for serving as the chairman and member of the thesis committee, respectively.

The author also thanks for the research financial supports from the Petrochemistry and Polymer Science Program of Chulalongkorn University and Center for Petroleum, Petrochemical, and Advanced Materials, National Research University Project of CHE, Faculty of Science, Chulalongkorn University. The author wishes to express her thankfulness to technicians of the Department of Chemical Technology, Faculty of Science, Chulalongkorn University for providing the chemicals and facilities throughout this research.

Thanks are going towards all of her friends in the laboratory for their friendships, assistance, suggestion, advice concerning the experimental techniques and the encouragement during the the course of her graduate research.

Finally, and most of all, the author wishes to express her deepest gratitude to her family; especially her parents for their love, support and encouragement throughout her entire study.

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LIST OF ABBREVIATIONS

ATR-FTIR : The attenuated total reflectance Fourier transform infrared spectroscopy

BPO : Benzoyl peroxide

BR : Butadiene rubber

DSC : Differential scanning calorimetry

GPPS : General purpose polystyrene

HIPS : High impact polystyrene

MPa : Megapascal

NMR : Nuclear magnetic resonance

NR : Natural rubber

PB : Polybutadiene

PS : Polystyrene

PVA : Poly(vinyl alcohol)

RPM : Revolutions per minute

SEM : Scanning electron microscopy

ST : Styrene

TEM : Transmission electron microscopy

TGA : Thermogravimetric analysis

CHAPTER 1

INTRODUCTION

1.1 The Statement of Problem

Polystyrene (PS), one of general purpose plastics, is widely used in various industries such as packaging application, electronic parts, household goods etc. due to its advantage in terms of transparent, light weight, good dimensional stability and inexpensive [Odian G., (2004)]. However, PS has high brittleness resulting in low impact strength (20 J/m) which limits its applications. There are many attempts to improve mechanical properties of brittle plastics by incorporating with reinforcing inorganic fillers such as halloysite nanotubes (HNTs) [Lin Y. et al., (2011)] or blending with elastomers such as butadiene rubber (BR) [Ronco L.I. et al., (2015)], butadiene-styrene, butyl rubber, nitrile rubber [Trifonova D. et al., (1992)], natural rubber (NR) [Aiamsen P. et al., (2003)], polystyrene-modified natural rubber (SNR) [Neoh S. et al., (2011)], and ethylene propylene diene rubber (EPDM) [Lourenco E. et al., (2008)]. The obtained product consisting of rubbers dispersed in a PS matrix is called as “High Impact Polystyrene (HIPS)” providing a good balance between rigidity and elasticity more than a general purpose PS (GPPS).

HIPS is commercially produced by continuous bulk polymerization of styrene (ST) containing polybutadiene (PB, 8.2 wt%). This HIPS has high stress crack resistance or environmental stress crack resistance (ESCR) as 40.3 % retained toughness [Sun L. et al., (2011)]. However, the addition of PB in the PS matrix in this process is limited as 12 wt% owing to the difficulty of agitation for stirring high viscous solution [Bucknall C.B., (1977)]. Moreover, the control of temperature for bulk polymerization of vinyl monomer is difficult since this reaction is highly exothermic leading the heat accumulation [Dowding P.J. et al., (2000)]. Furthermore, the bulk polymerization needs pelletization unit for making HIPS resin beads. To solve the problem of heat accumulation during polymerization and addition of pelletization unit for preparing

HIPS beads, the suspension polymerization has been suggested for synthesis of several polymers. Additionally, the final product is composed with rigid spherical polymer beads leading the ease of manufacturing feature for processing, transportation and storage [Dowding P.J. et al., (2000)].

To evaluate the significance of each parameters and their interaction for HIPS preparation via suspension polymerization, the factorial experimental design was applied in this study. The previous literatures studying the bulk polymerization to produce HIPS showed that the main effects on particle size of rubber dispersed in the PS matrix were concentration of initiator, reaction temperature, agitation rate and amount of BR [Cunha F. et al., (2013)]. Besides, the temperature and stirring speed of the system were intensively significant on monomer conversion. For the mechanical properties aspect, it was observed that the impact strength of HIPS was only depended on the rubber content [Cunha F. et al., (2013)]. On the other hand, the stabilizer such as poly(vinyl alcohol) (PVA) hinders the coalescence of the monomer droplet and stabilizes the polymer beads. Thus, the size of obtained polymer beads decreased with increasing the stabilizer concentration [Nanjwade B.K. et al., (2010)].

According to the trend of green materials, NR has been expected to replace the products derived from petroleums because of its high performance in mechanical properties and availability with low price. Although several articles have investigated the improvement of thermal and mechanical properties of PS by blending with elastomers [Asaletha R. et al., (1998, (1999)] The relationship of parameters for the synthesis of HIPS via suspension polymerization has not been statistically studied and reported. Therefore, the effects of reaction parameters: benzoyl peroxide (BPO), NR and PVA concentrations and reaction time including agitation rate on monomer conversion and particle size distribution of HIPS bead were individually studied by using univariate experimental design. The significant effects and their interaction on %ST conversion, green HIPS bead size and mechanical properties of HIPS obtained from suspension polymerization of ST containing NR were also evaluated by using 2^k factorial experimental design. The thermal properties of green HIPS bead such as glass transition temperature and decomposition temperature were also investigated. The mechanical properties in terms of tensile strength, elongation at break, hardness and impact strength including the morphology of green HIPS beads after sheeting were also examined.

1.2 Objectives of Research Work

The objectives of this research were stated as followed:

1. To prepare the green HIPS beads by using NR via suspension polymerization.
2. To characterize the structure of the obtained HIPS beads
3. To investigate the effects of the initiator BPO, NR and PVA concentrations, reaction time and agitation rate on %ST conversion, bead size of the green HIPS beads and mechanical properties of the green HIPS after sheeting.
4. To investigate the morphology of the tensile fractural surface and the thermal properties of the obtained green HIPS beads.

1.3 Scope of Research Work

The details of experimental procedure for this research were presented as followed:

1. Surveyed the previous literatures and related research works.
2. Prepared the HIPS beads by using NR via suspension method initiated and stabilized by BPO and PVA, respectively.
3. Characterized the structure of the obtained green HIPS beads by using attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) and nuclear magnetic resonance spectroscopy (NMR).

4. Evaluated the effects of the initiator, rubber and stabilizer concentrations and reaction time including agitation rate on %ST conversion, bead size of the green HIPS beads and the mechanical properties of the green HIPS sheets by using a univariate and 2^3 factorial design experiments.
5. Studied the morphology of the tensile fractural surface of the green HIPS sheets using scanning electron microscopy (SEM) and transmission electron microscope (TEM).
6. Investigated the effect of NR content on the thermal stability of PS phase of the obtained green HIPS beads by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).
7. Summarized and concluded the results.

CHAPTER 2
THEORY AND LITERATURE REVIEWS

2.1 Styrene and polystyrene

2.1.1 Definition and properties

Styrene (ST) has been well known since the mid-nineteenth century [Scheirs J. et al., (2003)] It is as an organic compound with the chemical formula of $C_6H_5CH=CH_2$. ST is clear organic liquid and pungent odour. Additionally, it is easily evaporated. Polystyrene (PS) is a synthetic aromatic polymer made from polymerization of ST. The chemical structure of PS is shown in Figure 2.1.

In general, PS is classified as two main groups: general purpose polystyrene (GPPS) and high impact polystyrene (HIPS). GPPS is thermoplastic and its structure is amorphous resulting in an atactic polymer. Therefore, PS is transparent, clear and rigid at room temperature. It also exhibits high stiffness, good dimensional stability, moderately high heat deflection and excellent electrical insulating properties [Sastri V., (2010)]. PS can be melted at higher temperature than its glass transition temperature. Some properties of PS are shown in Table 2.1.

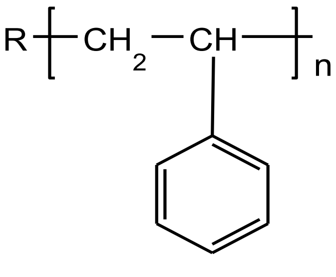


Figure 2.1 Stucture of Polystyrene.

Table 2.1 Properties of GPPS [Sastri V., (2010)]

Properties	Value
Density (g/cc)	1.05
Refractive index	1.589
Melting point (°C)	-
Glass transition temperature (°C)	90-95
HDT at 0.46 MPa	85-95
HDT at 1.8 MPa	90-100
Softening point (°C)	75-85
Tensile strength (MPa)	40
Elongation at break (%)	1-40
Flexural modulus (GPa)	3
Impact strength, notched (J/m)	20-50
% Crystallinity	-
Light transmission	Clear

PS is one of the major commercial plastics and it is extensively used as food containers, packaging, toys and electronic parts since it has high transparency, dimensional stability, light weight and low price. However, PS has poor resistance to UV, oxygen and ozone including organic solvents such as benzene and toluene due to its labile benzylic hydrogen. Moreover, the major drawback of PS is poor impact strength because of the stiff PS chains leading the brittleness [Odian G., (2004)].

2.1.2 Production process

The commercial PS in the grade of GPPS has been manufactured by BASF since 1930. Four techniques for production of PS are bulk, solution, suspension and emulsion polymerizations. Nevertheless, PS is mostly produced either by bulk or suspension polymerization.

2.1.2.1 Bulk polymerization

Bulk (or mass) polymerization is commonly used to produce several polymers because of the simplest theory and equipment. The component of bulk process is consisted of monomers and initiators leading the less contamination in the obtained polymers. However, the temperature in the bulk polymerization of vinyl monomers is difficult to be controlled since this reaction provides highly exothermic, high activation energy and trends toward Trommsdorff effect. To solve these problems, the production is divided as two parts as shown in Figure 2.2 [Scheirs J. et al., (2003)]. The first step is the pre-polymerization, which is the thermal polymerization of ST at 90 °C until the ST conversion achieved to 30-35%. The pre-polymerization syrup is then transferred to the top of the reactor to increase the ST conversion to 97%. This reactor is divided as 3 zones, which are operated at 100, 150 and 200 °C from top to bottom zone. The high bottom temperature not only ensures a higher conversion, but it also boils off the residual ST monomer from the PS polymer. Finally, the polymeric syrup is fed into an extruder for the production of PS pellet. However, the problem of

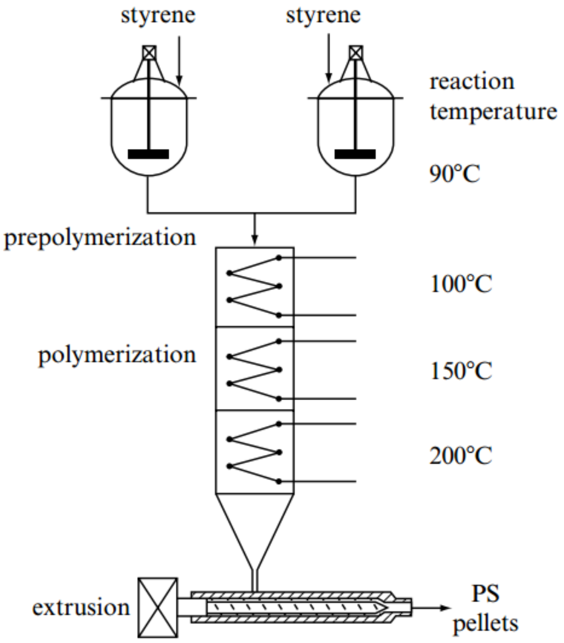


Figure 2.2 Continuous bulk polymerization of ST [Scheirs J. et al., (2003)].

heat accumulation is normally occurred because of the high viscosity development at the earlier stage of process. The difficulty to control the temperature of the process and the high energy consumption to agitate is also required to be solved. Additionally, the obtained product has a broad molecular weight distribution [Odian G., (2004)].

2.1.2.2 Solution polymerization

To solve the disadvantages of bulk polymerization, the solvent is introduced into the system and called as solution polymerization. The solvent is used as a media to enhance the ease of agitation and decrease the viscosity of polymeric syrup. The solvent is also used to receive the heat generated from the polymerization. The temperature control in the solution polymerization process is easier than that in the bulk system. The solvents generally used in this process are organic solvents such as toluene, benzene and cyclohexane. Additionally, solvent is also control the molecular weight of the obtained polymer by promoting chain transfer (although chain transfer agents are used). This process also provides polymeric products with narrow molecular weight distribution. Nevertheless, the limitation of this process are the hazard and the expensive cost of solvents. Moreover, the obtained products may be contaminated by unremoved solvent.

Figure 2.3 shows a generalized solution process for the production of PS. ST, solvent (usually methylbenzene in the amount of 2-30%), and initiators are fed into to 3 units of reactor to complete polymerization. The 1st reactor is performed at 120 °C for thermal polymerization. Then, the temperature in the 1st reactor is decreased to 90 °C when initiators are added. The reaction are operated at successively increasing temperatures to 180 °C in the 3rd reactor. Both single- and two-initiator systems can be applied. The final conversion of 60-90% are achieved. The reaction mixture is passed through a vacuum devolatilizer to remove solvent and unreacted monomer that are then condensed and recycled to the 1st reactor. The devolatilized PS (at 220-260 °C) is fed into the extruder and then pelletized [Odian G., (2004)].

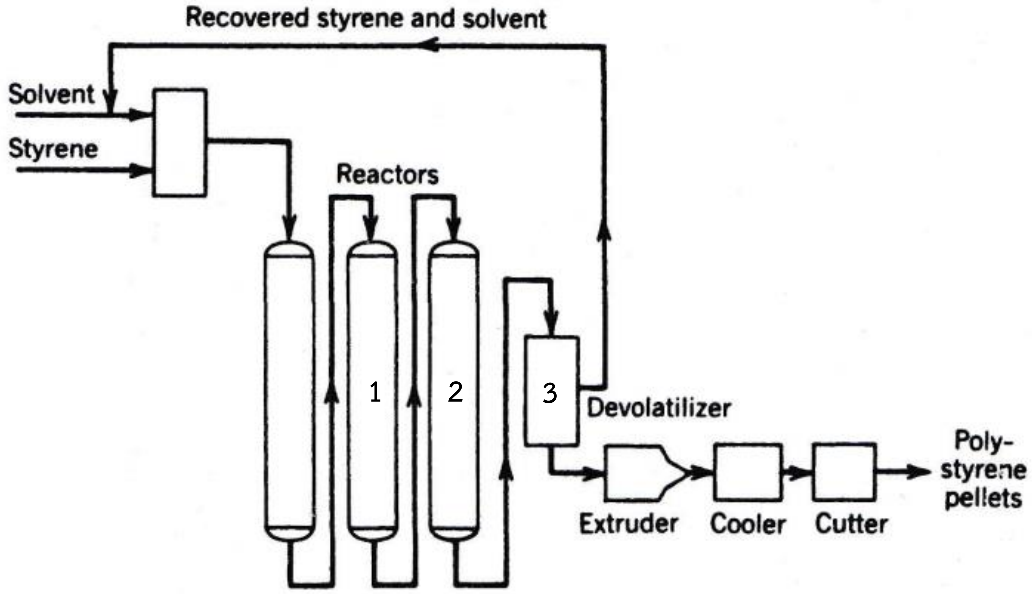


Figure 2.3 Continuous solution polymerization of ST [Odian G., (2004)].

2.1.2.3 Suspension polymerization

Since the presence of solvent in the solution polymerization may cause some problems in terms of high operating cost and contamination in the obtained product including toxicity and flammability of solvents. To solve these problems, suspension polymerization provides more benefit than the solution process since it is performed in the presence of water instead of organic solvents. This process is consisted of the monomer (discontinuous or dispersed phase) as droplets (50-500 μm diameter) and water (continuous phase). The initiator is dissolved in the monomer phase. Therefore, each monomer droplet is similar to the miniature bulk polymerization reactor [Odian G., (2004)]. The monomer droplets subsequently converted as polymer particles are prevented from coalescing and break-up of droplet during polymerization by stabilizer and agitation. The stabilizer is classified as two types: inorganic stabilizers such as tricalcium phosphase [Kaghan W.S. et al., (1953)] and organic stabilizer such as poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP) and salt of acrylic acid polymer. The volume fraction of the monomer phase in water is usually within the range of 0.1-0.5 [Dowding P.J. et al., (2000)]. The suspension process has many advantages; especially, the ability to control the thermal and viscosity of the system. Additionally, the obtained product is in a form of the rigid spherical polymer beads. The several commercial polymers such as poly(vinyl chloride), poly(vinyl acetate), PS [Kaghan W.S. et al., (1953)] and poly(tetrafluoroethylene) [Odian G., (2004)], poly(methyl methacrylate) and styrene-acrylonitrile copolymer (SAN) [Yuan H. et al., (1991)] are synthesized via suspension polymerization.

The flow diagram of suspension polymerization of ST is shown in Figure 2.4 [Yuan H. et al., (1991)]. The water fed into the reactor will be heated to 95 °C. The ST monomer is heated to 85 °C before charging. The initiators and stabilizer are premixed in ST and discharged by gravity into the reactor. When the conversion is almost completed, the obtained product in the bead form is separated from the water media by using centrifugation and then dried in air. Unreacted monomer may be removed by steam distillation. In addition, the centrifuge and dryer units are necessary to remove water from the obtained product to have only 0.03%. The pressure and time of reaction are in the ranges of 12.5-15.2 kPa and 14-15 h, respectively.

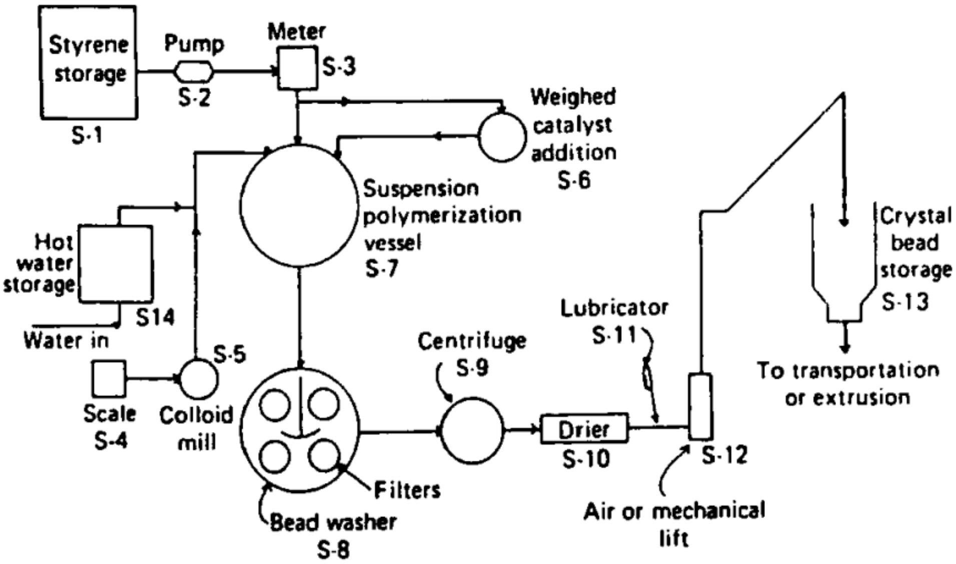


Figure 2.4 Suspension polymerization of ST [Yuan H. et al., (1991)].

The recipe of the production of PS is shown in Table 2.2. A combination of two initiators is normally used to reduce the polymerization time. However, the disadvantage of this process is the difficulty to be scaled up as the continuous mode [Brydson J.A., (1999)].

2.1.2.4 Emulsion polymerization

The emulsion polymerization is similar to the suspension one. They are different in mechanism and reaction characteristics because the emulsion system uses the water-soluble initiator such as potassium persulfate ($K_2S_2O_8$) whereas the suspension system uses initiators, which can be dissolved in the organic phase. The styrene particles in a form of latex or colloid is stabilized by emulsifier (or surfactant). The obtained latex product can be directly applied in many applications (Odian, 2004). In addition, this process is generally used for polymerization of styrene with other monomers or polymers such as acrylonitrile-butadiene-styrene (ABS). Nevertheless, the

Table 2.2 A recipe for the PS production via suspension process [Yuan H. et al., (1991)]

Ingredients	Parts by weight
Styrene	100
Water	100
Tricalcium phosphate	0.73
Sodium-β-naphthalene sulfate	1.19
Azobisisobutyronitrile	0.0735
Benzoyl peroxide	0.0365
Tertiary butyl perbenzoate (TBPB)	0.9

obtained latex is contaminated by the emulsifier. This process is not generally commercialized for producing GPPS because of the large quantities of soap left in the polymer, which adversely affects clarity, electrical and insulation properties [Brydson J.A., (1999)].

From the detail of all polymerization processes given above, the advantage and disadvantage of each technique are compared as shown in Table 2.3. Suspension polymerization process shows various advantages over the actual bulk polymerization in terms of the ease of heat transfer from the reaction, excellent

Table 2.3 Advantages and disadvantages of each polymerization process

Processes	Advantages	Disadvantages
Bulk	• Less contamination • Simple equipment for casting	• Strong exothermics • Heat accumulation • Broad molecular weight distribution at high conversion • High viscosity syrup
Solution	• Ability to control of heat generated from polymerization	• Difficulty to remove organic solvent to dry polymer
Emulsion	• Ability to control heat generated from polymerization • Rapid polymerization to high molecular weight and narrow distribution	• Contamination with emulsifier etc. • Requirement of washing and drying process
Suspension	• Ability to control heat generated from polymerization • Usable rigid granular polymer beads for transportation or process	• Requirement of continuous agitation • Contamination with stabilizer • Requirement of washing and drying processes

temperature and viscosity control throughout the polymerization. In addition, the obtained product is in the form of rigid polymer beads leading the ease of manufacturing feature for processing, storage and transportation. To compare with the emulsion polymerization, the suspension polymerization produces polymer with lower contamination and the separation cost can be neglected [Dowding P.J. et al., (2000)].

2.2 Natural rubber

Natural rubber (NR) in a form of latex or a milky colloid is produced by tapping the Brazilian rubber-tree (Hevea Brasiliensis). This tree is an original native of the tropical rain forest in the Amazon Basin in Brazil. In present, the production source of NR in the world is supplied from the tropical Alfrica and Asia [Brydson J.A., (1978)].

The chemical structure of NR is cis-1, 4-polyisoprene as shown in Figure 2.5. NR latex is comprise of 15,000-20,000 repeating isoprene units. Additionally, NR composes of approximately 36% total solid content (including a dry rubber content (DRC) of 33%) and 5% non-rubber components such as proteins, lipids, carbohydrates, alcohol and mineral substances. Its composition is varied according to the clones of rubber, age of rubber tree and tapping method [Blackley D.C., (1977)].

NR is extensively used in many applications such as medical equipments, tire industry, synthetic rubber and engineering thermoplastic materials because of its excellent mechanical properties: high tensile strength, flexibility, tear strengths, resilience, abrasion resistance and low heat build-up. Some physical

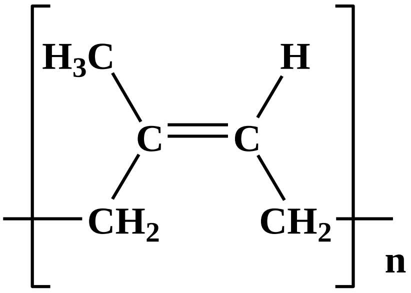


Figure 2.5 Natural rubber or cis-1,4-polyisoprene [Brydson J.A., (1978)].

properties of NR is shown in Table 2.4. However, the presence of double-bond and alpha-methylene in NR structure induces NR is deteriorated to heat, oxygen and ozone [Brydson J.A., (1978)].

2.3 High impact polystyrene

Thermoplastic elastomer (TPE) is one of the important developments in the field of polymer science and technology in recent years. It combines the properties of the elastomeric rubbers with the ease of processability of thermoplastics. Rubbers are generally used as the impact modifier for the rigid plastic region [Neoh S. et al., (2011)]. Since NR has an excellent tackiness property with high performance of mechanical properties, the modification of several thermoplastics normally uses NR to improve the toughness of materials to extend their applications.

Table 2.4 Physical properties of NR [Brydson J.A., (1978)]

Properties	Value
Density (g/cm^3)	0.92
Refractive index (1.52 at 20 °C)	1.52
Coefficient of cubical expansion (°C^{-1})	0.00062
Cohesive energy density (cal/cc)	63.7
Heat of combustion (cal/g)	10,700
Thermal conductivity (cal/sec/cm^3/°C)	0.00032
Dielectric constant	2.37
Power factor (1000 cycles)	0.15-0.2
Volume resistivity (Ω/cc)	10^{15}
Dielectric strength (V/mm)	1,000

2.3.1 Definition and properties

HIPS is one of the well known commercial rubber toughnened-plastics. It is also classified as one of TPE. HIPS has two phases consisting of a continuous PS phase and a dispersed rubber phase (polybutadiene (PB), 6-8.5 wt%), which ends up being 15-30 vol% due to PS occlusions [Alfarraj A. et al., (2004)] PB plays an important role as an impact modifier, while PS has good dimensional stability. Therefore, HIPS is used in many applications due to theirs excellent impact strength. The factors controlling the properties of HIPS are rubber particle size and its distribution, morphology of rubber, degree of adhesive, glass transition temperature (T_g) of rubber and the molecular mass of PS [Trifonova D. et al., (1992)]. Unfortunately, the increase in the rubber content in the PS matrix is limited to only 12 wt% due to the difficulty of agitation in the HIPS preparation [Bucknall C.B., (1977)].

Table 2.5 Properties of HIPS [Sastri V., (2010)]

Properties	Value
Density (g/cc)	0.8-1.04
Refractive index	-
Melting point (°C)	-
Glass transition temperature (°C)	85-95
HDT at 0.46 MPa	75-85
HDT at 1.8 MPa	85-95
Softening point (°C)	60-110
Tensile strength (MPa)	11-45
Elongation at break (%)	10-100
Flexural modulus (GPa)	0.6-3
Impact strength, notched (J/m)	70-100
% Crystallinity	-
Light transmission	Opaque

Some properties of commercial HIPS are shown in Table 2.5. To compare mechanical properties between HIPS and PS (Table 2.1 and Table 2.5), the tensile strength of HIPS decreases with increasing elongation at break and impact strength due to the salami morphology. The salami structure is composed of graft copolymer of butadiene and styrene (PBgS). Substructured salami phase domains of the PBgS are embedded in a matrix of PS. Crazes can be initiated from large rubber particles, passed through “craze-bridge” rubber particles, and ended to neighboring small one. Rubber particles prevent excessive crazes to form cracks. They also absorb energy and finally enhanced the toughness of PS [Zhu L.D. et al., (2013)].

2.3.2 Production process

There are several different routes to toughen PS. The most important processes are bulk, bulk-suspension and emulsion polymerizations. Significant amount of toughened plastics are also made by melt blending. Each process has its own technical and economic advantages, which are often specific to the type of produced materials. The typical recipe for production of HIPS is shown in Table 2.6.

Bulk or bulk-suspension polymerization is the generally process for manufacture HIPS as shown in Figure 2.6. The process for HIPS production involves three basics steps:

Table 2.6 Typical recipe for production of HIPS [Bucknall C.B., (1977)]

Ingredients	Part by weight
Styrene monomer	92.0
Polybutadiene	8.0
Benzoyl peroxide	0.05
Dicumyl peroxide	0.05
Tertiary dodecyl mercaptan	0.20

(i) Dissolution stage – uncrosslinked rubber is dissolved in ST monomer.

(ii) Pre-polymerization stage – the ST is partially polymerized, with stirring.

(iii) Finishing stage – the polymerization is completed with or without stirring.

In the pre-polymerization stage, it has two important processes: phase separation and phase inversion. First, the system is homogenized until 2% conversion was received and the phase separation occurs [Bucknall C.B., (1977)]. Meira G.R. et al. [Meira G.R. et al., (2007)] explained the phase inversion phenomenon. Before phase inversion, the continuous phase is rich in PB and the dispersed phase is rich in PS (Figure 2.7a and 2.7c). The phase inversion was occurred in the range of 5-25% ST conversion, and co-continuous morphology is occurred during that process. After the phase inversion, the PS-rich phase remains as the continuous phase as shown in Figure 2.7b and 2.7d. Rubber grafting is mainly produced by attack of primary initiator radicals onto the allylic H of the BD repeating units. The ST-PB graft copolymer, which is generated at earlier stages of the pre-polymerization, reduces the interfacial tension, promotes phase inversion, and controls the particle size. Figure 2.7c and 2.7d show that the graft copolymer molecules place themselves at the interfaces. Fischer and Hellmann [Fischer M. et al., (1996)] suggested that:

a) the phase inversion occurs when the volume of the PS-rich phase equals the volume of the PB-rich phase; and

b) after phase inversion, the graft copolymer molecules with two or more PS branches place themselves at the external interface of the rubber particles, while the molecules with a single PS branch place themselves at the interface of occlusions (Figure 2.7d). The particle occlusions also contain free PS of a relatively lower molar mass. Both the phase inversion and the particle morphology are governed by stirring and the grafting efficiency (i.e., the fraction of grafted ST with respect to the total polymerized ST) [Meira G.R. et al., (2007)].

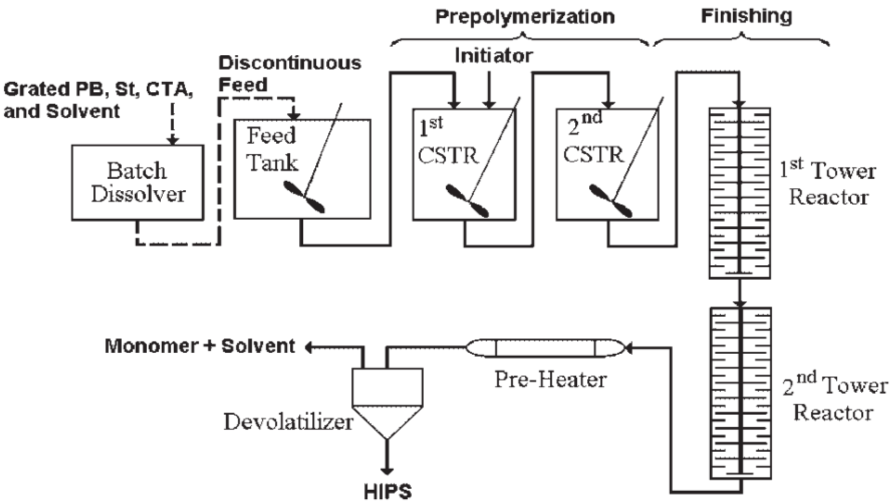


Figure 2.6 Continuous bulk polymerization of high impact polystyrene [Meira G.R. et al., (2007)].

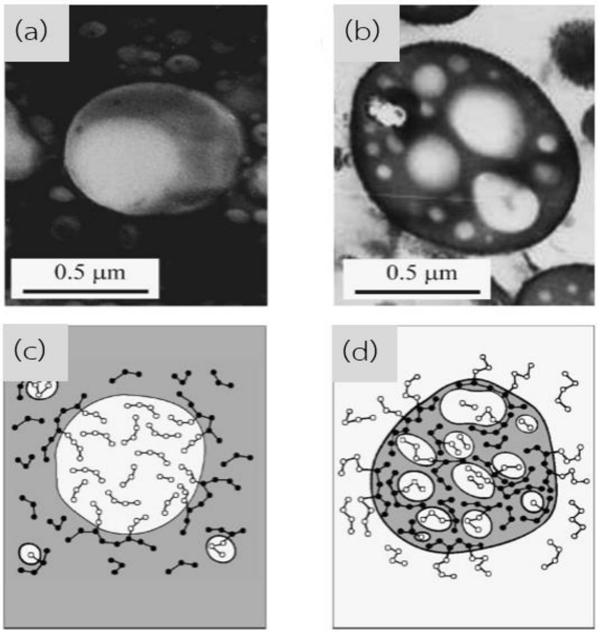


Figure 2.7 Evolution of particle morphology along a pre-polymerization: (a, b) TEM micrographs taken before and after the phase inversion and (c, d) molecular interpretations before and after the phase inversion by Fischer and Hellmann, where the white and black circles represents the ST and PB repeating units [Meira G.R. et al., (2007)].

2.3.2.1 Bulk and solution process

Nowadays, HIPS is predominantly produced by the continuous bulk and solution processes. In the dissolution section, PB is dissolved in styrene at 70 °C for thermal polymerization [Meira G.R. et al., (2007)]. The rubber is dissolved in ST containing a diluent (ethylbenzene or toluene) to give a 2 to 15% solution. If they are necessary, lubricants, regulators (tert-dodecyl mercaptan) or initiators (predominantly peroxides or hydroperoxides) are added. Figure 2.8 shows a pre-polymerization kettle reactor for bulk continuous process of HIPS production. The pre-polymerization stage is carried out between 80 and 100 °C until ST conversion achieves to 30%. The average time for pre-polymerization stage is 4 h. Then, pre-polymeric syrup is fed into the finishing stage which its temperature increases from 100 to 200 °C to complete polymerization. The average time in this stage is 10 h. Figure 2.9 shows the tower reactor used in the finishing stage of continuous bulk process. The polymer syrup is fed into a devolatilizer and then heated to 250 °C for evaporation of the residual monomer and solvent from the HIPS product. Finally, the obtained HIPS is transferred into an extruder unit to produce the HIPS pellets for shipment [Bucknall C.B., (1977)].

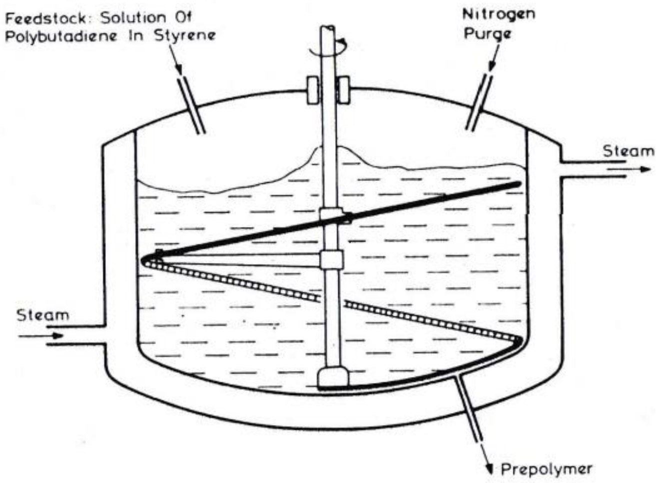


Figure 2.8 Pre-polymerization kettle reactor for the HIPS production [Bucknall C.B., (1977)].

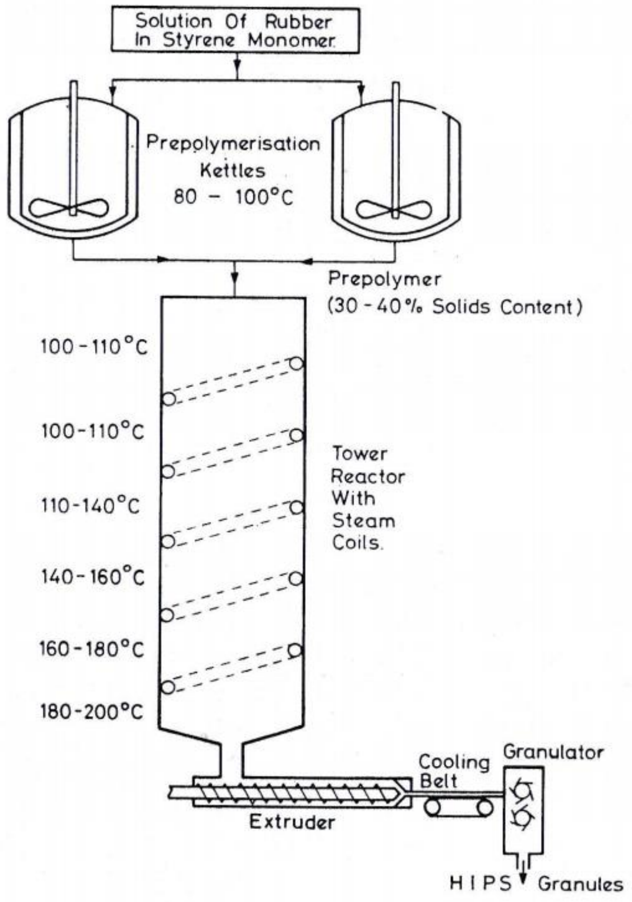


Figure 2.9 Continuous bulk polymerization for HIPS by the tower process [Bucknall C.B., (1977)].

2.3.2.2 Bulk-suspension process

The bulk-suspension process for HIPS was developed and used by Monsanto [Wünsch J.R., (2000)]. The suspension process avoids the problems of channeling and heat transfer. This bulk-suspension process is consisted of bulk pre-polymerization and finishing stages. The amount of rubber (2-15 wt%) is dissolved in the ST monomer. The mixture is fed into the bulk pre-polymerization stage. The bulk stage is carried out in the presence of initiators which are soluble in monomer. Typical initiators are benzoyl peroxide (BPO), di-t-butyl-peroxide, di-cumyl peroxide, t-butyl peracetate, tertiary butyl perbenzoate (TBPB), and azobisisobutyronitrile (AIBN). The solution of rubber in ST is gently agitated and heated to 80-100 °C until the %ST conversion reaches to 20-40%. The pre-polymeric syrup is fed into an aqueous suspension containing stabilizer in the finishing stage. The typical stabilizer are PVA, hydroxyethyl cellulose, and carboxmethyl cellulose. The amount of stabilizer is in the range of 0.1 and 1.0%. The suspension polymerization is carried out at 130 °C for 12 h to complete the polymerization. At the end of this process, water is removed from the polymeric beads by a settling tank, centrifuge unit, and a rotary dryer. The advantage of this process is the high flexibility with heat dissipation to complete ST conversion [Arthur L., (1971)].

2.3.2.3 Emulsion process

For emulsion process, this process is not suitable for the manufacture of HIPS production because the rubber particle size of the obtained HIPS product generated from emulsion process is limited to a maximum about 1 μm due to the low stability of lattices containing larger particles. Nevertheless, HIPS requires rubber particles 1-10 μm for providing the maximum toughness. The emulsion process is more suitable for the production of ABS because ABS requires rubber particles 0.1-1 μm [Brydson J.A., (1999)].

2.3.3 Comparison of TPE processes

The choice of a process for making a toughened plastics is governed by a variety of technical and economic factors [Bucknall C.B., (1977)]. The different techniques give the different morphology of the obtained product. For example, ABS is made by three processes such as bulk-suspension and emulsion polymerizations and blending techniques. The product obtained from bulk-suspension (Figure2.10a) and emulsion (Figure2.10b) techniques have spherical rubber particles, whereas the product obtained from blending technique (Figure2.10c) has irregularly shaped rubber particles.

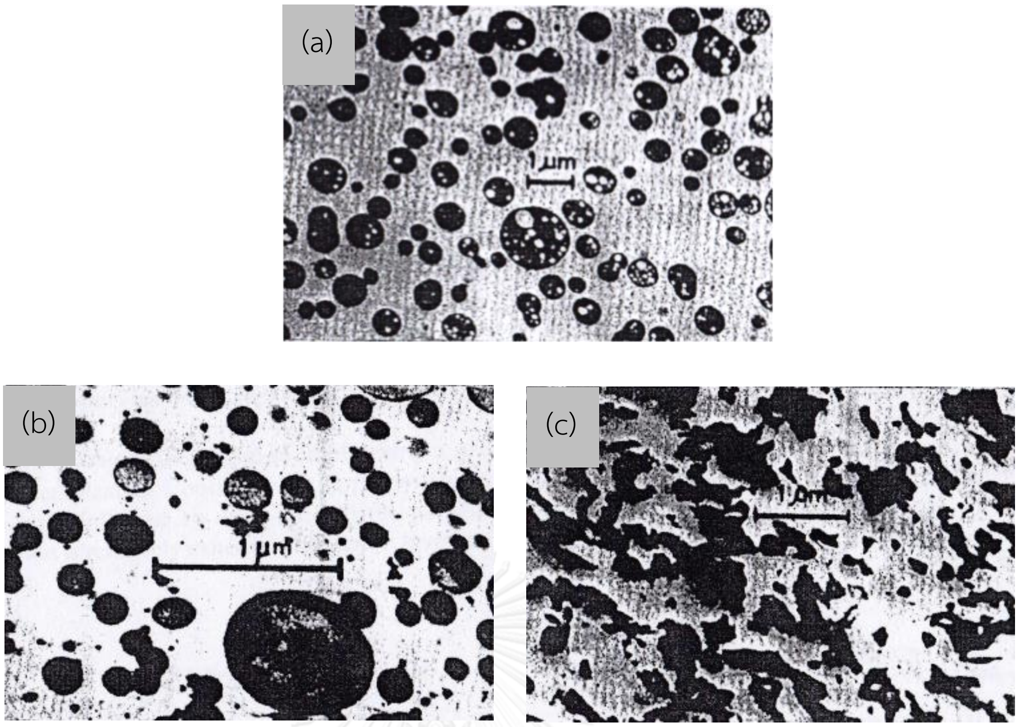


Figure 2.10 TEM of ABS polymer prepared by three processes: (a) bulk-suspension and (b) emulsion polymerizations and (c) blending process [Bucknall C.B., (1977)].

A major advantage of the product obtained from bulk and emulsion techniques is the good control of the grafting and crosslinking properties. For blending ones, there is no grafting and little control over crosslinking result in the inferior mechanical properties of the product. However, the disadvantages of the emulsion technique is the high impurity of the obtained product. Unless these impurities are removed by thorough washing, they cause degradation problems during drying and subsequent process. Bulk polymers contain the smallest amounts of impurities and suspension polymers occupy the middle place.

The economic factors are a major consideration in choosing a process for manufacturing toughened plastics. Continuous bulk polymerization is the cheapest process, followed by bulk-suspension polymerization. Emulsion polymerization is relatively expensive because it involves washing and drying units.

2.4 Literature reviews

The following previous literatures studied the effect of parameters on %ST conversion, beads size and mechanical properties of the preparation of PS with or without the addition of rubber.

Nogueira et al. [Nogueira A.L. et al., (2006)] prepared the PS via batch suspension polymerization. The BPO and PVP concentrations were 0.9101 wt% (based on ST monomer) and 2.0 g/L, respectively. This process was carried out in the stirred vertical tubular reactor (tower reactor) at 84 °C with a stirring rate of 300 rpm. The obtained PS had narrow particle size distribution and monomodal characteristics. In addition, Nogueira and coworker [Nogueira A. et al., (2012)] also studied the effect of BPO concentration (0.57 and 4.9 wt%) on particle size distribution of the PS beads. It showed that the PS particle size decreased with increasing the BPO concentration. This result was correspond to the report of [Kaghan W.S. et al., (1953)]. The influence of BPO concentration affected the particle size, average molecular weight (M_w) and yield. It was found that the increase in the BPO concentration led the higher yield and lower average M_w with decreasing the particle size. Furthermore, the influence of pH on the ability of stabilizer was investigated. The organic stabilizers such as PVA was effective more than inorganic stabilizers such as tricalcium phosphate because the inorganic stabilizers were very sensitive to pH modification resulting in the generation of large PS beads, whereas the organic stabilizers produced small PS beads and could be effective to protect the colloids in the wide pH range of water media.

Form the previous literatures, the modification of PS with elastomers in the process of polymerization is attractive. It is observed that the improvement of toughness properties of PS could be conducted by using two main processes:

2.4.1 Blending process

Trifonova et al. [Trifonova D. et al., (1992)] modified PS by using different elastomer types such as isoprene, butadienestyrene, α-methylstyrene, butyl rubber and nitrile rubber to enhance the physical and mechanical performance of the obtained HIPS produced by an extruder. It was found that the impact strength of HIPS obtained from PS blending with isoprene and butadiene-styrene (34-35 kJ/m^2) was higher than that of unmodified PS (15 kJ/m^2). The PS modified with butyl rubber had lowest impact strength. The optimal content of elastomers for improving the impact strength of PS was 12.5 parts per hundred of resin (phr). To explain the increase in the impact strength of the obtained HIPS by using isoprene and butadiene-styrene, the addition of isoprene with low glass transition temperature (T_g) and flexibility induced high impact strength. For the HIPS containing butadiene-styrene elastomer, this HIPS also had high impact strength because of the good adhesion between the PS and elastomer phase. In addition, the increase in the elastomer content decreased the tensile and flexural strengths of HIPS. However, the impact strength of the modified HIPS increased.

Asaletha et al. [Asaletha R. et al., (1998)] investigated the thermal properties of NR/PS blends with compatibilizer. The immiscibility and incompatibility of NR and PS could be improved by the addition of graft copolymer of NR and PS (NR-g-PS) synthesized via polymerization of styrene in NR latex using gamma-radiation. The blends were prepared by casting film technique. From the TGA results, the 50/50 of NR/PS blend with the addition of 1.5% NR-g-PS improved the thermal stability of the blend (the degradation temperature increased from 190 °C to 214 °C) due to the higher compatibility of the obtained blend. However, DSC measurement showed two T_g of PS/NR blend reflecting the phase separation and incompatibility of these blend constituents.

Asaletha et al. [Asaletha R. et al., (1999)] investigated the effect of blend ratio, processing conditions and vulcanizing system on mechanical properties of the blends of NR/PS. The samples were prepared by the melt mixing or the solution casting techniques. For the melt mixing process, there were three vulcanizing systems: dicumyl peroxide (DCP), sulfur and mixed system. In the case of melt mixed system, the mixing torque increased with increasing the rubber content due to the higher viscosity of NR phase than that of PS. For both of the melt mixing and solution casting techniques the tensile and tear strength of the obtained product decreased with increasing the NR content, whereas the impact strength of the NR/PS blends increased with increasing the NR content. For the comparison of vulcanizing system, the DCP system provided NR/PS blends with the maximum value of tensile strength due to the fine particle size of NR phase and the high crosslink density of NR/PS. In contrast, the DCP system showed the minimum value of impact strength. This exhibited that the mechanical properties of NR/PS blends related on the crosslink density of the samples.

Lourenco et al. [Lourenco E. et al., (2008)] prepared the modified PS via in situ polymerization of ST in the presence of ethylene-propylene-diene terpolymer (EPDM; 8, 11, 14 and 17 wt%). EPDM had excellent stability such as weather, ozone and oxidation resistance. It was obsereved that PS/EPDM contained only 8 wt% EPDM had higher impact resistance and it was more stable than the neat PS. Moreover, the blend containing 17 wt% EPDM showed an increase in the impact strength of 210% higher than that of the neat PS. In addition, the PS/EPDM blends showed the higher thermal stability than the neat PS owing to the stabilization generated by EPDM which

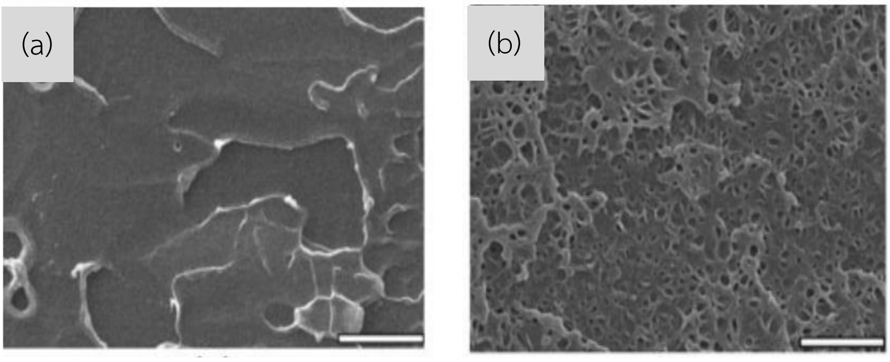


Figure 2.11 SEM of fractural surfaces of (a) PS and (b) 8 wt% EPDM in PS/EPDM blend [Lourenco E. et al., (2008)].

could deactivate PS macroradicals through intermolecular reaction. From SEM result as shown in Figure 2.11, it showed that HIPS had rubber granules dispersed in the PS matrix leading the rougher surface which could absorb more energy during the deformation of polymer. Therefore, the lower roughness led the poor impact resistance [Lourenço E. et al., (2006)].

Li et al. [Li D. et al., (2007)] studied the radiation of nano-powdered styrene- butadiene rubber (NRSBR) as an impact modifier. NRSBR was synthesized by adding two functional monomers such as 2-ethyl hexyl acrylate (2-EHA) or trimethylpropane triacrylate (TMPTA) in SBR latex via the gamma radiation. NPSBR was obtained after spray drying of the irradiated latex. The NPSBR toughened blends was carried out on a two screw extruder. It was found that the blending of 15 wt% NRSBR with PS induced higher impact strength (99.5 J/m) than the neat PS (31 J/m).

Neoh et al. [Neoh S. et al., (2011)] studied the mechanical properties of the modified PS by using polystyrene-modified natural rubber (SNR) used as an elastomeric phase. SNR was prepared by emulsion polymerization of PS in the presence of deproteinized natural rubber (DPNR) latex. The obtained SNR containing 25% PS and 75% NR. PS-SNR blends were produced by in situ vulcanization. It was found that the 20 %SNR loading gave the highest impact resistance. Figure 2.12 showed the fractural surface of PS/DPNR and PS/SNR blends. The PS/SNR blends had the rougher surface than the PS/DPNR blends. The rougher surface area indicated

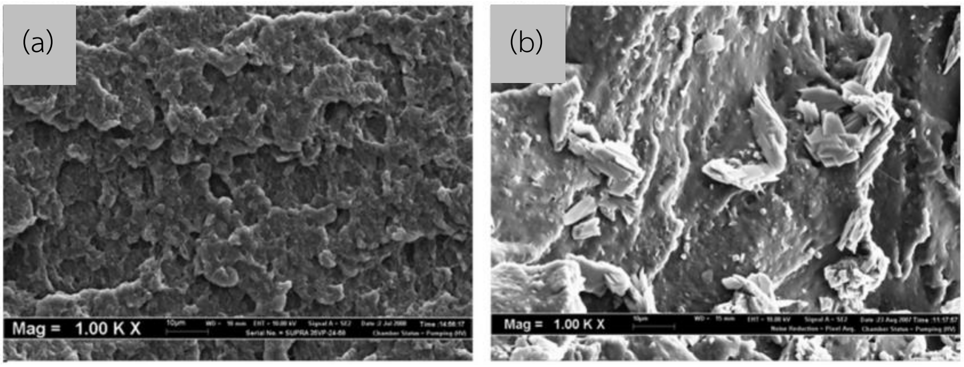


Figure 2.12 SEM of the fractural surface of (a) PS/SNR and (b) PS/DPNR [Neoh S. et al., (2011)].

the more energy which could be adsorbed during the impact strength testing. In addition, the SEM result of PS/DPNR showed the heterogeneous surface due to the agglomeration of rubber particles. These agglomeration led the reduction of mechanical properties of PS/DPNR. It indicated that SNR was more compatible with PS providing homogeneous dispersity in the PS matrix resulting in the higher mechanical properties.

2.4.2 Polymerization process

Aiamsen et al. [Aiamsen P. et al., (2003)] studied the modification of PS by using 5% of gamma-radiation vulcanized natural rubber (RVNR) prepared via suspension polymerization. This process used BPO, PVA and Kraton® 1107 as an initiator, a stabilizer and a compatibilizer, respectively. The reaction was carried out in 1 L glass reactor at 90 °C with a stirring rate at 300 rpm for 5 h of polymerization. The impact strength of the modified PS was higher than that of the neat PS. Moreover, it was found that HIPS containing Kraton® concentration of 10 wt% had the highest impact strength. The TEM result of HIPS beads showed the salami structure which was the characteristics of HIPS as shown in Figure 2.13.

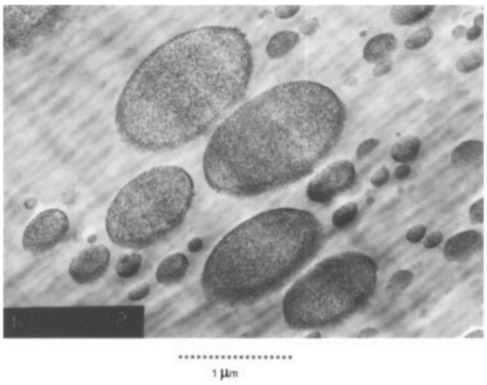


Figure 2.13 TEM of the RVNR/PS bead [Aiamsen P. et al., (2003)].

Ronco et al. [Ronco L.I. et al., (2015)] prepared the PB toughened PS nanoparticles via miniemulsion polymerization. The polymerization was carried out in 0.2 L glass reactor using 0.75-2.1 wt% BPO concentration 5-10 wt% PB loading at 90 °C for 3 h. It was observed that the use of high BPO concentration (2.1 wt%) in the obtained products gave high grafting properties and the obtained product was brittle due to the reduction of M_w of both free ST and PS branches. However, the tensile strength and elongation at break of the PB-toughened PS were improved when the BPO concentration was decreased.

Sun et al. [Sun L. et al., (2011)] produced HIPS using a continuous flow process as shown in Figure 2.6. The reactor used in the production of HIPS was continuous stirred tank reactor (CSTR) and plug flow reactors (PFR). 8.2 wt% Polybutadiene (Firestone diene 70) was used as an elastomer phase. L531/L233 (Luperox® 531/233) ratio used as an initiator was controlled as 80/40 mg/L. The elastomer, initiator and ST monomer were mixed in the CSTR. Then, the mixture was transferred to 4 units of PFR to complete polymerization before feeding to a devolatilizer for purification of HIPS. Finally, the obtained HIPS was sent to pelletizer unit and storage section.

Cunha et al. [Cunha F. et al., (2013)] studied of the effect of three parameters (agitation rate, PB content and initiator concentration) on the weight-average molecular weight (M_w), polydispersity (PD), volume-average diameter of PB particles (D(4,3)) and impact strength of HIPS produced by bulk polymerization. For the M_w, it showed that the initiator concentration and PB concentration affected M_w value of HIPS. The M_w of HIPS decreased with increasing the initiator concentration, while this value increased with decreasing PB content because the increase in the initiator concentration provided the higher rates of polymer grafting leading the production of HIPS with larger M_w. However, the increase in the PB concentration increased the relative double bond concentration to reduce the relative probability of grafting and crosslinking for individual PB chains. For the PD and D(4,3), it was observed that these values increased with decreasing agitation rate and initiator concentration. However, they decreased with increasing PB content. As explained in the Mw section, when the initiator concentration increased, the PD value decreased and the relative concentration of double bonds increased when the PB concentration increased. The increase in the D(4,3) could be explained in a term of the increasing PB content that it led the higher rates of particle nucleation and coalescence. The increase in the agitation rate induced the higher shear rates resulting in the lower rates of particle coalescence. Moreover, the increase in the initiator concentration enhanced the stabilization of occluded PS domains, the amount of the rubbery particle phase and the corresponding D(4,3) values. For the mechanical property aspect, the impact strength of HIPS was only depended on the rubber content.

CHAPTER 3

EXPERIMENTAL

3.1 Chemicals

Styrene (ST) monomer was purchased from Acros (Geel, Belgium). The solid NR (STR-5L) was supplied by PAN Innovation Industry Co., Ltd (Bangkok, Thailand). Benzoyl peroxide (BPO) from Panreac Quimica (Barcelona, Spain) and poly(vinyl alcohol) (PVA) from Ajax Finechem (Australia) were used as an initiator and a stabilizer, respectively. Sodium sulfate (Na_2SO_4) from Merck (Darmstadt, Germany), sodium hydroxide (NaOH), toluene and ethanol from Qrec (New Zealand) were used as received. The analytical grades of petroleum ether (PE) and methyl ethyl ketone (MEK) were recieved from Fisher Scientific (Leicestershire, UK). Butadiene (BR) from Thai Synthetic Rubbers Co., Ltd. was used as received. The commercial general purpose polystyrene (GPPS; Diarex®, THH102, Thai Styrenics Co, Ltd.) and high impact polystyrene (HIPS; Diarex®, H350, Thai Styrenics Co, Ltd., $\phi < 3.5$ mm) were used for comparison. Nitrogen gas (N_2) with 99.9% purity was supplied by Praxair (Samutprakan, Thailand).

3.2 Typical preparation of green high impact polystyrene

3.2.1 Purification of ST monomer

The ST monomer (b.p. 145.2 °C/760 mmHg) contained a trace amount of p-tert-butylcatechol as an inhibitor. This inhibitor was removed by sequentially washing with 10% NaOH solution and distilled water. The purified ST monomer was then dried with anhydrous Na_2SO_4 and was distilled under reduced pressure (50-60 °C/20 mmHg). The purified ST monomer was stored in a refrigerator.

3.2.2 Preparation of green HIPS

The PS containing NR for producing toughening product was called as green high impact polystyrene (green HIPS). It was prepared by suspension polymerization performed in a three-necked round glass bottom (1 L) equipped with a stirrer, a thermometer and a condenser as shown in Figure 3.1. The deionized water (DI water) containing PVA (0.1-3.0 % (w/v)) was transferred into the reactor and then it was deoxygenated by passing nitrogen gas and heated to 90 °C about 60 min. NR was masticated by using a two roll-mill at room temperature for 10 min to reduce its molecular weight (M_w) from $10.8\text{x}10^5$ to $3.2\text{x}10^5$ g/mol by Gel permeation chromatography (GPC). The total amount of purified ST monomer used in this experiment was divided as 2 parts. The 90 wt% purified ST monomer was used to dissolve the masticated NR (1-6 wt% NR based on ST content). The mixture was then added into the reactor and heated to 90 °C under stirring for 10 min. For the another part of the purified ST monomer (10 wt%), it was used to dissolve BPO (0.6 wt% based on ST content). The ST monomer containing BPO solution was then slowly dropped into the reaction mixture. The reaction was carried out under N_2 atmosphere for 6 h with a desired agitation rates (250-450 rpm). To terminate the reaction, the reactor was cooled down by immersing in an ice-bath for 30 min. Then, the obtained polymeric product was precipitated in ethanol, filtered and dried in a vacuum oven at 40 °C until a constant weight was received and kept in a desiccator. The %ST conversion was

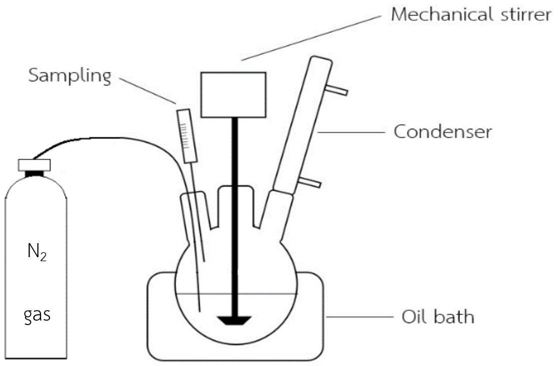


Figure 3.1 The drawing apparatus for suspension system to prepare the green HIPS.

Table 3.1 Recipe for preparation of green HIPS

Condition	Description
Purified ST monomer (g)	60
BPO (wt%)*	0.3-2.0
NR content (wt%)*	1-6
PVA concentration (% (w/v))**	0.1-3.0
Agitation rate (rpm)	250-450
Reaction temperature (°C)	90
Reaction time (h)	6-12

* BPO concentration and NR content were based on ST content

** PVA concentration was based on 360 mL DI water

calculated by gravimetric method. The standard recipe used for suspension polymerization to produce the green HIPS is shown in Table 3.1.

3.3 Determination of green HIPS beads size distribution

Differential granulometric analysis (sieving) is used to estimate the green HIPS beads size distribution. 3 sieves used to classify the size of HIPS beads were placed on a sieve shacker as a stack, which was sorted from the bottom to the top of the stack in the order of No. 4, 8 and 16 (No. 16 was the biggest sieve size). The dried HIPS beads (60 g) was transferred into the top of the sieve stack. Then, the sieve shaker was operated for 30 min. The residual amount of HIPS beads in each sieved was calculated as the retained mass fraction following Eq. 3.1 (ASTM D 1921).

$$Retained\ mass\ fraction\ in\ each\ sieve\ (\%) = \frac{Weight\ of\ sample\ remaining\ in\ each\ sieve}{Weight\ of\ total\ sample\ used} \qquad (3.1)$$

3.4 Structural characterization of green HIPS

The attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR, Perkins-Elmer spectrometer (USA)) was used to determine the presence of NR in the obtained HIPS product. All samples were carried out at room temperature over the wavenumber in the range of 515-4000 cm^{-1} with 64 scans in a 4 cm^{-1} resolution using a model spectrum. To confirm the FT-IR results, the nuclear magnetic resonance spectroscopy (NMR) was also used to analyze. ^1H-NMR spectrum obtained on the Varian Inova 600 MHz spectrometer was used to determine the specific functional groups: aromatic and double bonds in the structure of HIPS. Before analysis by using NMR, the sample (0.1 g) was swollen in 3-4 mL $CDCl_3$.

3.5 Mechanical properties evaluation of green HIPS

The obtained green HIPS beads were crushed as powder (ϕ < 1 mm) using the cutting mill (PULVERISETTE 15, Fritsch) and then dried in a vacuum oven at 40 °C until a constant weight. The HIPS powder was sheeted by using a compression-molding machine at 200 °C with a pressure of 120 kg/cm^2. Table 3.2 showed appropriate time for sheeting the green HIPS powder.

Table 3.2 Time in each step for compression of the green HIPS powder (T = 200 °C)

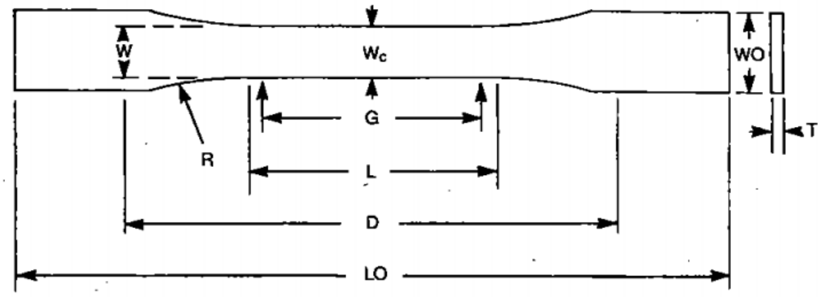
Time condition	Description (min)
Preheating	8
Venting	3 s/cycle for 3 times
Heating	3
Cooling	7

3.5.1 Tensile strength

The obtained green HIPS sheets were cut as dumbbell-shaped pieces (Type V) as illustrated in Figure 3.2. The thickness of the test specimens was 3.2 ± 0.4 mm. The tensile strength and elongation at break of HIPS dumbell were performed on a universal testing machine (INSTRON model 4206) with a cross-head speed of 1.0 mm/min. Each sample was tested for five measurements (ASTM D 638). The average value was reported.

3.5.2 Notched impact strength

The specimens used for impact strength testing had a dimension of 12.7 x 63.5 x 3.0 mm^3. The impact resistance of the five notched samples was measured using an Pendulum Impact Tester (Zwick 5113). The breaking energy of specimens was estimated and the weight hammer with 2 J was applied for the specimens. The pendulum was released and an excess energy remaining in the pendulum was recorded after breaking the specimens (ASTM D 256). The average value from five measurements was reported.



W : 3.18 mm WO : 9.53 mm G : 7.62 mm R : 12.7 mm T : 3.2 mm

L : 9.53 mm LO : 63.5 mm D : 25.4 mm RO : 25 mm

Figure 3.2 Diagram of tensile test specimens (type V) (ASTM D 638).

3.6 Univariate experiments

The univariate experiments of the central composite design of the factors were individually carried out to determine their influence on the %conversion, HIPS beads size and mechanical properties. The central condition and ranges of studied parameters were shown in Table 3.3.

3.7 Statistical analysis using two level factorial design experiments

Factorial designs are generally used for experimental systems involving several factors in order to study the main parameter effects and their interaction on the system response, and to evaluate the significance of the studied parameter [Douglas C.M., (2001)]. In this research, the three factors the green HIPS bead size and its mechanical properties were the NR content (A), PVA concentration (B) and agitation rate (C). When two-level factorial design was applied to calculate the effect of parameters on the response in the experiment, the level of these factors was assigned as “low (-1)” and “high (+1)” (Table 3.4). The range were 1-4 wt% for NR content (A),

Table 3.3 Condition of univariate experiment used for production of HIPS

Effect name	Central condition	Quantities
BPO (wt%)*	0.6	0.3, 0.6, 0.8, 1.0, 2.0
NR content (wt%)*	3	1, 2, 3, 4, 5, 6
PVA (% (w/v))**	1.6	0.1, 0.5, 1.0, 1.6, 2.0, 2.5, 3.0
Agitation rate (rpm)	350	250, 350, 450
Reaction time	6	6, 8, 12

* BPO concentration and NR content were based on ST monomer.

** PVA concentration was based on DI water volume.

1.0-2.0 % (w/v) for PVA concentration (B) and 300-400 rpm for agitation rate (C). The statistical model for a 2^3 design includes three main effects, three two-factor interactions and one three-factor interactions. The general procedure to the statistical analysis of the 2^3 design is divided as five steps [Douglas C.M., (2001)].

The first step is to compute the factor effects and the sum of squares for each effect. The contrast associated with each effect is firstly calculated.

In general, the contrast for effect *"ABC"* is determined by expanding the right-hand side of Eq. 3.2.

$$Contrast_{ABC} = (a \pm 1)(b \pm 1)(c \pm 1) \tag{3.2}$$

Once the contrasts for the effects are computed, the estimated factor effects and the sums of squares are calculated according to Eq. 3.3 and 3.4, respectively (where *n* denotes as the number of replicates).

$$Effect\ estimate_{ABC} = \frac{2}{n2^3}(Contrast_{ABC}) \tag{3.3}$$

$$SS_{ABC} = \frac{2}{n2^3}(Contrast_{ABC})^2 \tag{3.4}$$

For the second step, the 8 experiments obtained from 2^3 factorial design contains main effects and theirs interactions.

Table 3.4 Actual factors and their levels used for 2^3 factorial design experiment

Parameters	Parameter code	Low level (-1)	High level (+1)
NR content (wt%)	A	1	4
PVA (% (w/v))	B	1.0	2.0
Agitation rate (rpm)	C	300	400

Condition: ST = 60 g, BPO = 0.6 wt% based on ST content at 90 °C for 6 h.

The third step relates to the analysis of variance (ANOVA) to evaluate the significant effects and their interaction. Table 3.5 shows the general form of variance analysis for a 2^3 factorial design with *n* replicates. The F test was used to evaluate if a factor has a significance.

The forth step is to refine the model by removing any non-significant effects. When the significant effect estimates are obtained, the coefficient estimates are then calculated (Eq. 3.5). The standard deviation (S) associated with the experiment is given by the square root of the error mean square ($\sqrt{MS_E}$) (Eq. 3.6). The standard error (*se*) for the effect estimates and the coefficient estimates are then computed according to Eq. 3.7 and 3.8, respectively. These standard errors are used to construct the confidence intervals on the effect estimates and coefficient estimates.

$$Coefficient\ estimate_{ABC} = \frac{Effect\ estimate_{ABC}}{2} \tag{3.5}$$

$$S = \sqrt{MS_E} \tag{3.6}$$

$$se\ (Effect\ estimate) = \frac{2S}{\sqrt{n2^3}} \tag{3.7}$$

$$se\ (Coefficient\ estimate) = \frac{S}{\sqrt{n2}} \tag{3.8}$$

The standard error of an effect estimates is twice the standard error of an coefficient estimates in the regression model for the 2^3 factorial design.

In the final step, the usual residual analysis is provided to check the model adequacy.

Table 3.5 Analysis of variance for a 2^3 design [Douglas C.M., (2001)]

Model term	Sum of squares	Percent contribution	Degrees of freedom	Mean square	F_0
Main effects					
A	SS_A	$= (SS_A/SS_T)\times 100$	1	$MS_A = SS_A/1$	$= MS_A/ MS_E$
B	SS_B	$= (SS_B/SS_T)\times 100$	1	$MS_B = SS_B/1$	$= MS_B/ MS_E$
C	SS_C	$= (SS_C/SS_T)\times 100$	1	$MS_C = SS_C/1$	$= MS_C/ MS_E$
Two-factor interactions					
AB	SS_{AB}	$= (SS_{AB}/SS_T)\times 100$	1	$MS_{AB} = SS_{AB}/1$	$= MS_{AB}/ MS_E$
AC	SS_{AC}	$= (SS_{AC}/SS_T)\times 100$	1	$MS_{AC} = SS_{AC}/1$	$= MS_{AC}/ MS_E$
BC	SS_{BC}	$= (SS_{BC}/SS_T)\times 100$	1	$MS_{BC} = SS_{BC}/1$	$= MS_{BC}/ MS_E$
Three-factor interactions					
ABC	SS_{ABC}	$= (SS_{ABC}/SS_T)\times 100$	1	$MS_{ABC} = SS_{ABC}/1$	$= MS_{ABC}/ MS_E$
Error	SS_E	$= (SS_E/SS_T)\times 100$	$2^3(n\text{-}1)$	$MS_E = SS_E/2^3(n\text{-}1)$	
Total	SS_T		$n2^3\text{-}1$		

where SS_T = Total of sum of squares of each effect

$$SS_B = SS_T - SS_{Subtotals} \tag{3.9}$$

by $SS_{Subtotals} = SS_A + SS_B + SS_C + SS_{AB} + SS_{AC} + SS_{BC} + SS_{ABC}$ (3.10)

3.7.1 Validation of residuals and model adequacy

Before the conclusions from ANOVA, the adequacy of the underlying model should be validated. The primary diagnostic tool is *residual analysis*. The residuals (e) as shown in Eq. 3.11

$$e = Y - \hat{Y} \tag{3.11}$$

where Y is the observed values

$\hat{Y}$ is the predicted values

Model adequacy can be easily validated by using the graphical analysis of residuals.

3.7.1.1 Normal probability plot of the residuals

A normal probability plot of the residuals is an extremely useful procedure. In the analysis of variance, it is usually more effective to do this with the residuals. If the underlying error distribution is normal, this plot will resemble a straight line. In visualizing the straight line, place more emphasis on the central values of the plot than on the extremes.

3.7.1.2. Plot of residuals versus predicted values

A simple check to validate the model adequacy is to plot the residuals (e) versus the predicted values. They should be unrelated to any other variable including the predicted response. If the model is correct, the residuals should be structureless pattern.

3.7.2 Regression model

The general regression model could be applied to explain the relationship between the main effect and theirs interaction on the response [Douglas C.M., (2001)]. Because the 2^k is just a factorial design, the either an effects or a means model could be used. However, the regression model approach is much more natural and intuitive. For any predicted value, the regression model is presented as shown in Eq. 3.12.

$$\hat{Y}_i = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_k X_k \qquad (i = 1, 2, \dots, m) \qquad (3.12)$$

$\hat{Y}_i$ is any predicted value (i = number of response is available)

X_k is any coded factor (k = number of main effects)

β_0 is the average reponse of 2^k factorial design (y-intercept)

β_k is the coefficient estimates (regression coefficients)

3.8 Morphology of HIPS

3.8.1 Scanning Electron Microscopy

The morphology of tensile fractural surface of the HIPS obtained from the test of the tensile properties was also investigated using a JEOL model JSM-6400 scanning electron microscopy at 15 kV with a magnification of 1,000X. The specimens were mounted on a SEM stub using a double-side tape and the fractural surface of specimens was coated with gold.

3.8.2 Transmission electron microscope

The morphology of the tensile fractural surface of the HIPS was examined by using a JEOL model JEM-1400) and the accelerating voltage was 120 kV. Thin cross-section were cut using Reichert-Jung Ultracut E ultramicrotome with a diamond knife at room temperature. 1% aq. OsO_4 solution was added and allowed to stain the NR phase in the HIPS for 2 days. The sample was then placed on a grid and dried before evaluation.

3.9 Thermal properties of the green HIPS

3.9.1 Differential scanning calorimetry

Differential scanning calorimetry (DSC) was carried out on a METTLER model DSC822e to evaluate the effect of the addition of NR on the glass transition temperature (T_g) of the obtained HIPS. The thermogram signal was obtained from the temperature difference between the sample and the reference. The sample (5±0.3 mg) in an aluminium pan was cool down to -100 °C by using liquid nitrogen and then heated up to 270 °C with a constant heating rate of 10 °C/min under N_2 atmosphere. The T_g value was calculated from the midpoint of the baseline shift of the DSC thermogram.

3.9.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the green HIPS was performed on Perkin-Elmer Pyris Diamond (USA). Samples (5 mg) was placed in an alumina pan and heated from room temperature to 900 °C at a constant heating rate of 10 °C/min under N_2 atmosphere with a flow rate of 50 mL/min. The initial decomposition temperature (T_{id}) was determined from the intersection of two tangents at the onset of the decomposition temperature. The temperature at the maximum of mass-loss rate (T_{max}) was obtained from the peak maxima of the differential thermogravimetric (DTG) curve.

CHAPTER 4
RESULTS AND DISCUSSION

The green high impact polystyrene (HIPS) was prepared by suspension polymerization by using benzoyl peroxide (BPO) and poly(vinyl alcohol) (PVA) as an initiator and stabilizer, respectively. Natural rubber (NR) was used as a toughness modifier due to the excellent tensile and tack properties. The structure of the obtained product was characterized by using the attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) and proton nuclear magnetic resonance spectroscopy (^{1}H-NMR). The investigation of the effect of significant parameters on %ST conversion, HIPS beads size and mechanical properties was divided into two parts: univariate and 2^3 factorial design experiment. The studied parameters of the green HIPS production were BPO, NR, and PVA concentrations and reaction time including agitation rate on %ST conversion, beads size of green HIPS and mechanical properties of the sheeted green HIPS. The fractural surface of the green HIPS specimens obtained from the tensile testing was observed by using transmission electron microscope (TEM) and scanning electron microscopy (SEM). The thermal properties such as glass transition temperature (T_g) and decomposition temperature of polystyrene (PS), NR and HIPS were investigated by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

4.1 Characterization of structure of green HIPS

4.1.1 ATR FT-IR spectroscopic characterization

The functional groups of the PS, NR and obtained green HIPS were identified using ATR FT-IR spectroscopy as shown in Figure 4.1. The ATR FT-IR spectra of the obtained green HIPS (loading 5 wt% NR) had CH stretching vibration at 2,920 and 2,850 cm^{-1}, C-H bending of CH_2 vibration at 1,450 cm^{-1} and =C-H out of plane

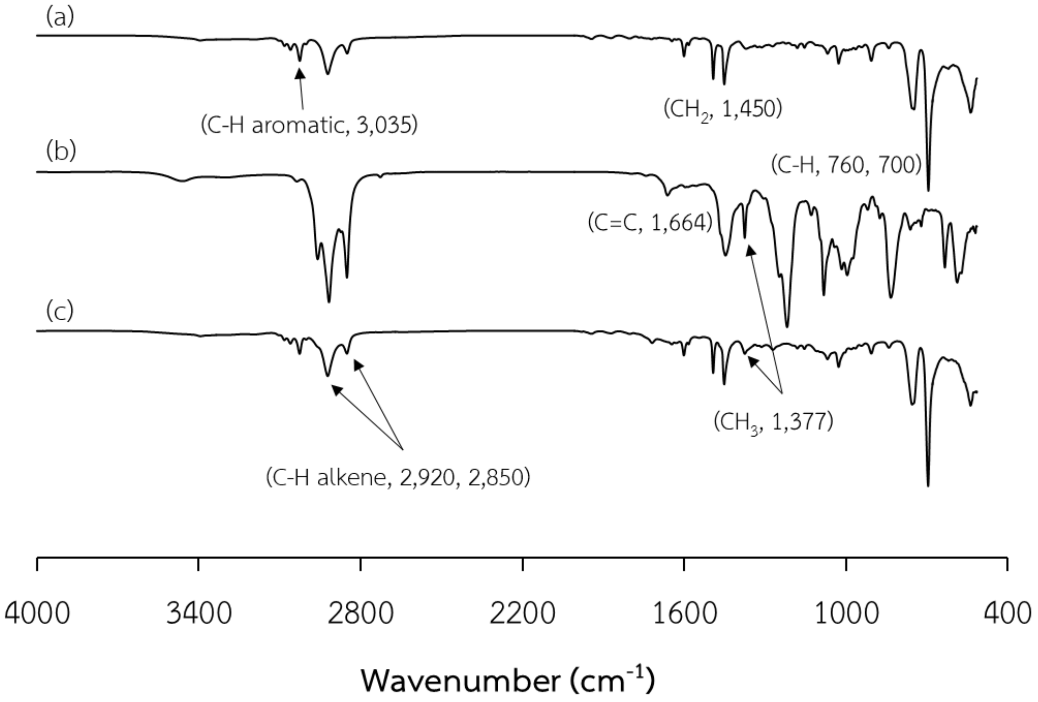


Figure 4.1 ATR FT-IR spectra of (a) PS, (b) NR and (c) green HIPS (NR 3 wt%).

within the same range of wavenumber. The C-H stretching of aromatic ring peaks at 3,035, 1,601, 1,490, 760 and 700 cm^{-1} and C=C in aromatic ring at 2,000-1,660 cm^{-1} which are characteristic peaks of PS were also found {[Kaewtatip K. et al., (2008)] and [Lin Y. et al., (2011)]}. Moreover, the new signal appeared at 1,377 cm^{-1} attributed to the CH_3 deformation of NR was presented in the green HIPS spectrum [Nallasamy P. et al., (2004)]. This result confirmed that the suspension polymerization method could successfully insert NR portion into the PS matrix for producing the green HIPS beads.

4.1.2 ^{1}H-NMR spectroscopic characterization

To confirm the ATR FT-IR result, the structure of green HIPS were analyzed using ^{1}H-NMR spectroscopy. Figure 4.2a presents the ^{1}H-NMR of PS, which

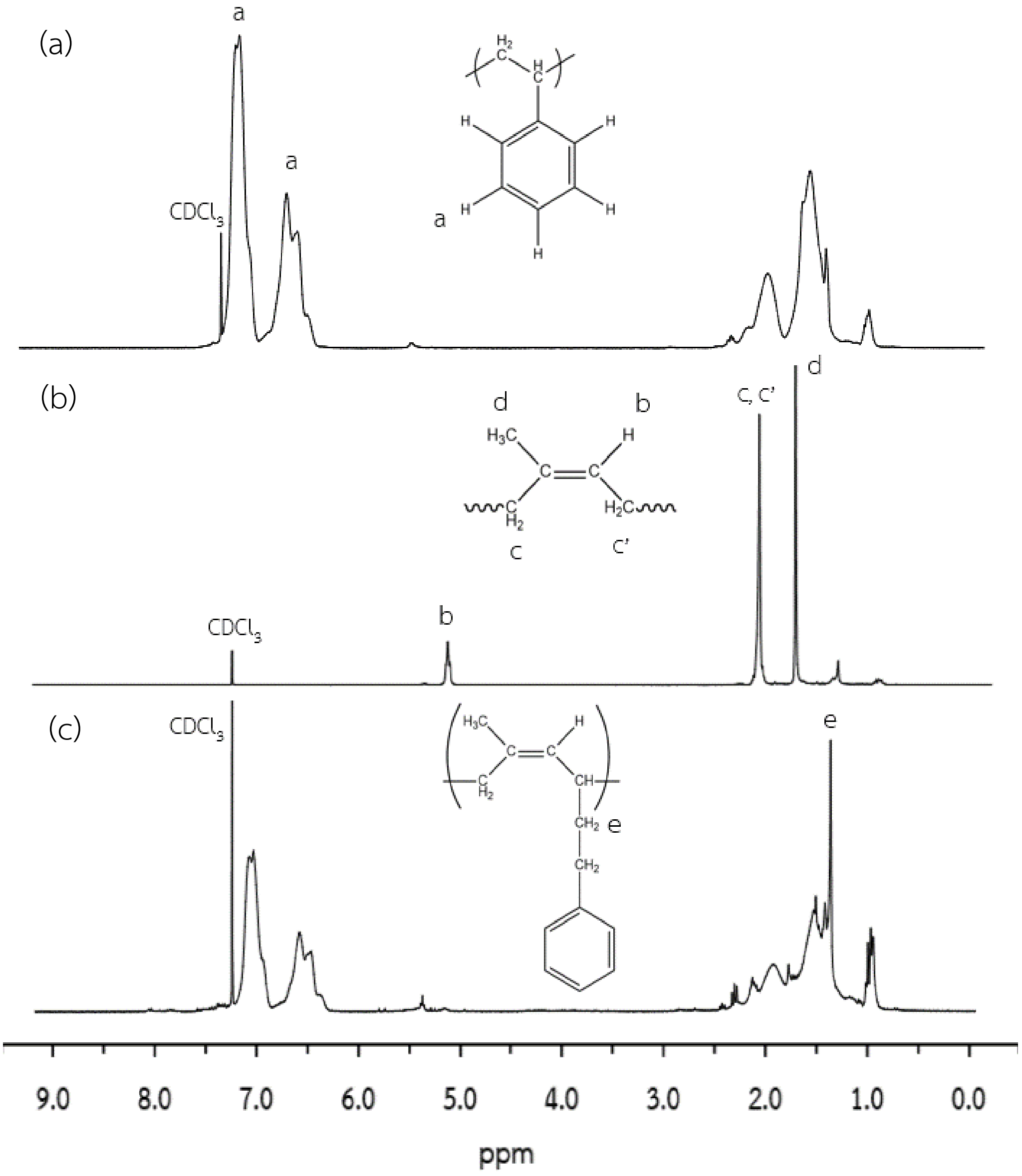


Figure 4.2 ^{1}H-NMR spectra of (a) PS, (b) NR and (c) HIPS (NR 3 wt%).

showed the important signals at 6.5-7.5 ppm assigned to the peaks of aromatic protons (a). The ^{1}H-NMR of NR (Figure 4.2b) showed two major signals at 1.64 (-CH_3) and 2.01 ppm (-CH_2-) that were attributed to the aliphatic group (d, c and c') and at 5.15 ppm (-HC=CH-) that was attributed to the cis-olefinic proton (b). After the suspension polymerization of PS in the presence of NR, the green HIPS had new signals at 0.8-1.5 ppm defined as the overlaps signals of methylene and methane protons obtained from ST and NR, respectively, and their peak intensity tended to be decreased (Figure 4.2c) {[Pisuttisap A. et al., (2013)] and [Sondari D. et al., (2010)]}. Thus, this result implied that the ST was grafted onto the NR during the suspension polymerization.

4.2 Univariate experiment

The univariate experiment was carried out in this research in order to individually investigate the influence studied parameters on %ST conversion, HIPS beads size and mechanical properties for the obtained green HIPS and compared with the neat PS. The central condition applied for the univariate experiments was 0.6 wt% BPO and 3 wt% NR based on ST content, 1.6 % (w/v) PVA based on volume of DI water and 350 rpm agitation rate at 90 °C for 6 h as shown in Table 3.3. The monomer/water was kept constant at 1/6 (w/w).

4.2.1 Effect of BPO concentration on appearances, bead size and shaping ability of PS

Before preparing the green HIPS, the effect of BPO on the bead size and ability for sheeting of PS was firstly investigated. The BPO concentration was varied from 0.3 to 2.0 wt% based on ST content. The ST monomer was kept constant at 60 g under 350 rpm at 90 °C for 6 h. Table 4.1 showed %ST conversion and PS appearance (in bead and sheet forms). It was indicated that the increase in the BPO concentration in the range of 0.3-0.8 wt% slightly increased %ST conversion (95-97%). It is possible that the higher initiator concentration produced the higher amount of free radicals. When the initiator concentration was above 0.8 wt%, %ST conversion tended to be decreased. This was caused by combination of free radicals [Charmondusit K. et al., (1998)]. In addition, it could be explained that the higher

Table 4.1 Effect of BPO concentration on %ST conversion and PS appearance in the bead and sheet forms

BPO concentration (wt%)	%ST Conversion*	PS appearance	
		Bead form	Sheet form***
0.3	94.9 (2.00)**		
0.6	95.3 (0.71)		
0.8	96.7 (0.58)		
1.0	89.7 (1.16)		
2.0	90.3 (0.61)		

* Condition: ST = 60 g, [PVA] = 0.1 % (w/v), stirring speed = 350 rpm at 90 °C for 6 h.

** The number in parenthesis is a standard deviation.

*** Samples were sheeted by compression mold at 200 °C and 120 kg/cm^2.

initiator concentration produced the higher amount of free radicals resulting in the shorter polymer chains [Charmondusit K. et al., (1998)] Therefore, the PS bead size decreased with increasing the initiator concentration as shown in Table 4.1 and Figure 4.3. Figure 4.3 showed that the mass fraction of the PS bead size at <1.18 mm increased from 0.10 to 0.82 with increasing the BPO concentration from 0.3 to 2.0 wt%, while the mass fraction of the larger PS bead size between 1.18-2.36 mm decreased from 0.75 to 0.18 with increasing the initiator concentration from 0.6 to 2.0 wt%.

The effect of BPO concentration on the shaping ability of PS product was also studied. The temperature and the pressure for compressing the PS sheet was at 200 °C and 120 kg/cm^2, respectively. From Table 4.1, it was found that when the BPO concentration was 0.3 wt%, the products showed the air bubbles over the obtained sheet. Moreover, the overdose of BPO (>0.8 wt% based on ST monomer) tended to produce the cracked PS sheets. This result was similar to the previous report which the PS-*g*-PB polymer contained with 2.1 wt% BPO gave the brittle product with low tensile strength and elongation at break [Ronco L.I. et al., (2015)]. It was possible

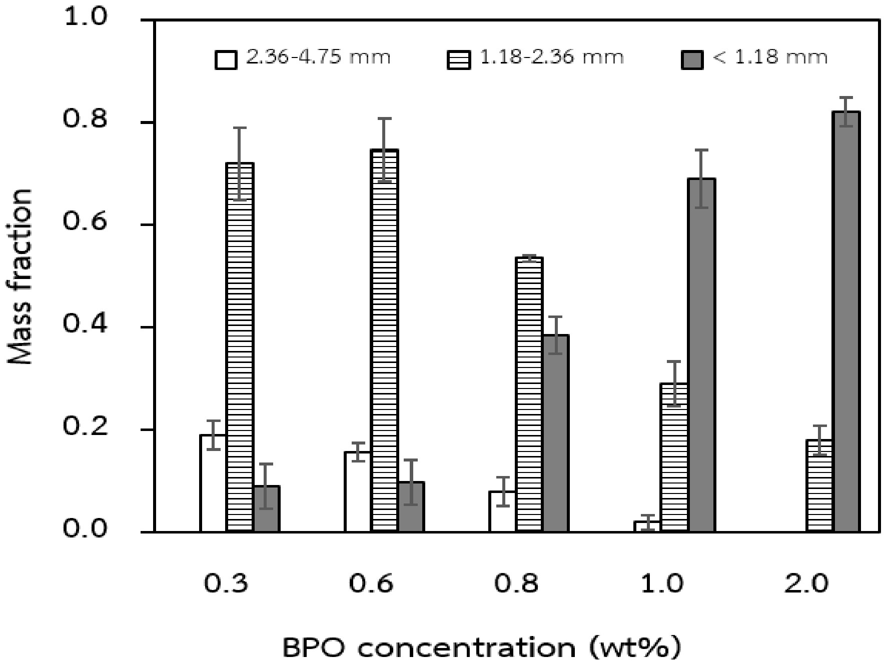


Figure 4.3 Effect of BPO concentration on the PS bead size distributions (Condition: ST = 60 g, [PVA] = 0.1 % (w/v), stirring speed = 350 rpm at 90 °C for 6 h).

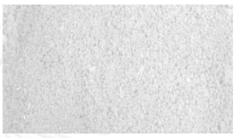
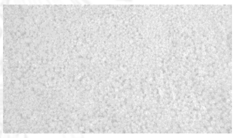
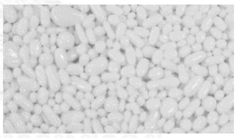
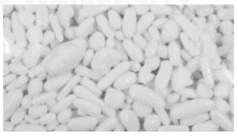
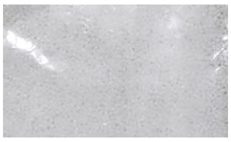
to explain that the higher BPO concentration produced the high free radicals owing to many shorter polymer chains [Charmondusit K. et al., (1998)]. The lower BPO concentration produced the bigger PS bead size than the higher BPO concentration. Some portion of water might be blocked inside the PS beads resulting in the formation of bubble inside the PS sheet due to the evaporation during compression in the hot compression mold. The BPO concentration at 0.6 wt% produced the fine, transparent and smooth PS sheet. Therefore, the BPO concentration at 0.6 wt% was selected to produce the green HIPS beads in further experiments.

4.2.2 Effect of NR content on appearances, bead size and mechanical properties of green HIPS

4.2.2.1 Green HIPS appearance

The effect of NR content in the range of 1-6 wt% based on ST monomer on %ST conversion, bead size and appearance of green HIPS was shown in Table 4.2. The production of green HIPS was carried out by using 0.6 wt% BPO based on ST content and 1.6 % (w/v) PVA based on the volume of DI water. This system was under 350 rpm agitation rate and 90 °C for 6 h. It was observed that the increase in the NR content from 1 to 3 wt% did not affect %ST conversion (93-95%), whereas the increase in the NR content from 3 to 5 wt% slightly decreased the %ST conversion from 95.1 to 91.2%. It was possible that the viscosity of the polymeric syrup increased with increasing NR content over 4 wt% resulting in the difficult mobility to polymerize ST monomer. Moreover, the addition of 6 wt% NR caused very high viscosity of the polymeric syrup. The polymer formed was clustered and fused into a big lump. As the solution viscosity of the rubber increased, it became more difficult to break the rubber phase down into small droplets. In that limit, the system completely failed to invert [Bucknall C.B., (1977)]. Therefore, the suspension polymerization technique could not synthesize the green HIPS when NR content above 6 wt% was applied.

Table 4.2 Effect of NR content on %ST conversion and green HIPS appearance in the bead and sheet forms

NR content (wt% based on ST)	%ST Conversion*	High impact polystyrene appearance	
		Bead form	Sheet form****
1	94.2 (0.52)**		
2	93.2 (0.38)		
3	95.1 (0.23)		
4	92.9 (0.88)		
5	91.2 (1.10)		
6	NA***	-	-
HIPS commercial	-		

* Condition: ST = 60 g, [BPO] = 0.6 wt%, [PVA] = 1.6 % (w/v), stirring speed = 350 rpm at 90 °C for 6 h.

** The number in parenthesis is a standard deviation.

*** NA = could not be synthesized.

**** Samples were sheet using by compression mold at 200 °C and 120 kg/cm^2.

Figure 4.4 showed the effect of NR content on the green HIPS bead size distribution. It indicated that the mass fraction of the HIPS bead size as <1.18 mm decreased from 0.35 to 0.10 with increasing the NR content from 1 to 3 wt%. Furthermore, the bead size of green HIPS containing 4 wt% NR was bigger than 1.18 mm. Moreover, the higher NR loading as 5 wt% induced the green HIPS bead size bigger than 4.75 mm. This could be explained that the high NR content could promote the higher rates of particle nucleation and coalescence due to the high viscosity of polymeric syrup [Cunha F. et al., (2013)].

The effect of NR contents on the shaping ability of green HIPS product was shown in Table 4.2. The temperature for compressing the HIPS sheet was 200 °C under the pressure of 120 kg/cm^2. All of green HIPS sheets containing various NR content in the range of 1-5 wt% produced yellow transparency sheets. The green HIPS sheets containing higher NR contents showed the more yellowness than the neat PS sheet.

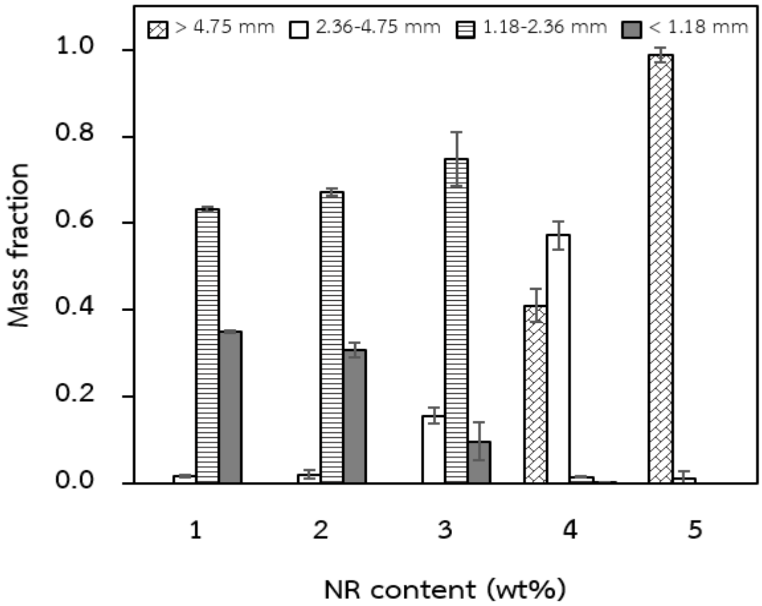


Figure 4.4 Effect of NR content on the green HIPS bead size distributions (Condition: ST = 60 g, [BPO] = 0.6 wt%, [PVA] = 1.6 % (w/v), stirring speed = 350 rpm at 90 °C for 6 h).

4.2.2.2 Effect of NR content on mechanical properties of green HIPS

The effect of NR content in the range of 1-5 wt% on the mechanical properties of the green HIPS was shown in Figure 4.5. The studied mechanical properties were tensile strength, elongation at break, impact strength and hardness. For the tensile strength as shown in Figure 4.5a, it was shown that the increase in the NR content in the range of 1-5 wt% enhanced the tensile strength from 13.0 MPa to 20.4 MPa due to the excellent tensile property of NR dispersed in the PS matrix. The previous reports were observed that BPO were more effective in the grafting efficiency of rubber particles which was classified as “internal grafting”. This internal grafting gave the small rubber particles with small occlusions of the PS/PB-*g*-PS that improved the storage modulus of rubber particles {[Gao G. et al., (2007)] and [Soto G. et al., (2004)]}. Moreover, the increase in the NR content in the range of 1-3 wt%, increased the elongation at break of the obtained green HIPS sheet. However, the NR content higher than 3 wt% did not affect its elongation at break. This might be explained that the crosslinked NR particles was dispersed in PS matrix of the obtained green HIPS leading the reduction of rubber elasticity. Furthermore, the obtained green HIPS was more plasticity than elasticity since this synthesis technique could add only 5 wt% of NR in the PS matrix. This result was similar to the observation of the PS-NR blends [Neoh S. et al., (2004)]. At 5 wt% NR loading, the green HIPS sheet had high tensile strength with low elongation at break (0.2-0.4%) as shown in Figure 4.5a and 4.5b. This implied that the green HIPS had high brittleness. Above 5 wt% NR loading, Neoh et al. [Neoh S. et al., (2004)] observed that the tensile strength of green HIPS tended to decrease with increasing the elongation at break.

For the hardness (Figure 4.5c), it was observed that the hardness of the green HIPS sheet slightly increased from 74.0 to 84.3 of shore B with increasing the NR content from 1 to 5 wt%. This result was conform to the tensile result that the addition of NR caused the high crosslink of NR particles due to the increase in the grafting site.

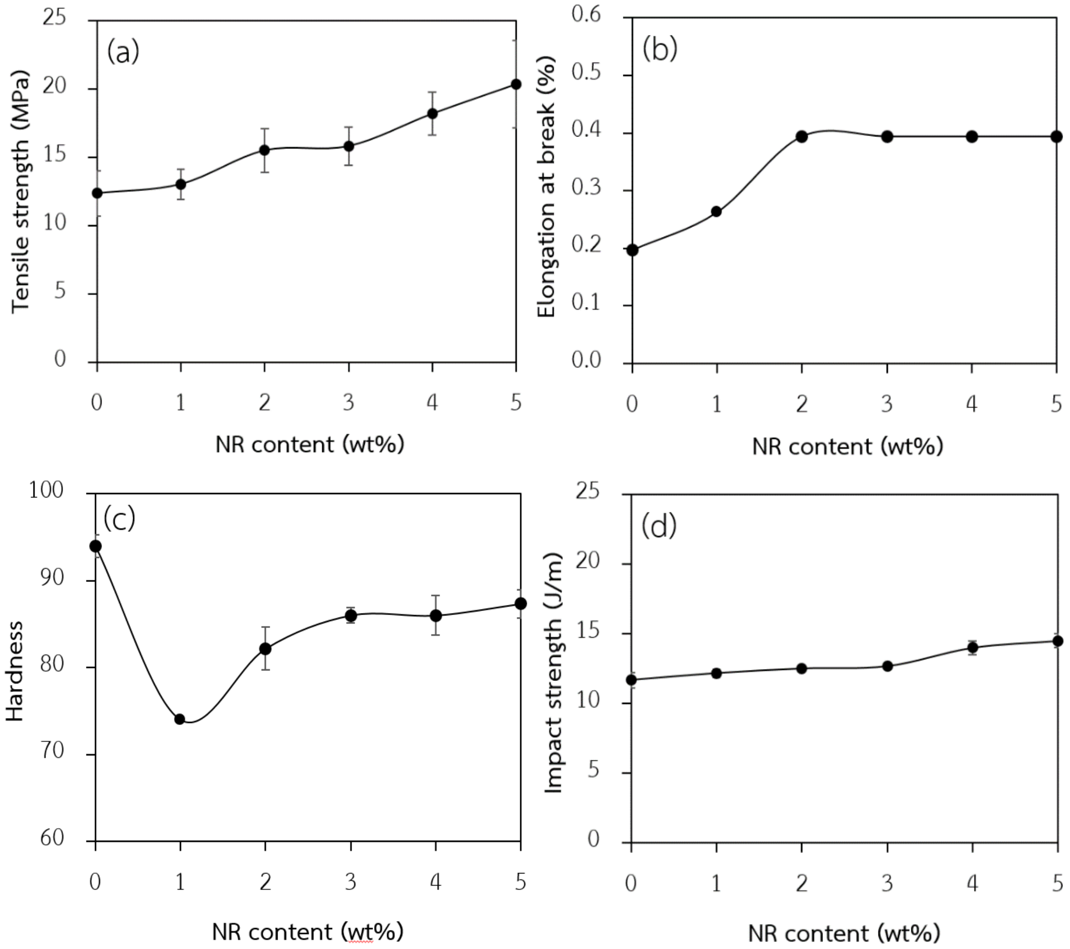


Figure 4.5 Effect of NR content on (a) tensile strength, (b) elongation at break, (c) hardness and (d) impact strength of the green HIPS sheets containing 3 wt% NR.

To consider the impact strength, Figure 4.5d showed that the green HIPS sheet containing 5 wt% NR had the higher impact strength (14.5 J/m) than the neat PS also prepared by suspension polymerization (11.7 J/m). Nevertheless, the commercial HIPS had much higher impact strength (83.8 J/m) than the synthesized one. This result was possibly related to very low amount of NR inducing the small rubber particle size dispersed inside the obtained green HIPS. The morphology of the green HIPS sheet after tensile testing was attested by TEM as shown in Figure 4.6 and explained in the next section.

4.2.2.3 The effect of NR content on morphology of green HIPS

The previous literatures indicated that the increase in the NR content could enhance the impact energy absorption of the brittle materials. However, the real criterion defining impact resistance is the volume fraction of the dispersed phase, the grafted PS chains and the free PS contained in the particle occlusion [Meira G.R. et al., (2007)]. General morphologies of HIPS are salami (PS multi- occlusion) and core-shell (PS mono-occlusion). Salami morphology particles or an adequate combination of submicrometer rubber particles [Zhu L.D. et al., (2013)] contribute the high volume fraction. Salami morphology is non-transparent due to the difference in the refractive index between PS and rubber phases and the relatively large particle sizes with respect to the visible wavelengths [Meira G.R. et al., (2007)]. The commercial HIPS beads was sheeted by using a compression molding machine at 200°C with a pressure of 120 kg/cm^2. The condition was also appropriate for sheeting the green HIPS. It showed that the commercial HIPS sheet was white, whereas the green HIPS containing various NR content in the range of 1-5 wt% NR produced yellow transparency sheets (Table 4.2).

Figure 4.6 presented the fractural surface obtained from tensile specimens of the green HIPS containing 3 and 5 wt% NR (Figure 4.6a-4.6b, respectively) and the commercial HIPS (Figure 4.6c) by using TEM. Two-phase morphology of crosslinked rubber particles (dark color) dispersed in the PS matrix (light color) was observed. Figure 4.6a and 4.6b indicated the crazes appeating around a rubber particle in the fractural surface. For the commercial HIPS (Figure 4.6c), its morphology was salami type having the large volume fraction of rubber particles resulting in the high impact resistance (83.8 J/m) since the rubber particles are craze terminators to prevent the growth of very large crazes. This multiple crazes occurring throughout rubber-modified materials induces the high energy absorption in the fracture tests [Perkins W.G., (1999)]. The optimal rubber particle size in the range of 1–5 μm could improve the impact resistance. Moreover, the reduction of both diameter and volume fraction of the rubber particles in the obtained green HIPS leading the tensile rises as the impact falls [Bucknall C.B., (1977)]. This indicated that the small rubber particles in the green HIPS less than 1 μm had more effect on the tensile properties of the green HIPS than its impact property.

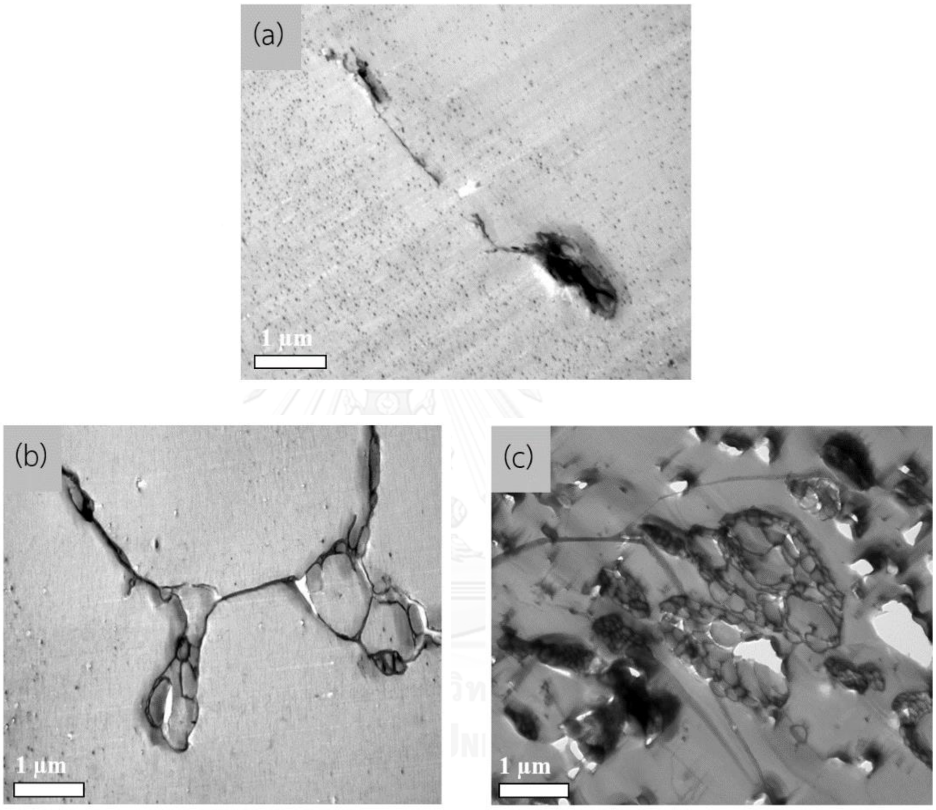


Figure 4.6 TEM micrographs of the tensile fractural surface of the obtained green HIPS containing various NR contents: (a) 3 wt%, (b) 5 wt% and (c) commercial HIPS.

Figure 4.7 shows the fractural surface of tensile specimens by SEM to explain the surface morphology of the 3 and 5 wt% NR loading in the green HIPS. The SEM of pure PS as shown in Figure 4.6a had a large crazes that are the characteristic morphology of the brittle materials. The addition of NR to produce the green HIPS indicated the hackle-like texture (Figure 4.6b and 4.6c), which is classified as a ductile failure characteristics [Neoh S. et al., (2004)]. This result implied that the green HIPS had rubber granules dispersed in the PS matrix leading the rougher surface area [Vilaplana F. et al., (2007)]. The surface roughness provided the more energy during the tensile testing [Sekharan R.V. et al., (2012)]. Therefore, the presence of NR in the PS matrix reduced the rampant crack propagation in the specimens.

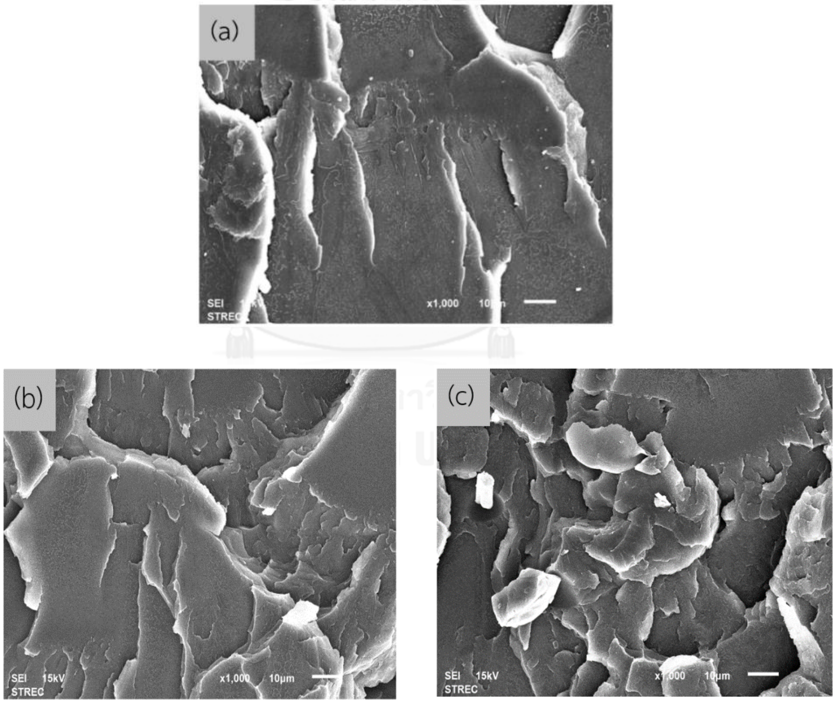


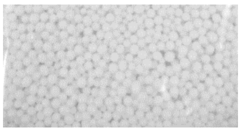
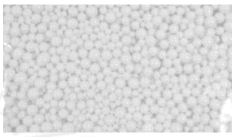
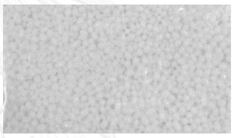
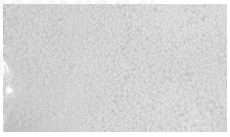
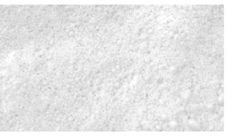
Figure 4.7 SEM micrographs of the tensile fractural surface of (a) pure PS and green HIPS containing various NR contents; (b) 3 and (c) 5 wt% produced by suspension polymerization.

4.2.3 Effect of PVA concentration on appearances, bead size and mechanical properties of green HIPS

4.2.3.1 Green HIPS appearance

The effect of PVA concentration on %ST conversion, bead size and appearance of the green HIPS was shown in Table 4.3. The range of PVA concentration was varied between 0.1-3.0 % (w/v) based on DI water volume. The ST, BPO and NR contents were kept constant at 60 g, 0.6 wt% and 3 wt%, respectively, under 350 rpm agitation rate at 90 °C for 6 h. It was found that the increase in the PVA concentration from 0.1 to 2.0 wt% provided %ST conversion as 93-95%. When PVA concentration increased from 2.0 to 3.0 % (w/v), the %ST conversion decreased from 94.0% to 81.7%. It could be explained that the presence of PVA-stabilizer decreased the interfacial surface tension resulting in the higher solubility of the monomer in the aqueous phase. Consequently, the high PVA concentration reduced monomer and polymer droplets [Nanjwade B.K. et al., (2010)]. Thus, it was possible that the PVA blocked the mobility of ST monomer for polymerization. When the PVA concentration increased from 0.1 to 3.0 % (w/v) as shown in Figure 4.8, the mass fraction of green HIPS bead with a the smallest size (<1.18 mm) increased from 0.01 to 0.60, while the mass fraction of green HIPS bead with the biggest size (>4.75 mm) decreased from 0.62 to 0.00. Moreover, it was observed that the green HIPS bead used 0.1 % (w/v) PVA almost gave the larger bead size than 2.36 mm. Nevertheless, the green HIPS bead that used 3.0 % (w/v) PVA gave the smaller bead than 2.36 mm. It was possible to explain that the higher PVA concentration could hindrance the rates of particle nucleation and coalescence leading the occurrence of smaller syrup droplets [Kiatkamjornwong S. et al., (2001)].

Table 4.3 Effect of PVA concentration on %ST conversion and green HIPS appearance in the bead and sheet forms

PVA concentration (% w/v of water media)	%ST conversion*	High impact polystyrene appearance	
		Bead form	Sheet form***
0.1	92.6 (1.59)**		
0.5	93.1 (0.38)		
1.0	93.1 (0.53)		
1.6	95.1 (0.23)		
2.0	94.0 (1.47)		
2.5	88.2 (0.64)		
3.0	81.7 (1.31)		

* Condition: ST = 60 g, [BPO] = 0.6 wt%, [NR] = 3 wt%, stirring speed = 350 rpm at 90 °C for 6 h.

** The number in parenthesis is a standard deviation.

*** Samples were sheet using by compression mold at 200 °C and 120 kg/cm^2.

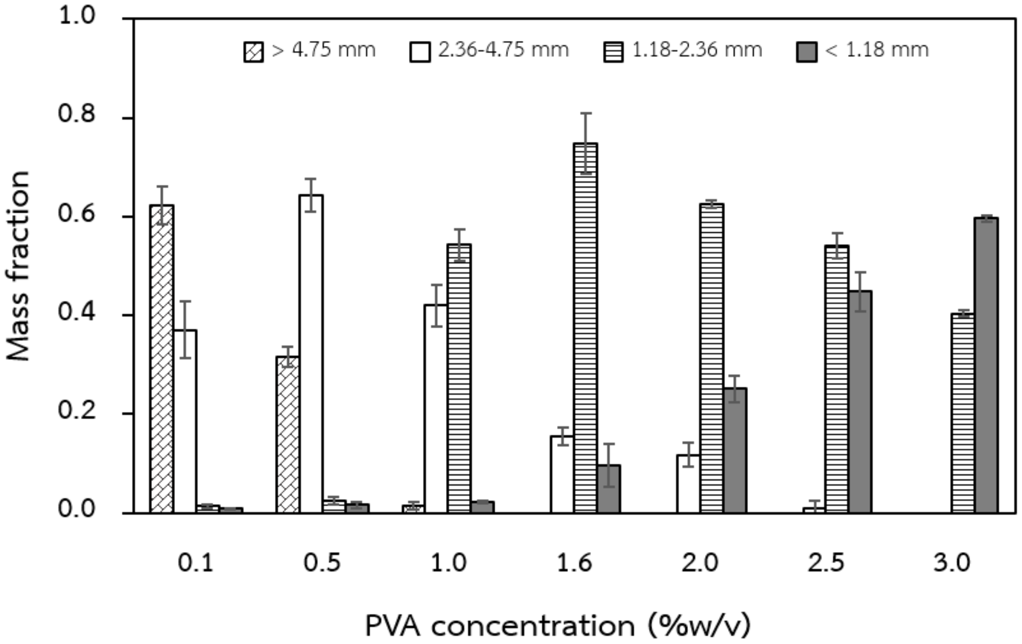


Figure 4.8 Effect of PVA concentration on the green HIPS bead size distributions (Condition: ST = 60 g, [BPO] = 0.6 wt%, [NR] = 3 wt%, stirring speed = 350 rpm at 90 °C for 6 h).

The effect of PVA concentration on the shaping ability of HIPS product also showed in Table 4.3. The temperature and pressure for compressing the HIPS sheet were carried out at 200 °C and 120 kg/cm^2. The result showed that all samples were yellowness transparency caused by the effect of NR.

4.2.3.2 Effect of PVA concentration on mechanical properties of green HIPS

Figure 4.9 shows the effect of PVA concentration in the range of 0.1-3.0 % (w/v) on the mechanical properties of the green HIPS. From Figure 4.9a and 4.9b, they indicated that the increase in the PVA concentration from 0.1 to 3.0 % (w/v) increased the tensile strength from 11.0 to 19.7 MPa with slightly increasing the elongation at break from 0.26 to 0.39%. Above 1.0 % (w/v) PVA, the elongation at break

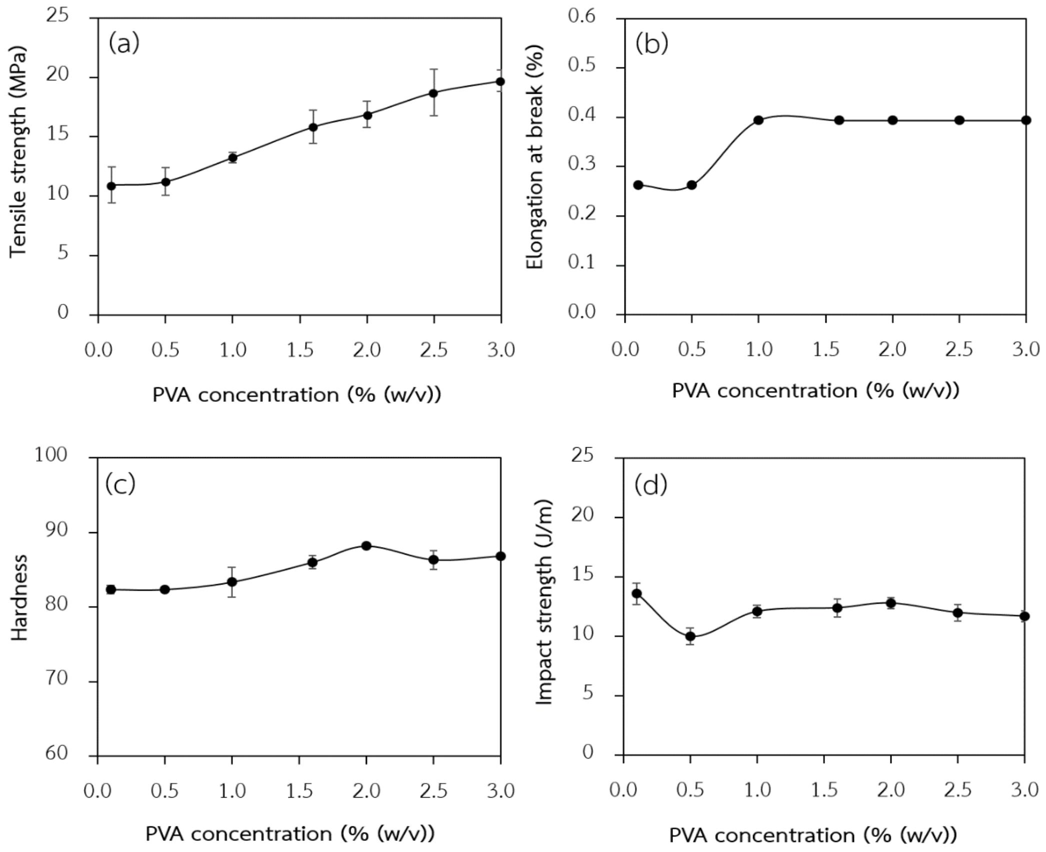


Figure 4.9 Effect of PVA concentration on (a) tensile strength, (b) elongation at break, (c) hardness and (d) impact strength of the green HIPS sheets containing 3 wt% NR.

of the green HIPS was independent on the PVA concentration. The higher PVA concentration caused the smaller particles and lower volume fraction of NR particle resulting in the higher stiffness of the green HIPS. This indicated that the green HIPS was more rigid materials with increasing the PVA concentration.

From Figure 4.9c, the increase in the PVA concentration from 0.1 to 3.0 % (w/v) slightly increased the hardness of the green HIPS sheets from 82.3 to 86.8 shore B. For the impact strength as shown in Figure 4.9d, the green HIPS produced from the use of 0.1 % (w/v) PVA concentration showed the highest impact strength. However, the increase in PVA concentration decreased the impact strength. It could be explained that the decrease in the HIPS bead size in the section 4.2.3.1 might decrease the NR particle size. Therefore, the obtained green HIPS had low volume fraction of NR particles leading the high young’s modulus, high tensile strength and low impact strength [Bucknall C.B., (1977)].

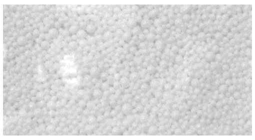
4.2.4 Effect of agitation rate on appearances, bead size and mechanical properties of green HIPS

4.2.4.1 Green HIPS appearance

The effect of agitation rate in the range of 250-450 rpm on %ST conversion, bead size and appearance of green HIPS is shown in Table 4.4. The production of green HIPS was carried out by using 0.6 wt% BPO, 3 wt% NR based on ST and 1.6 % (w/v) PVA at 90 °C for 6 h. It was shown that the increase in the agitation rate from 250 to 450 rpm increased %ST conversion from 66.1 to 91.3. It could be explained that the higher shear rate produced the high interfacial area for polymerization. Furthermore, the higher agitation rate led the lower rate of particle coalescence and the smaller monomer droplet {[Cunha F. et al., (2013)] and [Kiatkamjornwong S. et al., (2001)]}. The effect of agitation rate on the HIPS bead size distribution was shown in Figure 4.10. It indicated that the mass fraction of the smallest green HIPS bead size (<1.18 mm) increased from 0.01 to 0.13 with increasing the agitation rate from 250 to 450 rpm, while the mass fraction of the green HIPS bead with the size of >4.75 mm decreased from 0.10 to 0.00.

For the effect of PVA concentration on the shaping ability of green HIPS beads is shown in Table 4.4. The result indicated that all samples showed the yellow transparency sheet due to the effect of NR phase dispersed in the PS matrix.

Table 4.4 Effect of agitation rate on %ST conversion and green HIPS appearance in the bead and sheet forms

Agitation rate (rpm)	%ST conversion*	High impact polystyrene appearance	
		Bead form	Sheet form***
250	66.1 (2.70)**		
350	95.1 (0.23)		
450	91.3 (0.25)		

* Condition: ST = 60 g, [BPO] = 0.6 and [NR] = 3 wt%, [PVA] = 1.6 % (w/v) at 90 °C for 6 h.

** The number in parenthesis is a standard deviation.

*** Samples were sheet using by compression mold at 200 °C and 120 kg/cm^2.

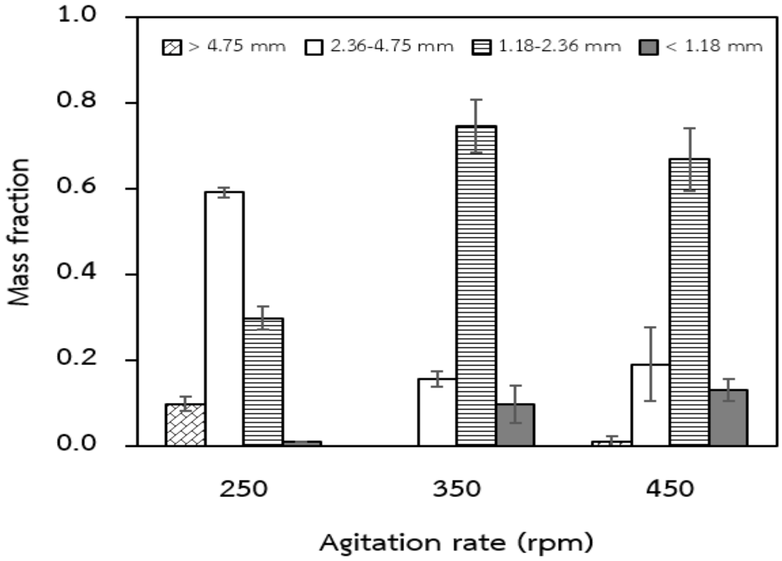


Figure 4.10 Effect of agitation rate on the green HIPS bead size distributions (Condition: ST = 60 g, [BPO] = 0.6 and [NR] = 3 wt%, [PVA] = 1.6 % (w/v) at 90 °C for 6 h

4.2.4.2 Effect of agitation rate on mechanical properties of green HIPS

The mechanical properties of green HIPS containing 3 wt% NR with various agitation rates in the range of 250-450 rpm were investigated as shown in Figure 4.11. It was found that the agitation rate drastically affected the tensile strength of the green HIPS sheet (Figure 4.11a). The highest agitation rate used in the production of the green HIPS gave the highest tensile strength value (23.3 MPa). It could be explained that the increase in the agitation rate leading the high shear

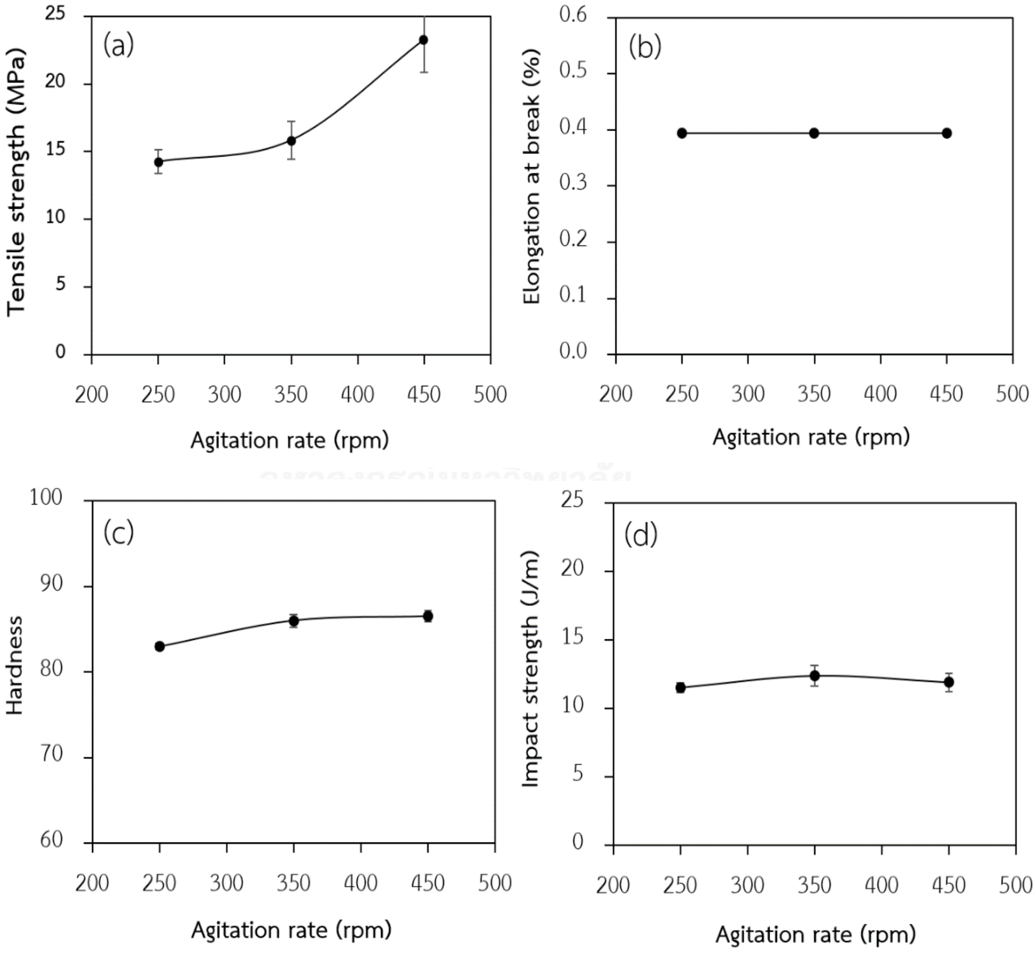


Figure 4.11 Effect of agitation rate on (a) tensile strength, (b) elongation at break, (c) hardness and (d) impact strength of the green HIPS sheets containing 3 wt% NR.

force and caused the lower rate of particle coalescence. Therefore, the obtained green HIPS had the small diameter and volume fraction of the rubber particles resulting in the higher young's modulus and tensile strength values. Bucknall [Bucknall C.B., (1977)] found that the excess agitation rates required for phase inversion resulted in the small rubber particles consisting of a single small droplet of PS enclosed within a skin of rubber (or core shell type). The larger rubber particles (or salami type) were formed by the aggregation of the smaller rubber particles at lower shear rates [Bucknall C.B., (1977)]. However, the agitation rate did not significantly influence on the elongation at break, impact strength and hardness of the green HIPS sheets. It was possible that the used of 3 wt% NR was too low to induce the elasticity properties. Hence, the obtained green HIPS still showed plasticity.

4.2.5 Effect of reaction time on appearances, bead size and mechanical properties of green HIPS

4.2.5.1 Green HIPS appearance

The effect of the reaction time varied in the range of 6-12 h on %ST conversion and green HIPS appearance (bead and sheet forms) was investigated as shown in Table 4.5. The reaction was performed by using 0.6 wt% BPO, 3 wt% NR and 1.6 % (w/v) PVA under 350 rpm at 90 °C. It was observed that the reaction time did not affect the %ST conversion and green HIPS bead size. It could be explained that the extent of initiation and propagation of copolymer increased with increasing the reaction time at the induction period (<5 h). Most of monomer was polymerized to form new polymeric radicals until this ST monomer was completely consumed to reach the maximum conversion. This result was similar to the observation for suspension polymerization of ST in the presence of gamma-radiation vulcanized natural rubber (RVNR) initiated and stabilized by BPO and PVA at 90 °C for 5 h. They showed that the %ST conversion was completed within 4 h for 0.6 wt% BPO concentration [Aiamsen P. et al., (2003)]. Moreover, the HIPS bead size distribution at various reaction times in range of 6-12 h similarly tended as shown in Figure 4.12.

Table 4.5 Effect of reaction time on %ST conversion and green HIPS appearance in the bead and sheet forms

Reaction time (h)	%ST conversion	High impact polystyrene appearance	
		Bead form	Sheet form
6	95.1 (0.23)		
8	92.8 (1.87)		
12	95.1 (0.16)		

* Condition: ST = 60 g, [BPO] = 0.6 wt%, [NR] = 3 wt%, [PVA] = 1.6 % (w/v), stirring speed = 350 rpm at 90 °C.

** The number in parenthesis is a standard deviation.

*** Samples were sheet using by compression mold at 200 °C and 120 kg/cm^2.

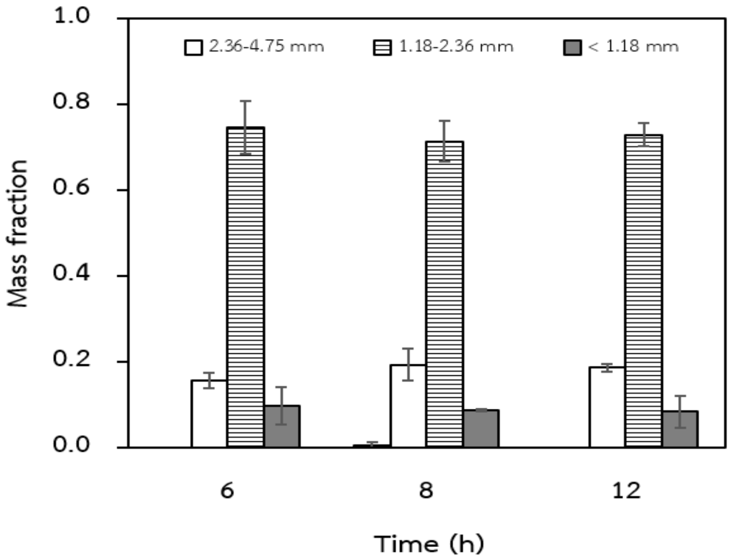


Figure 4.12 Effect of reaction times on the green HIPS bead size distributions (Condition: ST = 60 g, [BPO] = 0.6 wt%, [NR] = 3 wt%, [PVA] = 1.6 % (w/v), stirring speed = 350 rpm at 90 °C).

The effect of reaction time on the shaping ability of HIPS product was shown in Table 4.5. The temperature and pressure for compressing the HIPS sheet was at 200 °C and 120 kg/cm^2, respectively. The result presented that all samples showed the yellow sheet due to the effect of NR phase dispersed in the PS matrix.

4.2.5.2 Effect of reaction time on mechanical properties of green HIPS

Figure 4.13 shows the effect of reaction time on the mechanical properties of the green HIPS sheets. The reaction time was varied from 6 to 12 h. For the tensile strength as shown in Figure 4.12a, this value increased from 15.4 to 23.6 MPa with increasing the reaction time from 6 to 12 h. It might be explained that the increase in the reaction time might cause induce the obtained green HIPS having more high molar mass of the free PS polymer. This led the higher tensile strength [Meira G.R. et al., (2007)]. However, it observed that the reaction time did not affect the elongation at break, impact strength and hardness. This result was similar to the results from the effect of the agitation rate.

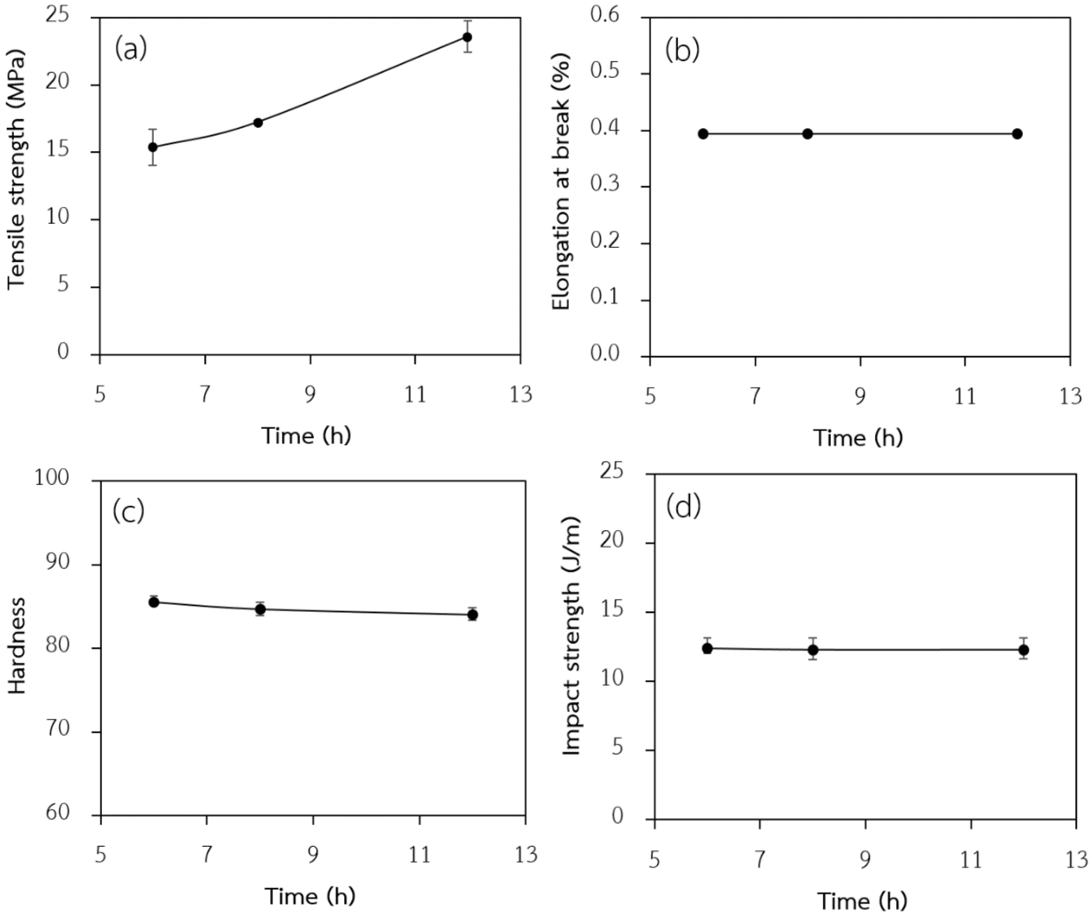


Figure 4.13 Effect of reaction time on (a) tensile strength, (b) elongation at break, (c) hardness and (d) impact strength of the green HIPS sheets containing 3 wt% NR.

4.3 2^3 factorial design experiment

Factorial design experiment was carried out in this research to investigate the influence of studied factors on the %ST conversion, green HIPS bead size and mechanical properties (tensile strength and impact resistance). To study the size of green HIPS beads, the green HIPS beads with the size of <1.18 mm was selected for the response of the significant parameters because this size provided the ease of transportation and storage. Moreover, the small size bead is easy to be melted during sheeting without trituration. The previous literatures and text book reported that rubber content and agitation rate effected on size of rubber particles and mechanical properties of HIPS. No one reported that PVA concentration effected on mechanical properties of HIPS. However, PVA played a role important to hinder the coalescence of the monomer droplet for suspension polymerization method. Therefore, NR content (A), PVA concentration (B) and agitation rate (C) were chosen to investigate the influence of studied factors on the %ST conversion, green HIPS bead size, tensile strength and impact strength of the synthesize green HIPS. The results obtained from 2^3 factorial design experiment of the production of green HIPS were shown in Table 4.6. The design matrix and the average response data obtained from two replicates were shown in Table 4.7. The 16 runs were made in random order. The analysis of these data was started by constructing a normal probability plot of the effect estimates. The table of plus and minus signs for the calculation of contrast constants for the 2^3 factorial design are shown in Appendix E. From the obtained contrasts, the 8 factorial effects estimates and the sum of squares are shown in Appendix E.

Table 4.6 Results from 2^3 factorial design experiment for the production of green HIPS

Exp.	Design Factor			%ST conversion	Mass fraction*	Tensile strength (MPa)	Impact strength (J/m)
	NR (wt%)	PVA (%w/v)	AR (RPM)				
HIPS 01	1	1	300	93.4	0.24	12.2	11.5
HIPS 02	1	1	300	91.1	0.13	9.7	11.5
HIPS 03	4	1	300	86.2	0.00	14.6	11.5
HIPS 04	4	1	300	90.5	0.00	15.4	12.0
HIPS 05	1	2	300	93.5	0.68	11.6	11.0
HIPS 06	1	2	300	96.9	0.66	11.3	11.0
HIPS 07	1	1	400	92.9	0.32	13.0	11.5
HIPS 08	1	1	400	95.4	0.45	11.2	11.5
HIPS 09	4	2	300	93.2	0.06	17.6	12.0
HIPS 10	4	2	300	93.5	0.00	17.0	12.5
HIPS 11	4	1	400	93.2	0.05	17.5	12.5
HIPS 12	4	1	400	91.1	0.01	18.3	12.0
HIPS 13	1	2	400	93.7	0.84	12.0	11.5
HIPS 14	1	2	400	95.6	0.74	14.9	11.5
HIPS 15	4	2	400	93.4	0.08	21.5	13.5
HIPS 16	4	2	400	93.3	0.10	20.8	13.5

* Mass fraction of green HIPS beads with the size of <1.18 mm.

Table 4.7 Design matrix of 2^3 factorial design experiment for the production of green HIPS

Exp.	Run label	Design Factor			%ST conversion	Mass fraction*	Tensile strength (MPa)	Impact strength (J/m)
		A	B	C				
HIPS 01	(1)	-	-	-	92.2 (1.6)**	0.19 (0.1)	11.0 (1.8)	11.5 (0.0)
HIPS 02	a	+	-	-	88.4 (3.0)	0.00 (0.0)	15.0 (0.6)	11.8 (0.4)
HIPS 03	b	-	+	-	95.2 (2.4)	0.67 (0.0)	11.5 (0.2)	11.0 (0.0)
HIPS 04	c	-	-	+	94.2 (1.8)	0.39 (0.1)	12.1 (1.3)	11.5 (0.0)
HIPS 05	ab	+	+	-	93.3 (0.3)	0.30 (0.0)	17.3 (0.4)	12.3 (0.4)
HIPS 06	ac	+	-	+	92.2 (1.5)	0.03 (0.0)	17.9 (0.6)	12.3 (0.4)
HIPS 07	bc	-	+	+	94.7 (1.4)	0.79 (0.1)	13.5 (2.1)	11.5 (0.0)
HIPS 08	abc	+	+	+	93.3 (0.1)	0.09 (0.0)	21.2 (0.5)	13.5 (0.0)

* Mass fraction of green HIPS beads with the size of <1.18 mm.

** The number in parenthesis is a standard deviation.

Figure 4.14 showed the normal probability plots of these effects. The effects following the line were negligible, whereas the important effects influencing the system were far from the straight line. For the %ST conversion, it was observed that the A and B factors only affected on %ST conversion, whereas A and B including C factors were significant on the mass fraction of the target size, tensile strength and impact strength of the green HIPS sheets.

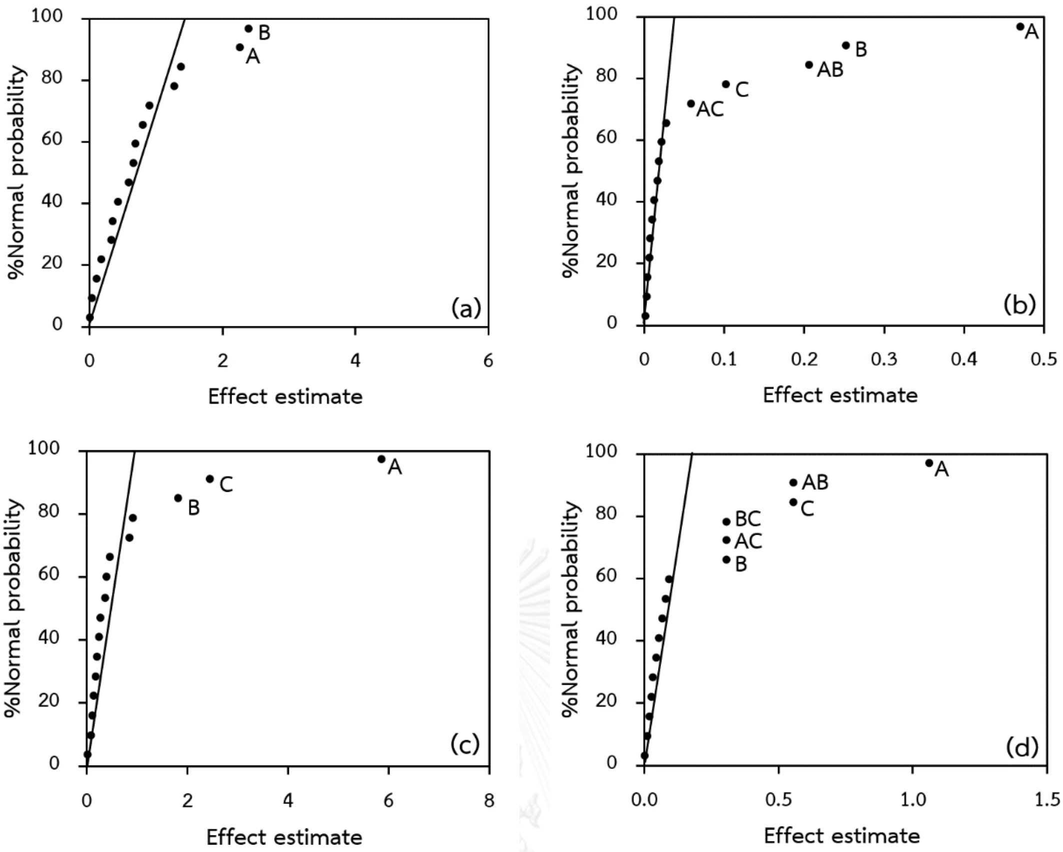


Figure 4.14 The normal probability plots of effect estimates on (a) %ST conversion, (b) mass fraction of green HIPS beads with the size of <1.18 mm (c) tensile strength and (d) impact strength.

The analysis of variance (ANOVA) of %ST conversion, mass fraction of green HIPS bead with the size of <1.18 mm and mechanical properties (tensile strength and impact resistance) was summarized in Table 4.8. The F test statistic was used to evaluate whether a factor has a significant effect ($F_0 > F_{\alpha,\nu_1,\nu_2}$ where α = 95% confidence interval or 0.05; ν_1 = degree of freedom for model and. ν_2 = degree of freedom for insignificant factors or error). This F values for each model and factors were obtained from the table of percentage points of the F distribution (Appendix Table IV in Montgomery, 2001). For example, the F_0 value of %ST conversion model (7.06) was higher than $F_{0.05,4,11}$ (3.18). Thus, this result was confirmed that A and B factors were slightly significant factor on %ST conversion. For mass fraction model,

F_0 (102.41) has more value than $F_{0.05,5,10}$ (3.33). Therefore, it is concluded that the bead size model is significant. This method is used to verify the significant of all models and selected factors as shown in Table 4.8.

Table 4.8 Analysis of variance for 2^3 factorial design experiment for the production of green HIPS

Model term	Sum of square	Degree of freedom	Mean square	F_0	F_{α,v_1,v_2} (F_{table})
1) %ST conversion					$F_{0.05,4,13}$
Model	43.75	4	10.94	7.06	3.18
					$F_{0.05,1,13}$
A	20.66	1	20.66	13.33	4.67
B	23.09	1	23.09	14.90	4.67
Error	20.20	13	1.55		
Total	63.95	15			
2) Mass fraction of green HIPS beads with the size of <1.18 mm					$F_{0.05,5,10}$
Model	1.34	5	0.27	102.41	3.33
					$F_{0.05,1,10}$
A	0.88	1	0.88	337.90	4.96
B	0.24	1	0.24	91.82	4.96
C	0.04	1	0.04	16.07	4.96
AB	0.16	1	0.16	61.19	4.96
AC	0.01	1	0.01	5.06	4.96
Error	0.03	10	0		
Total	1.37	15			

* A = NR content (wt% based on ST monomer), B = PVA concentration (% (w/v) based on volume of DI water) and C = agitation rate (rpm).

Table 4.8 Analysis of variance for 2^3 factorial design experiment for the production of green HIPS (continue)

Model term	Sum of square	Degree of freedom	Mean square	F_0	F_{α,v_1,v_2} (F_{table})
3) Tensile Strength					$F_{0.05,3,12}$
Model	174.29	3	58.10	39.79	3.49
					$F_{0.05,1,12}$
A	135.72	1	135.72	92.96	4.75
B	14.06	1	14.06	9.63	4.75
C	24.50	1	24.50	16.78	4.75
Error	17.54	12	1.46		
Total	191.86	15			
4) Impact strength					$F_{0.05,6,9}$
Model	8.34	6	1.39	34.75	3.37
					$F_{0.05,1,9}$
A	4.84	1	4.84	121.00	5.12
B	0.36	1	0.36	9.00	5.12
C	1.21	1	1.21	30.25	5.12
AB	1.21	1	1.21	30.25	5.12
AC	0.36	1	0.36	9.00	5.12
BC	0.36	1	0.36	9.00	5.12
Error	0.39	9	0.04		
Total	8.73	15			

* A = NR content (wt% based on ST monomer), B = PVA concentration (% (w/v) based on volume of DI water) and C = agitation rate (rpm).

The results obtained from the calculation of effect estimate and coefficient estimate including their standard errors is presented in Table 4.9. It showed that the increase in the NR content gave the negative effect for %ST conversion, mass fraction of green HIPS beads with the size of <1.18 mm. It could be explained that the higher NR content might cause the higher viscosity of polymeric syrup resulting in the difficult mobility to polymerize ST monomer and difficult to break the rubber phase down to small green HIPS droplets. However, the tensile and impact strength of green HIPS increased with increasing NR content due to the excellent mechanical properties of NR.

The increase in PVA concentration exhibited all positive effect for %ST conversion, mass fraction of green HIPS beads with the size of <1.18 mm, tensile strength and impact resistance. For green HIPS bead size result, it was possible to explain that the higher PVA concentration could hindrance the rates of particle nucleation and coalescence resulting in the smaller green HIPS beads. For mechanical properties, it was possible that the decrease in the HIPS bead size might decrease the NR particle size. Therefore, the green HIPS had low volume fraction of NR particles resulted in the high young's modulus, high tensile strength and low impact [Bucknall C.B., (1977)].

The agitation rate showed positive effect on mass fraction of green HIPS beads with the size of <1.18 mm, tensile and impact strength. This was possible that the higher shear rate produced the smaller monomer droplets due to the lower rate of particle coalescence. From the above reason, the tensile and impact strength increased with increasing the agitation rate because the obtained green HIPS had the small diameter and volume fraction of the rubber particles led the increase in the young's modulus and tensile strength value [Bucknall C.B., (1977)]. However, the agitation rate did not affect the %ST conversion because the studied range of agitation rate was too high (300-400 rpm) providing the higher %ST conversion.

Table 4.9 Calculation of effect estimate, coefficient estimate and standard error of 2^3 factorial design experiment for the production of green HIPS

Effect name	Effect estimate	±	Standard error	Coefficient estimate	±	Standard error
1) Average %ST conversion				92.94	±	0.47
Main effect						
NR content, A	-2.27	±	0.94	-1.13	±	0.47
PVA concentration, B	2.40	±	0.94	1.20	±	0.47
2) Average mass fraction of green HIPS beads with the size of <1.18 mm				0.27	±	0.01
Main effect						
NR content, A	-0.47	±	0.02	-0.24	±	0.01
PVA concentration, B	0.24	±	0.02	0.12	±	0.01
Agitation rate, C	0.10	±	0.02	0.05	±	0.01
Two-factors interaction						
A*B	-0.20	±	0.02	-0.10	±	0.01
A*C	-0.06	±	0.02	-0.03	±	0.01
3) Average tensile strength				14.91	±	0.30
Main effect						
NR content, A	5.83	±	0.60	2.91	±	0.30
PVA concentration, B	1.88	±	0.60	0.94	±	0.30
Agitation rate, C	2.48	±	0.60	1.24	±	0.30
4) Average impact strength				11.90	±	0.05
Main effect						
NR content, A	1.10	±	0.10	0.55	±	0.05
PVA concentration, B	0.30	±	0.10	0.15	±	0.05
Agitation rate, C	0.55	±	0.10	0.27	±	0.05
Two-factors interaction						
A*B	0.55	±	0.10	0.27	±	0.05
A*C	0.30	±	0.10	0.15	±	0.05
B*C	0.30	±	0.10	0.15	±	0.05

4.3.1 Regression model

The coefficient estimate of each response model obtained from the analysis of variance of four response models for the production of green HIPS. The coefficient estimate of each response model was used for the regression model. In this research, the regression models for predicting the %ST conversion, mass fraction of green HIPS beads with the size of <1.18 mm, tensile and impact strength were shown in Eq. 4.1 - 4.4.

$$\hat{Y}_1 = 92.94 - 1.13X_1 + 1.20X_2 \quad (4.1)$$

$$\hat{Y}_2 = 0.27 - 0.24X_1 + 0.12X_2 + 0.05X_3 - 0.10X_1X_2 - 0.03X_1X_3 \quad (4.2)$$

$$\hat{Y}_3 = 14.91 + 2.9X_1 + 0.94X_2 + 1.24X_3 \quad (4.3)$$

$$\hat{Y}_4 = 11.90 + 0.55X_1 + 0.15X_2 + 0.27X_3 - 0.27X_1X_2 - 0.15X_1X_3 - 0.15X_2X_3 \quad (4.4)$$

where $\hat{Y}_1$, $\hat{Y}_2$, $\hat{Y}_3$ and $\hat{Y}_4$ are the predicted values or fitted value of %ST conversion, mass fraction of green HIPS beads with the size of <1.18 mm, and tensile and impact strength, respectively. X_1, X_2 and X_3 are coded factor representing NR content (wt% based on ST content), PVA concentration (% (w/v) based on DI water volume) and agitation rate (rpm).

This regression model can be used to calculate the predicted value ($\hat{Y}$) in 16 experiments of 2^3 factorial design for the production of green HIPS as shown in Table 4.10.

4.3.2 Residuals and model adequacy checking

To validate the practicability of the regression model for 2^3 factorial design experiment for the production of HIPS. The residuals of 2^3 factorial design should be checked to confirm whether the model is correct and adequate.

For example, the ANOVA for tensile model indicates that the only significant factors are A = 2.91, B = 0.94 and C = 1.24. If model is true, the estimated tensile value is given by Eq. 4.3.

According to the definition, the residuals (e) are the differences between the observed values (Y) and predicted values ($\hat{Y}$). For example (HIPS 01), all factors (A, B and C) were at high level (+1). Thus, the predicted values of tensile value was calculated from Eq. 4.5.

$$\hat{Y} = 14.91 + 2.91(-1) + 0.94(-1) + 1.24(-1) \tag{4.5}$$

$$= 9.82$$

Because the observed tensile value (Y) is 21.50, the residual (e) is 1.50. The observed values, predicted values and residuals for all 16 experiments of %ST conversion, mass fraction of green HIPS beads with the size of <1.18 mm tensile and impact strength are shown in Table 4.10.

Figure 4.15 showed the normal probability plots of the residuals of %ST conversion, mass fraction of green HIPS beads size less than 1.18 mm, tensile and impact strength. All models showed that the points on these plots lie reasonably close to a straight line. For example, this result supports the conclusion that A, B and C are the only significant effects on tensile value from the ANOVA results. Furthermore, the tensile model was also checked by the plot of the residuals versus the predicted tensile value. The plots of the residuals versus the predicted values of %ST conversion, mass fraction of green HIPS beads with the size of <1.18 mm, tensile strength and impact strength were shown in Figure 4.16. These plots were now satisfactory due to not appear obvious pattern or structureless. It could be concluded that the tensile model for the production of green HIPS required only factor A, B and C. The method for this analysis was applied for all models of responses.

Table 4.10 The observed value, predicted value and residuals of %ST conversion, mass fraction of green HIPS beads with the size of <1.18 mm, tensile strength and impact strength

Exp.	Run label	%ST conversion			Mass fraction of green HIPS beads with the size of <1.18 mm		
		Observed values	Predicted values	Residuals	Observed values	Predicted values	Residuals
HIPS 01	(1)	93.41	95.27	-1.86	0.24	0.21	0.04
HIPS 02	(1)	91.10	95.27	-4.17	0.13	0.21	-0.08
HIPS 03	a	86.25	89.91	-3.66	0.00	-0.01	0.01
HIPS 04	a	90.54	89.91	0.63	0.00	-0.01	0.01
HIPS 05	b	93.47	95.27	-1.80	0.68	0.65	0.03
HIPS 06	b	96.90	95.27	1.63	0.66	0.65	0.01
HIPS 07	c	92.89	93.01	-0.12	0.32	0.37	-0.05
HIPS 08	c	95.44	93.01	2.43	0.45	0.37	0.09
HIPS 09	ab	93.15	93.01	0.14	0.06	0.04	0.02
HIPS 10	ab	93.51	93.01	0.50	0.00	0.04	-0.04
HIPS 11	ac	93.22	90.61	2.61	0.05	0.04	0.01
HIPS 12	ac	91.09	90.61	0.48	0.01	0.04	-0.03
HIPS 13	bc	93.70	95.27	-1.57	0.84	0.81	0.03
HIPS 14	bc	95.64	95.27	0.37	0.74	0.81	-0.07
HIPS 15	abc	93.38	93.01	0.37	0.08	0.08	0.00
HIPS 16	abc	93.30	93.01	0.29	0.10	0.08	0.02

* Mass fraction of green HIPS bead with the size of <1.18 mm.

Table 4.10 The observed value, predicted value and residuals of %ST conversion, mass fraction of green HIPS beads with the size of <1.18 mm, tensile strength and impact strength (continue)

Exp.	Run label	Tensile strength (MPa)			Impact strength (J/m)		
		Observed values	Predicted values	Residuals	Observed values	Predicted values	Residuals
HIPS 01	(1)	12.20	9.82	2.38	11.50	11.53	-0.03
HIPS 02	(1)	9.70	9.82	-0.12	11.50	11.53	-0.03
HIPS 03	a	14.60	15.66	-1.06	11.50	11.72	-0.22
HIPS 04	a	15.40	15.66	-0.26	12.00	11.72	0.28
HIPS 05	b	11.60	11.68	-0.08	11.00	10.97	0.03
HIPS 06	b	11.30	11.68	-0.38	11.00	10.97	0.03
HIPS 07	c	13.00	12.31	0.69	11.50	11.47	0.03
HIPS 08	c	11.20	12.31	-1.11	11.50	11.47	0.03
HIPS 09	ab	17.60	17.54	0.06	12.00	12.28	-0.28
HIPS 10	ab	17.00	17.54	-0.54	12.50	12.28	0.22
HIPS 11	ac	17.50	18.14	-0.64	12.50	12.28	0.22
HIPS 12	ac	18.30	18.14	0.16	12.00	12.28	-0.28
HIPS 13	bc	12.00	14.16	-2.16	11.50	11.53	-0.03
HIPS 14	bc	14.90	14.16	0.74	11.50	11.53	-0.03
HIPS 15	abc	21.50	20.02	1.48	13.50	13.47	0.03
HIPS 16	abc	20.80	20.02	0.78	13.50	13.47	0.03

* Mass fraction of green HIPS bead with the size of <1.18 mm.

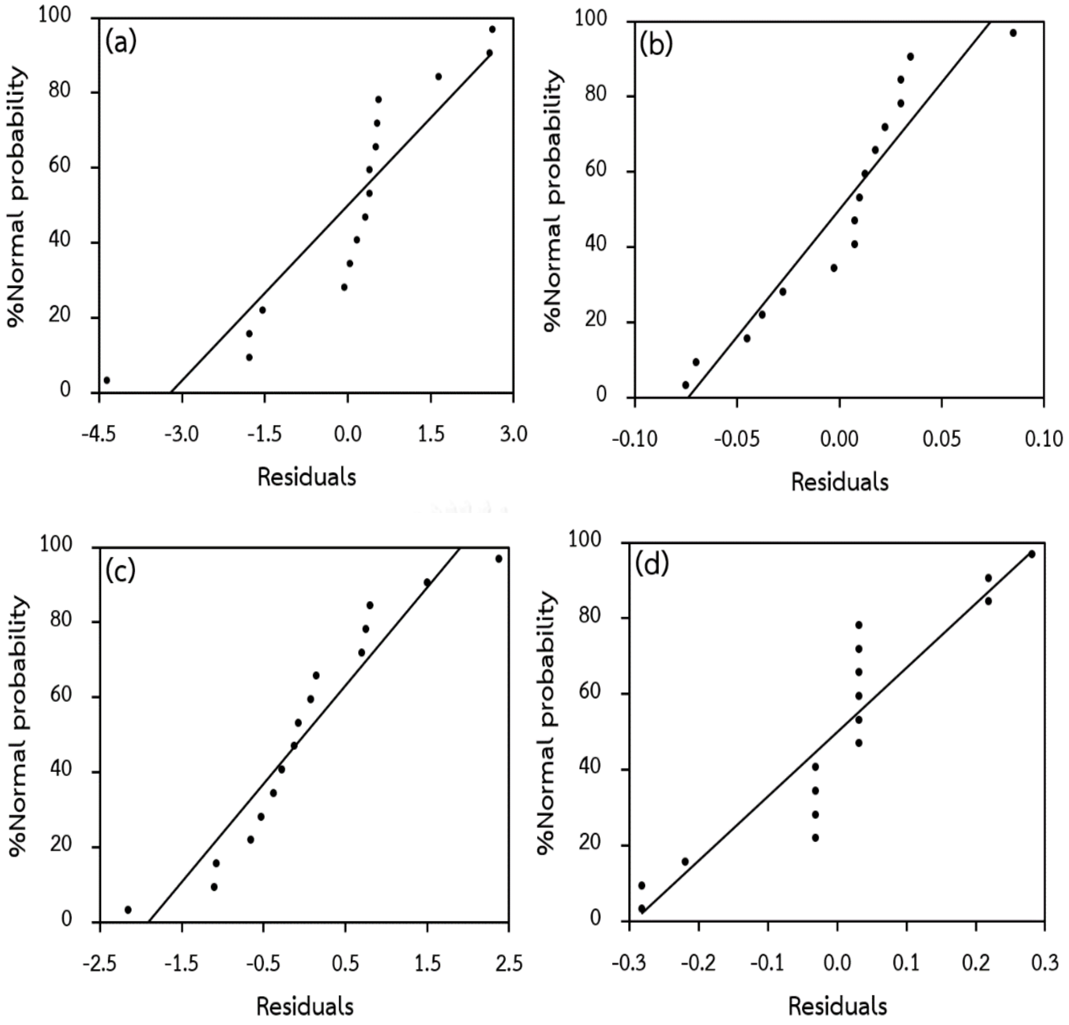


Figure 4.15 The normal probability plots of the residuals of (a) %ST conversion, (b) mass fraction of green HIPS beads with the size of <1.18 mm, (c) tensile strength and (d) impact strength.

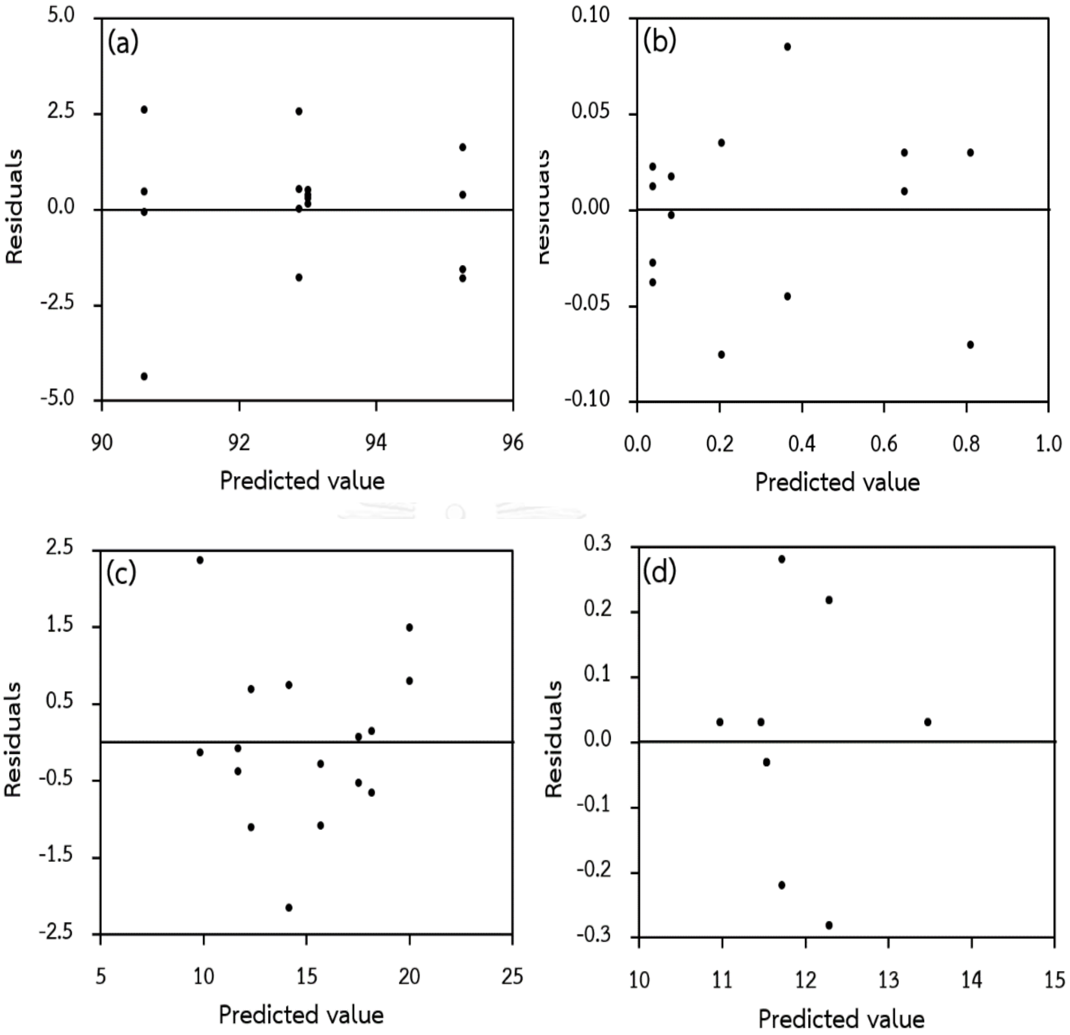


Figure 4.16 The plots of the residuals versus the predicted values of (a) %ST conversion, (b) mass fraction of green HIPS beads with the size of <1.18 mm, (c) tensile strength and (d) impact strength.

4.4 Thermal properties of green HIPS

4.4.1 Differencial scanning calorimetry (DSC)

The DSC thermograms of PS, NR and green HIPS containing 1-5 wt% NR were presented in Figure 4.17, 4.18 and Table 4.11. HIPS containing 1, 3 and 5 wt% NR based on ST monomer were coded as HIPS_NR1, HIPS_NR3 and HIPS_NR5, respectively. From DSC results shown in Table 4.11, it was found that the glass transition temperature (T_g) of pure PS and NR were 97.9 °C and -66.1 °C, respectively. Nevertheless, all sample thermogram could not present the melting temperature (T_m). It was possible that the structure of PS, NR and green HIPS could be fully amorphous [Brostow W. et al., (2004)]. Moreover, the T_g of NR could not be detected in the HIPS thermograms owing to the small amount of NR in the HIPS bead as shown in Figure 4.17. The effect of NR loading on T_g of green HIPS is shown in Figure 4.18. It was observed that the HIPS thermograms indicated one T_g with the range of 96-102 °C attributed to PS phase. The result showed the shift of T_g from 101.6 to 96.36 °C when the addition of NR content was 5 wt% NR.

Table 4.11 DSC data for PS, NR and green HIPS with various NR contents

Sample	Glass transition temperature (°C)
PS	97.9
NR	-66.1
HIPS_NR1	101.6
HIPS_NR3	98.7
HIPS_NR5	96.4

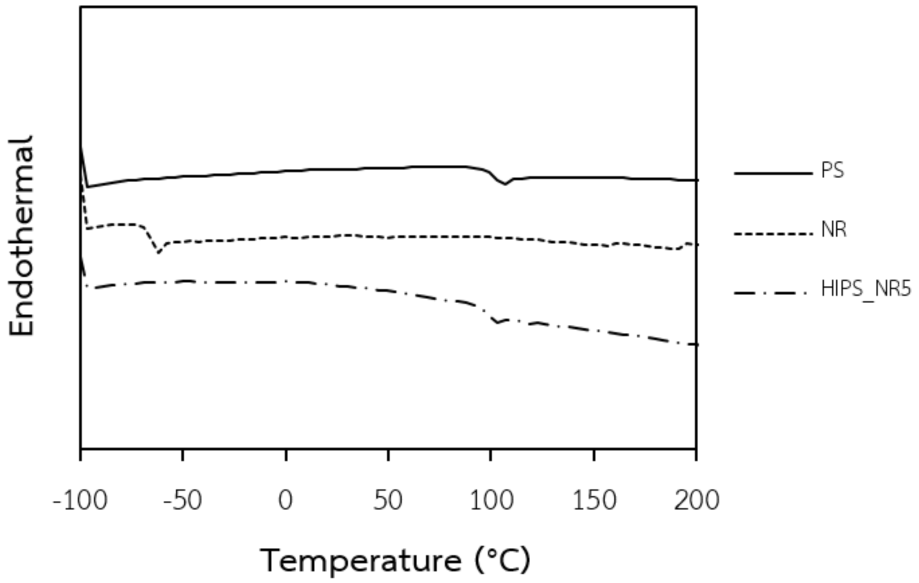


Figure 4.17 DSC thermograms of PS, NR and green HIPS containing 5 wt% NR.

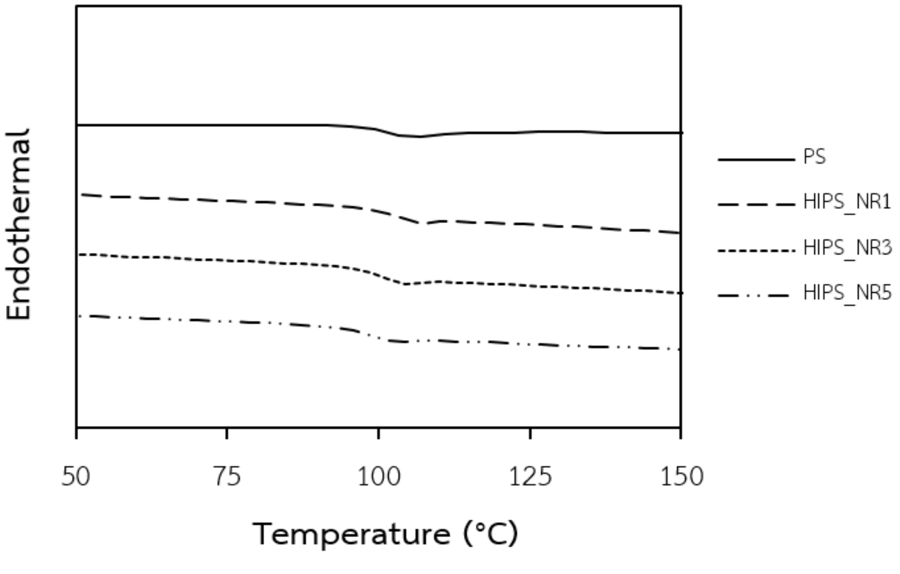


Figure 4.18 DSC thermograms of PS and green HIPS with various NR contents.

4.4.2 Thermogravimetric analysis

The TGA and DTG curves and data of PS, NR and green HIPS containing 1-5 wt% were shown in Figure 4.18 and Table 4.12. HIPS_NR1, HIPS_NR3 and HIPS_NR5 codes denoted HIPS containing 1, 3 and 5 wt% NR based on ST monomer, respectively. It indicated that the initial degradation temperature (T_{id}) and maximum degradation temperature (T_{max}) of pure PS were 384 °C and 412 °C, respectively. These were higher than the T_{id} (360 °C) and T_{max} (383 °C) of NR resulting in the existence of highly thermal stability of phenyl group in PS. Aseletha [Asaletha R. et al., (1998)] presented that the T_{max} of PS was 400 °C for the complete chain scission to volatile monomer and T_{max} of NR was 373 °C for complete distrillation of NR.

Table 4.12 TGA data for PS, NR and green HIPS with various NR contents

Sample	Temperature (°C)	
	Initial degradation (T_{id})	Maximum degradation (T_{max})
PS	384	412
NR	360	383
HIPS_NR1	388	415
HIPS_NR3	402	422
HIPS_NR5	402	422

For the green HIPS with various NR content, it was found that the T_{id} and T_{max} of the green HIPS increased with increasing the NR content. It could be explained the increase in the NR content provided the higher grafting site leading the higher crosslink polymer of ST and NR. This result was similar to the previous literatures that also used BPO as the initiator for graft polymerization of PS in the presence of NR [Asaletha R. et al., (1998)].

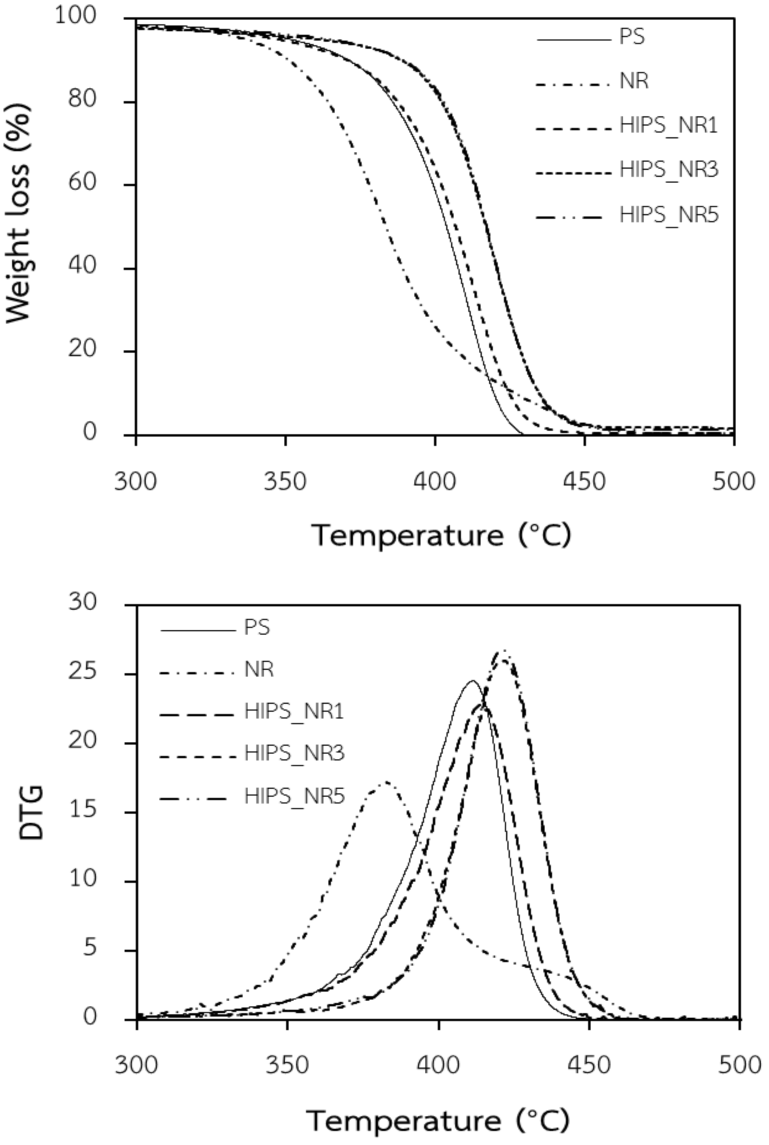


Figure 4.19 Thermogravimetric curves of PS, NR and green HIPS with various NR contents: (a) TGA and (b) DTG curves.

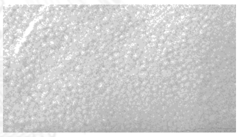
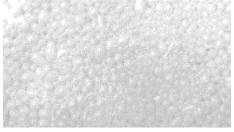
4.5 Effect of PB/NR ratio on HIPS bead size and mechanical properties of HIPS

4.5.1 HIPS appearance

The effect of PB content in NR for HIPS preparation was also individually investigated as shown in Table 4.13. The wt ratio of NR/PB in the HIPS beads was varied in range of 0 to 100 (the rubber content in HIPS beads was constant at 3 wt%). The synthesize of HIPS was carried out by using 0.6 wt% BPO based on ST content and 1.6 % (w/v) PVA based on the volume of DI water. This system was under 350 rpm agitation rate and 90 °C for 6 h. Table 4.13 shows %ST conversion and HIPS appearance (bead and sheet forms). It was indicated that the increase in the PB content slightly decreased %ST conversion. It could be explained that the PB had higher size average molecular weight (M_z) than the masticated NR that used in all experiments in this thesis. The molecular weight of NR and PB were shown in Table 4.14. Thus, the higher viscosity of PB caused the difficult mobility to polymerization of ST monomer resulting in the reduction of %ST conversion. From this reason, HIPS bead that contained 3 wt% PB was bigger size than HIPS bead that contained 3 wt% NR as shown in Table 4.13 and Figure 4.19. It showed that the HIPS bead size bigger than 4.75 mm was found in HIPS containing 3 wt% PB. However, it was not found in HIPS containing 3 wt% NR.

The effect of wt ratio of PB/NR on the shaping ability of HIPS product was shown in Table 4.13. The temperature and pressure for compressing the HIPS sheet was carried out at 200 °C and 120 kg/cm^2. The result showed that all sample produced the yellow transparency sheet owing to the existence of rubber dispersed in the PS matrix.

Table 4.13 Effect of PB/NR ratio on %ST conversion and HIPS appearance in the bead and sheet forms

PB/NR ratio (w/w)	%ST Conversion*	High impact polystyrene appearance	
		Bead form	Sheet form***
0/100	95.1 (0.90)**		
25/75	96.0 (1.77)		
50/50	95.2 (1.16)		
75/25	93.1 (1.07)		
100/0	82.4 (0.23)		

* Condition: ST 60 g, [rubber] = 3 wt%, [PVA] 1.6 % (w/v), stirring speed = 350 at 90 °C for 6 h.

** The number in parenthesis is a standard deviation.

*** Samples were sheet using by compression mold at 200 °C and 120 kg/cm^2.

Table 4.14 Molecular weight of NR, masticated NR and PB

Rubber	Molecular weight (x 10^5 g/mol)		
	Mn (x 10^5)	M_W (x 10^5)	M_Z (x 10^5)
NR	4.5	10.8	22.0
Masticated NR	1.8	3.2	5.4
PB	1.5	2.5	13.3

* Number average molecular weight (Mn)

Weight average molecular weight (M_W)

Z average or size average molecular weight (M_Z)

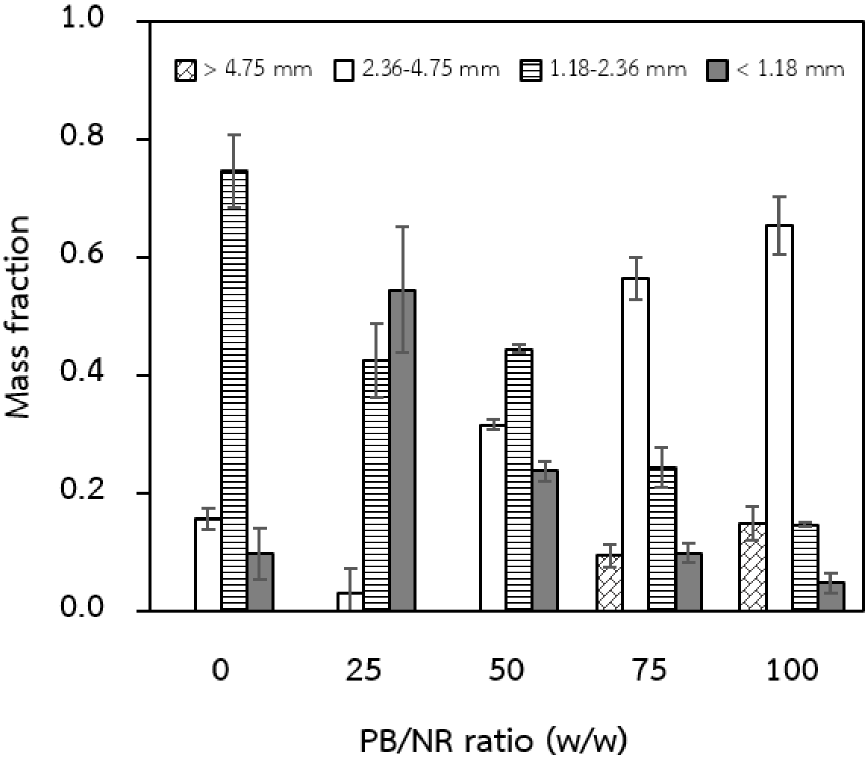


Figure 4.20 Effect of PB/NR ratio on the HIPS beads size distributions (Condition: ST 60 g, [rubber] = 3 wt%, [PVA] 1.6 % (w/v), stirring speed = 350 at 90 °C for 6 h).

4.5.2 Effect of PB/NR ratio on mechanical properties of green HIPS

The effect of green HIPS containing 3 wt% of rubber with various PB/NR ratios on tensile strength, elongation at break, hardness and impact strength was shown in Figure 4.20a. It indicated that HIPS produced from 50/50 PB/NR gave the highest tensile strength (21.9 MPa). It was possible that the green HIPS containing 50/50 PB/NR was more compatibility than green HIPS with another PB/NR ratio. From Figure 4.20b, the HIPS contained only PB gave low tensile strength and elongation at break due to the poor tensile properties of PB. Furthermore, it was found that the PB/NR ratio did not influence on the hardness and impact strength of the green HIPS sheets. It could be explained that the addition of 3 wt% rubber was too low to improve elasticity. Therefore, the obtained green HIPS showed plasticity.

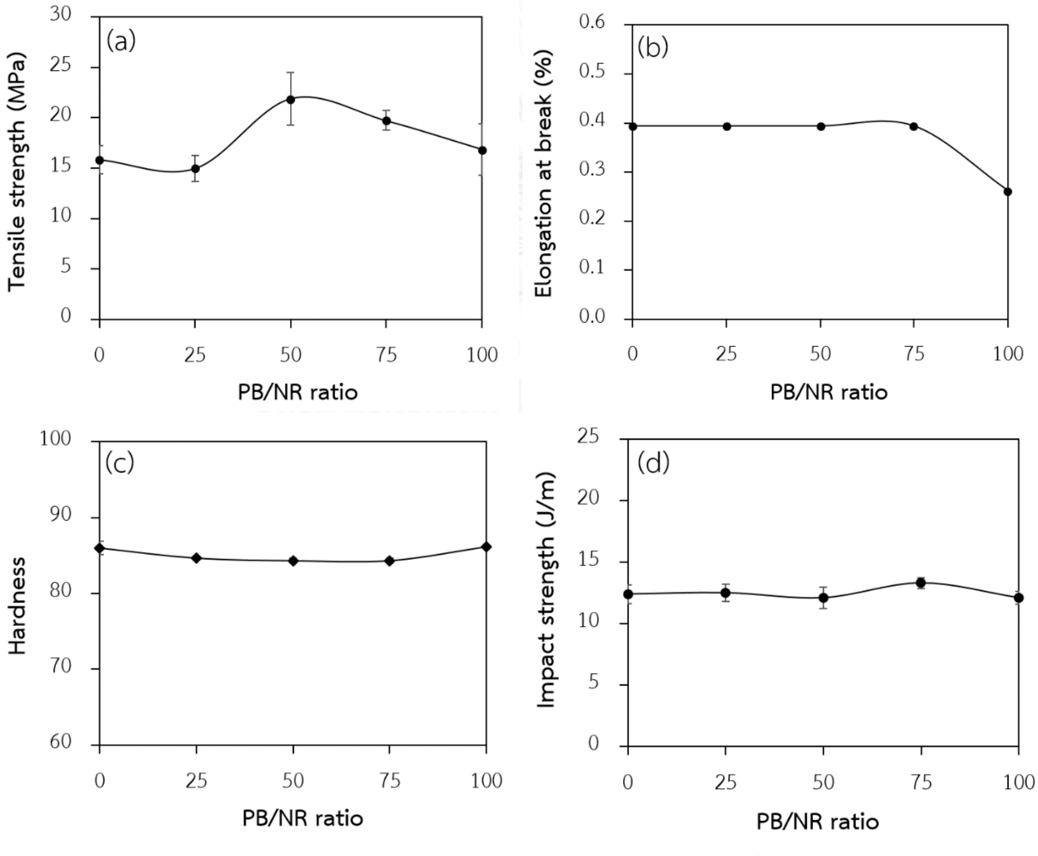


Figure 4.21 Effect of PB contents on (a) tensile strength, (b) elongation at break, (c) hardness and (d) impact strength of the HIPS sheets containing 3 wt% rubber.

CHAPTER 5

CONCLUSION

The green high impact polystyrene (HIPS) was successfully prepared via suspension polymerization of styrene (ST) in the existence of natural rubber (NR) by using benzoyl peroxide (BPO) and poly(vinyl alcohol) (PVA) as an initiator and stabilizer, respectively. The investigation of the significantly parameters on %ST conversion, HIPS beads size and mechanical properties was divided into two parts: univariate and 2^k factorial design experiment. The studied parameters of the production of HIPS were BPO, NR, and PVA concentrations and reaction time including agitation rate on %ST conversion, beads size of the green HIPS beads and mechanical properties of the green HIPS sheets. The fractural surface of the green HIPS specimens obtained from the tensile testing was observed by using transmission electron microscope (TEM) and scanning Electron Microscopy (SEM). The thermal properties such as glass transition temperature (T_g) and decomposition temperature of polystyrene (PS), NR and HIPS were investigated by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

5.1 Univariate experiment for the production of green HIPS

From the univariate experiment, the optimum BPO concentration was 0.6 wt% based on ST monomer produced the fine smooth sheets of the obtained PS and green HIPS. The central condition applied for the univariate experiments was 0.6 wt% BPO and 3 wt% NR based on ST content, 1.6 % (w/v) PVA based on volume of DI water and 350 rpm agitation rate at 90 °C for 6 h. The monomer/water (w/w) was kept constant at 1/6. The %ST conversion was depended on PVA concentration and agitation rate. The excess PVA concentration (above 2.0 % (w/v) provided the lower %ST conversion whereas the lower agitation rate (450 rpm) provided the lower %ST conversion. For PVA effect, the high PVA concentration generated the PVA radicals around the surface of syrup droplets which they blocked the mobility to polymerize of ST monomer. For agitation rate, the higher shear rate produced the high interfacial area for polymerization leading the higher %ST conversion. Moreover, it was observed that the incorporation of NR in the synthesize green HIPS gave more rigidity product due to its excellent tensile property. The green HIPS containing 5 wt% NR had the highest tensile strength (20.4 MPa), hardness (84.3 of shore B) and impact strength (14.5 J/m). However, NR content did not affected elongation at break owing to the limitation of the agitation rate of system was only used 5 wt% NR caused the obtained green HIPS showed plasticity. The increase in the PVA concentration and agitation rate also increased the tensile strength and provided the smaller HIPS bead size. Since the obtained green HIPS had low volume fraction of NR particles leading the high young's modulus, high tensile strength and low impact. The reaction time only affected the tensile strength value. The 12 h of reaction time gave the obtained HIPS that had the higher tensile strength. It was explained that the increase in the reaction time caused the obtaind green HIPS had more high molar mass of the free PS polymer leading the higher stiffness.

5.2 Statistical analysis using two level factorial design experiment

The range of each studied factors were 1-4 wt% for NR content (A), 1.0-2.0 % (w/v) for PVA concentration (B) and 300-400 rpm for agitation rate (C). The %ST conversion was depended only A and B factors. The sequence of the main effects of the variables of the production of green HIPS on the HIPS bead with the size of <1.18 mm was NR content (A) > PVA concentration (B) > agitation rate (C) > A-C interaction. For mechanical properties, the significant parameters were NR content (A) > agitation rate (C) > PVA concentration (B). Moreover, The AB and AC two-factor interaction effect were significant for the bead size and impact strength. NR content was strongly effect on HIPS bead size and mechanical properties. The optimum condition to give the highest tensile (21.2 MPa) and impact strength (13.5 J/m) was 4 wt% NR, 2.0 % (w/v) and 400 rpm agitation rate.

5.3 Morphology of the green HIPS

The fractural surface obtained from tensile specimens of the green HIPS by using TEM showed Two-phase morphology of small crosslinked rubber particles less than 1 µm (dark color) dispersed in the PS matrix (light color). The smaller diameter and volume fraction of the rubber particles in the obtained green HIPS affected the tensile properties more than its impact property. For SEM result, it was observed that the fractural surface from the tensile testing of the green HIPS indicated the rougher surface area than the neat PS. Therefore, the presence of NR in the PS matrix reduced the rampant crack propagation in the specimens.

5.4 Thermal properties of the green HIPS

For the DSC result, the glass transition temperature decreased from 101.6 to 96.36 °C when the addition of NR content was 5 wt% due to the elasticity of the rubber phase. Furthermore, the incorporation of 5 wt% NR in the PS matrix via suspension polymerization improved thermal resistance of the obtained green HIPS. The initial degradation and maximum degradation temperature were shifted from 384 °C and 412 °C to 402 °C and 422 °C, respectively.

5.5 Recommendations

A further study of production of the green HIPS via suspension polymerization by using NR should be design the reactor and speed motor for the applied of the higher NR content. Moreover, the NR-*g*-PS obtained from suspension method is blended with NR to improve stiffness property.

REFERENCES

Aiamsen, P., Paiphansiri, U., Sangribsub, S., Polpanich, D., & Tangboriboonrat, P. (2003). Toughness and morphology of radiation-crosslinked natural rubber modified polystyrene. *Polymer International, 52*(7), 1198-1202.

Alfarraj, A., & Nauman, E. B. (2004). Super HIPS: improved high impact polystyrene with two sources of rubber particles. *Polymer, 45*(25), 8435-8442.

Arthur, L. (1971). Suspension system for producing high impact polystyrene: Google Patents.

Asaletha, R., Kumaran, M., & Thomas, S. (1998). Thermal behaviour of natural rubber/polystyrene blends: thermogravimetric and differential scanning calorimetric analysis. *Polymer Degradation and Stability, 61*(3), 431-439.

Asaletha, R., Kumaran, M., & Thomas, S. (1999). Thermoplastic elastomers from blends of polystyrene and natural rubber: morphology and mechanical properties. *European Polymer Journal, 35*(2), 253-271.

Blackley, D. C. (1977). *Polymer lattices science and technology*. London: Chapman and Hall.

Brostow, W., Castano, V. M., Horta, J., & Martinez-Barrera, G. (2004). Gamma irradiation effects on impact strength and thermal properties of SBR-toughened polystyrene. *Polimery, 49*(1), 9-14.

Brydson, J. A. (1978). *Rubber chemistry*: Applied Science Publishers.

Brydson, J. A. (1999). *Plastics materials*: Butterworth-Heinemann.

Bucknall, C. B. (1977). *Toughened plastics*: Springer.

Charmondusit, K., Kiatkamjornwong, S., & Prasassarakich, P. (1998). Grafting of methyl methacrylate and styrene onto natural rubber. *The Journal of Scientific Research Chulalongkorn University, 23*(2), 167-181.

Cunha, F., Costa, J., Nele, M., Folly, R., Souza Jr, M., & Pinto, J. (2013). Influence of reaction operation conditions on the final properties of high impact polystyrene (hips). *Brazilian Journal of Chemical Engineering, 30*(3), 575-587.

Douglas, C. M. (2001). Design and analysis of experiments. *John Wiley and Sons*.

Dowding, P. J., & Vincent, B. (2000). Suspension polymerisation to form polymer beads. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 161*(2), 259-269.

Fischer, M., & Hellmann, G. (1996). On the evolution of phase patterns during the high-impact-modified polystyrene process. *Macromolecules, 29*(7), 2498-2509.

Gao, G., Zhou, C., Yang, H., & Zhang, H. (2007). Influence of core–shell rubber particles synthesized with different initiation systems on the impact toughness of modified polystyrene. *Journal of Applied Polymer Science, 103*(2), 738-744.

Kaewtatip, K., & Tanrattanakul, V. (2008). Preparation of cassava starch grafted with polystyrene by suspension polymerization. *Carbohydrate Polymers, 73*(4), 647-655.

Kaghan, W. S., & Shreve, R. N. (1953). Suspension Polymerization of Styrene. *Industrial & Engineering Chemistry, 45*(2), 292-297.

Kiatkamjornwong, S., Chientachakul, P., Prasassarakich, P., & Damronglerd, S. (2001). Kinetic studies on styrene–divinylbenzene copolymerization by suspension technique. *Journal of Applied Polymer Science, 82*(6), 1521-1540.

Li, D., Xia, H., Peng, J., Zhai, M., Wei, G., Li, J., & Qiao, J. (2007). Radiation preparation of nano-powdered styrene-butadiene rubber (SBR) and its toughening effect for polystyrene and high-impact polystyrene. *Radiation Physics and Chemistry, 76*(11), 1732-1735.

Lin, Y., Ng, K. M., Chan, C.-M., Sun, G., & Wu, J. (2011). High-impact polystyrene/halloysite nanocomposites prepared by emulsion polymerization using sodium dodecyl sulfate as surfactant. *Journal of Colloid and Interface Science, 358*(2), 423-429.

Lourenco, E., & Felisberti, M. I. (2008). PS/EPDM blends prepared by in situ polymerization of styrene. *Journal of Applied Polymer Science, 110*(3), 1804-1813.

Lourenço, E., & Felisberti, M. I. (2006). Thermal and mechanical properties of in situ polymerized PS/EPDM blends. *European Polymer Journal, 42*(10), 2632-2645.

Meira, G. R., Luciani, C. V., & Estenoz, D. A. (2007). Continuous bulk process for the production of high-impact polystyrene: recent developments in modeling and control. *Macromolecular Reaction Engineering, 1*(1), 25-39.

Nallasamy, P., & Mohan, S. (2004). Vibrational spectra of cis-1, 4-polyisoprene. *Arabian Journal for Science and Engineering, 29*(1; PART A), 17-26.

Nanjwade, B. K., R., P. S., Ravikumar, & F.V., M. (2010). Characteristics and evaluations of monomer for colloidal suspension polymerization. *Der Pharmacia Lettre, 2*(1), 245-252.

Neoh, S., Azura, A., & Hashim, A. S. (2011). Comparison of the different vulcanization techniques of styrene modified natural rubber (SNR) as an impact modifier of natural rubber-based high impact polystyrene (NRHIPS). *Polymer-Plastics Technology and Engineering, 50*(2), 121-126.

Neoh, S., & Hashim, A. S. (2004). Highly grafted polystyrene-modified natural rubber as toughener for polystyrene. *Journal of Applied Polymer Science, 93*(4), 1660-1665.

Nogueira, A., Quadri, M., Araújo, P., & Machado, R. (2012). Influence of semi-batch operations on morphological properties of polystyrene made in suspension polymerization. *Procedia Engineering, 42*, 1045-1052.

Nogueira, A. L., Machado, R. A., & Quadri, M. B. (2006). *Styrene suspension polymerization using a stirred vertical tubular reactor.* Paper presented at the Macromolecular Symposia.

Odian, G. (2004). *Principles of polymerization*: John Wiley & Sons.

Perkins, W. G. (1999). Polymer toughness and impact resistance. *Polymer Engineering and Science, 39*(12), 2445.

Pisuttisap, A., Hinchiranan, N., Rempel, G. L., & Prasassarakich, P. (2013). ABS modified with hydrogenated polystyrene-grafted-natural rubber. *Journal of Applied Polymer Science, 129*(1), 94-104.

Ronco, L. I., Minari, R. J., Passeggi, M. C., Meira, G. R., & Gugliotta, L. M. (2015). Toughened polystyrene nanoparticles through high-solids miniemulsion polymerization. *Chemical Engineering Journal, 263*, 231-238.

Sastri, V. (2010). Plastics in medical applications: properties, requirements and applications: Elsevier, PA, USA.

Scheirs, J., & Priddy, D. (2003). *Modern styrenic polymers: polystyrenes and styrenic copolymers* (Vol. 6): John Wiley & Sons.

Sekharan, R. V., Abraham, B. T., & Thachil, E. T. (2012). Utilization of waste expanded polystyrene: Blends with silica-filled natural rubber. *Materials & Design, 40*, 221-228.

Sondari, D., Haryono, A., & Ghozali, M. (2010). *Preliminary study of emulsion copolymerization of styrene on natural rubber latex* Paper presented at the Prosiding Seminar Nasional Sains Dan Teknologi Fakultas Teknik.

Soto, G., Nava, E., Rosas, M., Fuenmayor, M., Gonzalez, I., Meira, G., & Oliva, H. (2004). Bulk polymerization of styrene in the presence of polybutadiene: Effect of initiator type and prepolymerization conditions on particle morphology. *Journal of Applied Polymer Science, 92*(3), 1397-1412.

Sun, L., Sosa, J. M., Eon, S., Corleto, C., & Cooper, S. (2011). Methods of making high impact polystyrene: Google Patents.

Trifonova, D., & Vasileva, S. (1992). Rubber-modified polystyrene compositions. *Journal of Materials Science, 27*(13), 3657-3661.

Vilaplana, F., Karlsson, S., & Ribes-Greus, A. (2007). Changes in the microstructure and morphology of high-impact polystyrene subjected to multiple processing and thermo-oxidative degradation. *European Polymer Journal, 43*(10), 4371-4381.

Wünsch, J. R. (2000). *Polystyrene: Synthesis, production and applications* (Vol. 112): iSmithers Rapra Publishing.

Yuan, H., Kalfas, G., & Ray, W. (1991). Suspension polymerization. *Journal of Macromolecular Science, Part C: Polymer Reviews, 31*(2-3), 215-299.

Zhu, L. D., Yang, H. Y., Cai, G. D., Zhou, C., Wu, G. F., Zhang, M. Y., . . . Zhang, H. X. (2013). Submicrometer‐sized rubber particles as “craze‐bridge” for toughening polystyrene/high‐impact polystyrene. *Journal of Applied Polymer Science, 129*(1), 224-229.

APPENDIX

APPENDIX A

Table A-1 Properties of dry natural rubber (STR 5L)

Property	Limit
Dirt (retained on 44 aperture) (%wt)	0.04
Ash (%wt)	0.40
Volatile matter (%wt)	0.80
Nitrogen (%wt)	0.60
Colour lovibond scale	6.0
Initial wallance plasticity, Po (min)	35
Plasticity retention index, PRI (min)	60

APPENDIX B

Calculation of %ST conversion,

From the suspension polymerization of green HIPS, all obtained data for green HIPS (HIPS 01) was calculated as follow in below example:

Weight of ST (A)	= 60.2 g
Weight of NR (B)	= 0.6 g
Weight of product (C)	= 56.1

%ST conversion

%ST conversion = (C - B)/A x 100

= (56.1-0.60)/60.2 X 100

= 92.2

APPENDIX C

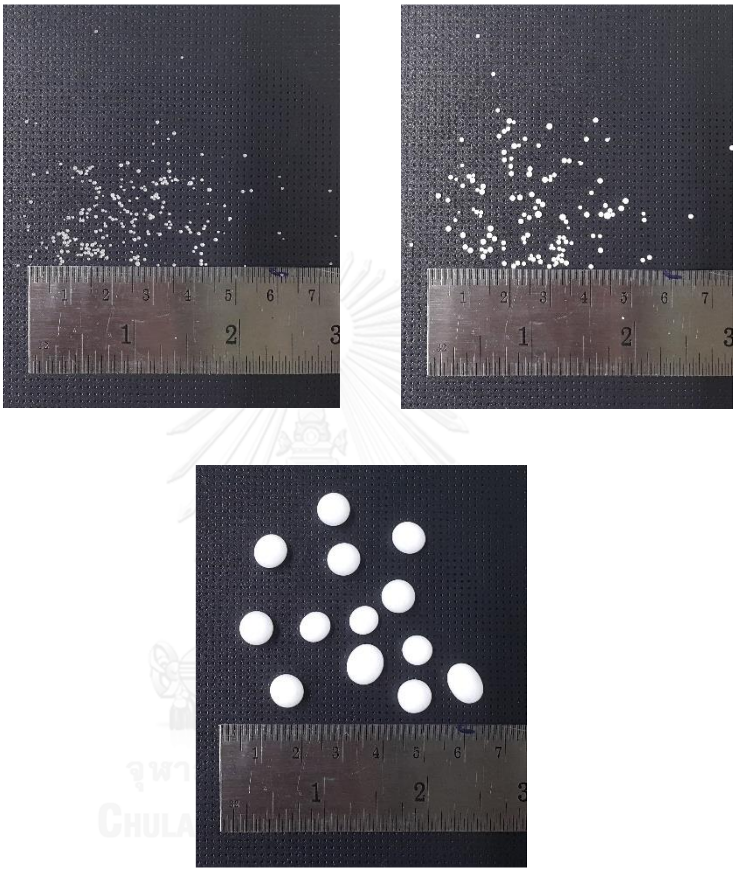


Figure C-1 Pictures of beads size of (a) PS and green HIPS containing; (b) 1 wt% NR and (c) 5 wt% NR.

APPENDIX D

DATA of the production of green HIPS

Table D-1 Univariate average data for the synthesis of green HIPS beads via suspension polymerization at 90°C

Exp.	BPO (wt%)	PS (g)	NR (wt%)	PVA (% (w/v))	Agitation rate (rpm)	Reaction time (h)	Product	%ST conversion	Mass fraction			
									>4.75 mm	2.36-4.75 mm	1.18-2.36 mm	<1.18 mm
BPO concentration												
1	0.3	60.6	-	0.1	350	6	60.6	94.9	0.00	0.19	0.72	0.09
2	0.6	60.1	-	0.1	350	6	60.1	95.3	0.00	0.16	0.75	0.10
3	0.8	60.4	-	0.1	350	6	60.4	96.7	0.00	0.08	0.54	0.39
4	1.0	60.2	-	0.1	350	6	60.2	89.7	0.00	0.02	0.29	0.69
5	2.0	60.2	-	0.1	350	6	60.2	90.3	0.00	0.00	0.18	0.82
NR content												
1	0.6	60.8	1	1.6	350	6	57.6	93.9	0.00	0.02	0.63	0.35
2	0.6	60.6	2	1.6	350	6	57.5	92.9	0.00	0.02	0.67	0.31
3	0.6	60.2	3	1.6	350	6	59.1	95.2	0.00	0.16	0.75	0.10
4	0.6	60.7	4	1.6	350	6	60.2	95.2	0.41	0.57	0.02	0.00
5	0.6	59.9	5	1.6	350	6	59.9	95.0	0.99	0.01	0.00	0.00
PVA concentration												
1	0.6	60.8	3	0.1	350	6	59.3	94.7	0.62	0.37	0.01	0.01
2	0.6	60.6	3	0.5	350	6	58.4	93.4	0.32	0.64	0.02	0.02
3	0.6	60.3	3	1.0	350	6	57.7	92.7	0.02	0.42	0.54	0.02
4	0.6	60.2	3	1.6	350	6	59.1	95.2	0.00	0.16	0.75	0.10
5	0.6	60.4	3	2.0	350	6	58.0	93.0	0.00	0.12	0.63	0.25
6	0.6	60.3	3	2.5	350	6	54.4	88.7	0.00	0.01	0.54	0.45
7	0.6	60.0	3	3.0	350	6	51.4	82.7	0.00	0.00	0.40	0.60

Table D-1 Univariate average data for the synthesis of green HIPS beads via suspension polymerization at 90ºC (continue)

Exp.	BPO (wt%)	PS (g)	NR (wt%)	PVA (% (w/v))	Agitation rate (rpm)	Reaction time (h)	Product	%ST conversion	Mass fraction			
									>4.75 mm	2.36-4.75 mm	1.18-2.36 mm	<1.18 mm
Agitation rate												
1	0.6	60.3	3	1.6	250	6	42.8	68.0	0.10	0.59	0.30	0.01
2	0.6	60.2	3	1.6	350	6	59.1	95.2	0.00	0.16	0.75	0.10
3	0.6	60.1	3	1.6	450	6	56.7	91.4	0.01	0.19	0.67	0.13
Reaction time												
1	0.6	60.2	3	1.6	350	6	59.1	95.2	0.00	0.16	0.75	0.10
2	0.6	60.2	3	1.6	350	8	58.5	94.1	0.01	0.19	0.71	0.09
3	0.6	60.9	3	1.6	350	12	59.8	95.2	0.00	0.19	0.73	0.08
PB/NR ratio												
0/100	0.6	60.2	3	1.6	350	6	59.1	95.2	0.00	0.16	0.75	0.10
25/75	0.6	60.2	3	1.6	350	6	59.1	95.2	0.00	0.03	0.42	0.55
50/50	0.6	60.1	3	1.6	350	6	59.0	95.1	0.00	0.32	0.44	0.24
75/25	0.6	60.3	3	1.6	350	6	57.2	91.8	0.09	0.56	0.24	0.10
100/0	0.6	60.1	3	1.6	350	6	51.8	83.1	0.15	0.65	0.15	0.05

Table D-2 Univariate average data for mechanical properties of green HIPS synthesize by suspension polymerization at 90°C

Exp.	BPO (wt%)	PS (g)	NR (wt%)	PVA (% (w/v))	Agitation rate (rpm)	Reaction time (h)	Green HIPS product (g)	%ST conversion	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore B)	Impact strength (J/m)
BPO concentration												
1	0.3	60.6	-	0.1	350	6	60.6	94.9	-	-	-	-
2	0.6	60.1	-	0.1	350	6	60.1	95.3	12.4	0.20	94.0	11.7
3	0.8	60.4	-	0.1	350	6	60.4	96.7	-	-	-	-
4	1.0	60.2	-	0.1	350	6	60.2	89.7	-	-	-	-
5	2.0	60.2	-	0.1	350	6	60.2	90.3	-	-	-	-
NR content												
1	0.6	60.8	1	1.6	350	6	57.6	93.9	13.0	0.26	74.0	12.2
2	0.6	60.6	2	1.6	350	6	57.5	92.9	15.5	0.39	82.2	12.5
3	0.6	60.2	3	1.6	350	6	59.1	95.2	15.8	0.39	86.0	12.4
4	0.6	60.7	4	1.6	350	6	60.2	95.2	18.2	0.39	86.0	14.0
5	0.6	59.9	5	1.6	350	6	59.9	95.0	20.4	0.39	87.3	14.5
PVA concentration												
1	0.6	60.8	3	0.1	350	6	59.3	94.7	11.0	0.26	82.3	13.6
2	0.6	60.6	3	0.5	350	6	58.4	93.4	11.2	0.26	82.3	10.0
3	0.6	60.3	3	1.0	350	6	57.7	92.7	13.3	0.39	82.3	12.1
4	0.6	60.2	3	1.6	350	6	59.1	95.2	15.8	0.39	86.0	12.4
5	0.6	60.4	3	2.0	350	6	58.0	93.0	16.9	0.39	88.2	12.8
6	0.6	60.3	3	2.5	350	6	54.4	88.7	18.7	0.39	86.3	12.0
7	0.6	60.0	3	3.0	350	6	51.4	82.7	19.7	0.39	86.8	11.7

Table D-2 Univariate average data for mechanical properties of green HIPS synthesize by suspension polymerization at 90°C **(continue)**

Exp.	BPO (wt%)	PS (g)	NR (wt%)	PVA (% (w/v))	Agitation rate (rpm)	Reaction time (h)	Green HIPS product (g)	%ST conversion	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore B)	Impact strength (J/m)
Agitation rate												
1	0.6	60.3	3	1.6	250	6	42.8	68.0	14.3	0.39	83.0	11.5
2	0.6	60.2	3	1.6	350	6	59.1	95.2	15.8	0.39	86.0	12.4
3	0.6	60.1	3	1.6	450	6	56.7	91.4	23.3	0.39	86.5	11.9
Reaction time												
1	0.6	60.2	3	1.6	350	6	59.1	95.2	15.8	0.39	86.0	12.4
2	0.6	60.2	3	1.6	350	8	58.5	94.1	17.3	0.39	84.7	12.3
3	0.6	60.9	3	1.6	350	12	59.8	95.2	23.6	0.39	83	12.3
PB/NR ratio												
0/100	0.6	60.2	3	1.6	350	6	59.1	95.2	15.8	0.39	86.0	12.4
25/75	0.6	60.2	3	1.6	350	6	59.1	95.2	15.0	0.39	84.7	12.5
50/50	0.6	60.1	3	1.6	350	6	59.0	95.1	21.9	0.39	84.3	12.1
75/25	0.6	60.3	3	1.6	350	6	57.2	91.8	19.7	0.39	84.3	13.3
100/0	0.6	60.1	3	1.6	350	6	51.8	83.1	16.9	0.26	86.2	12.1

Table D-3 The average of %ST conversion, mass fraction of green HIPS beads with various size, tensile strength and impact strength obtained from 2^3 factorial design

Exp.	BPO (wt%)	PS (g)	NR (g)	PVA (g)	Agitation rate (rpm)	Reaction time (h)	Green HIPS product	%ST conversion	Mass fraction				Tensile strength (MPa)	Impact strength (J/m)
									>4.75 mm	2.36-4.75 mm	1.18-2.36 mm	<1.18 mm		
HIPS 01	0.6	60.2	0.6	3.6	300	6	56.1	92.2	0.00	0.15	0.61	0.24	11.0	11.5
HIPS 02	0.6	60.5	2.4	3.6	300	6	55.9	88.4	0.95	0.03	0.02	0.00	15.0	11.8
HIPS 03	0.6	60.0	0.6	7.2	300	6	57.7	95.2	0.00	0.01	0.31	0.68	11.5	11.0
HIPS 04	0.6	60.7	0.6	3.6	400	6	57.8	94.2	0.00	0.11	0.57	0.32	12.1	11.5
HIPS 05	0.6	60.8	2.4	7.2	300	6	59.1	93.3	0.00	0.62	0.32	0.06	17.3	12.3
HIPS 06	0.6	60.5	2.4	3.6	400	6	58.2	92.2	0.29	0.29	0.37	0.05	17.9	12.3
HIPS 07	0.6	60.6	0.6	7.2	400	6	58.0	94.7	0.00	0.00	0.16	0.84	13.5	11.5
HIPS 08	0.6	60.2	2.4	7.2	400	6	58.5	93.4	0.00	0.25	0.68	0.08	21.2	13.5

APPENDIX E

Calculation of 2^3 factorial design experiments

Table E-1 Contrast constant, effect estimate and sum of squares of %ST conversion for the factorial design

Exp	Run label	Factorial effect							%ST conversion
		A	B	C	AB	AC	BC	ABC	
1	(1)	-1	-1	-1	1	1	1	-1	92.24
2	a	1	-1	-1	-1	-1	1	1	88.35
3	b	-1	1	-1	-1	1	-1	1	95.2
4	c	-1	-1	1	1	-1	-1	1	94.15
5	ab	1	1	-1	1	-1	-1	-1	93.31
6	ac	1	-1	1	-1	1	-1	-1	92.15
7	bc	-1	1	1	-1	-1	1	-1	94.65
8	abc	1	1	1	1	1	1	1	93.34
Contrast		-9.09	9.61	5.19	2.69	2.47	-6.23	-1.31	$\overline{X} = 92.9$
Effect estimate		-2.27	2.40	1.30	0.67	0.62	-1.56	-0.33	
Sum of squares		20.66	23.09	6.73	1.81	1.53	9.70	0.43	

Table E-2 Contrast constant, effect estimate and sum of squares of Mass fraction of green HIPS beads with the size of <1.18 mm for the factorial design

Exp	Run label	Factorial effect							Mass fraction*
		A	B	C	AB	AC	BC	ABC	
1	(1)	-1	-1	-1	1	1	1	-1	0.19
2	a	1	-1	-1	-1	-1	1	1	0.00
3	b	-1	1	-1	-1	1	-1	1	0.67
4	c	-1	-1	1	1	-1	-1	1	0.39
5	ab	1	1	-1	1	-1	-1	-1	0.03
6	ac	1	-1	1	-1	1	-1	-1	0.03
7	bc	-1	1	1	-1	-1	1	-1	0.79
8	abc	1	1	1	1	1	1	1	0.09
Contrast		-1.89	0.97	0.41	-0.79	-0.23	-0.05	0.11	$\overline{X}$ = 0.27
Effect estimate		-0.47	0.24	0.10	-0.20	-0.06	-0.01	0.03	
Sum of squares		0.88	0.24	0.04	0.16	0.01	0.00	0.00	

* Mass fraction of green HIPS beads with the size of <1.18 mm.

Table E-3 Contrast constant, effect estimate and sum of squares of tensile strength for the factorial design

Exp	Run label	Factorial effect							Tensile strength (MPa)
		A	B	C	AB	AC	BC	ABC	
1	(1)	-1	-1	-1	1	1	1	-1	11
2	a	1	-1	-1	-1	-1	1	1	15
3	b	-1	1	-1	-1	1	-1	1	11.5
4	c	-1	-1	1	1	-1	-1	1	12.1
5	ab	1	1	-1	1	-1	-1	-1	17.3
6	ac	1	-1	1	-1	1	-1	-1	17.9
7	bc	-1	1	1	-1	-1	1	-1	13.5
8	abc	1	1	1	1	1	1	1	21.2
Contrast		23.30	7.50	9.90	3.70	3.70	1.90	0.10	$\overline{X}$ = 14.97
Effect estimate		5.83	1.88	2.48	0.93	0.93	0.48	0.03	
Sum of squares		135.72	14.06	24.50	3.42	3.42	0.90	0.00	

Table E-4 Contrast constant, effect estimate and sum of squares of impact strength for the factorial design

Exp	Run label	Factorial effect							Impact strength (J/m)
		A	B	C	AB	AC	BC	ABC	
1	(1)	-1	-1	-1	1	1	1	-1	11.5
2	a	1	-1	-1	-1	-1	1	1	11.8
3	b	-1	1	-1	-1	1	-1	1	11
4	c	-1	-1	1	1	-1	-1	1	11.5
5	ab	1	1	-1	1	-1	-1	-1	12.3
6	ac	1	-1	1	-1	1	-1	-1	12.3
7	bc	-1	1	1	-1	-1	1	-1	11.5
8	abc	1	1	1	1	1	1	1	13.5
Contrast		4.40	1.20	2.20	2.20	1.20	1.20	0.20	$\overline{X}$ = 11.93
Effect estimate		1.10	0.30	0.55	0.55	0.30	0.30	0.05	
Sum of squares		4.84	0.36	1.21	1.21	0.36	0.36	0.01	

VITA

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Presentation

2014 Preparation of Green High Impact Polystyrene Beads via Suspension Polymerization, 6-11, International Conference on 2014 IUPAC World Polymer Congress or MACRO 2014, Chiang Mai, Thailand