

ผลของเอสเอเอ็นต่อสมบัติเชิงกลและสัณฐานวิทยาของเอบีเอส

นายศุภชัย รินสม



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2542

ISBN 974-333-155-7

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

**EFFECT OF SAN ON THE MECHANICAL PROPERTIES
AND MORPHOLOGY OF ABS**

Mr. Supachai Rinsom

**A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science**

Program of Petrochemistry and Polymer Science

Graduate school

Chulalongkorn University

Academic Year 1999

ISBN 974-333-155-7

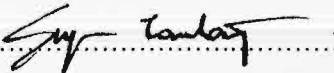
Thesis Title Effect of SAN on the mechanical properties and morphology of
 ABS
By Mr. Supachai Rinsom
Department Petrochemistry and Polymer Science
Thesis Advisor Associate Professor Supawan Tantayanon, Ph.D.
Thesis Co-advisor Mr. Pierre Priest, Ph.D.


Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment
of the Requirements for the Master's Degree


 Dean of Graduate School
(Associate Professor Suchada Kiranandana , Ph.D.)

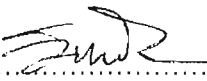
THESIS COMMITTEE

 Chairman
(Professor Pattarapan Prasassarakich , Ph.D.)

 Thesis Advisor
(Associate Professor Supawan Tantayanon , Ph.D.)

 Thesis Co-advisor
(Mr.Pierre Priest , Ph.D.)

 Member
(Associate Professor Wimonrat Trakarnpruk , Ph.D.)

 Member
(Ajarn Vipavee Phuvanartnuruk , Ph.D.)

ศุภชัย รินสม : ผลของเอสเอเอ็นต่อสมบัติเชิงกลและสัณฐานวิทยาของเอบีเอส (EFFECT OF SAN ON THE MECHANICAL PROPERTIES AND MORPHOLOGY OF ABS) อ.ที่ปรึกษา : รศ.ดร. ศุภวรรณ ตันตยานนท์, อ.ที่ปรึกษาร่วม : ดร.ปีแอร์ พริส ; 64 หน้า, ISBN 974-333-155-7

การศึกษาผลของความสามารถในการไหล และ ปริมาณอะคริโลไนไตรล์ ของเอสเอเอ็น ต่อสมบัติเชิงกล และสัณฐานวิทยาของอะคริโลไนไตรล์ บิวทาไดอีน สไตรีน พอลิเมอร์ (เอบีเอส) เอสเอเอ็น ที่มีความแตกต่างกันในความสามารถในการไหล และปริมาณอะคริโลไนไตรล์ ถูกนำมา ผสมกับ ยางกราฟฟอลิบิวทาไดอีน ช่วงของความสามารถในการไหลของเอสเอเอ็นที่ใช้ในการ ทดลองอยู่ระหว่าง 6.2 ถึง 84.7 กรัมต่อ 10 นาที และ ปริมาณอะคริโลไนไตรล์อยู่ในช่วงระหว่าง 23.5 ถึง 40 เปอร์เซ็นต์ ในขณะที่ปริมาณอะคริโลไนไตรล์ ในยางกราฟฟอลิบิวทาไดอีน มีค่า 25 เปอร์เซ็นต์ สัดส่วนของยางในการผสมอยู่ระหว่าง 13 ถึง 18 เปอร์เซ็นต์ ในรายงานได้เสนอสมการ ที่ใช้ในการคำนวณการทนแรงกระแทกไอซอด และ ความสามารถในการไหลของเอบีเอส จาก ความสามารถในการไหล และ ปริมาณ อะคริโลไนไตรล์ของเอสเอเอ็น และสัดส่วนของยางกราฟ ฟอลิบิวทาไดอีน ภาพถ่ายโดยใช้ ทรานสมิซชัน อิเล็กตรอน ไมโครสโคป ของเอบีเอสที่มียาง 15.5 เปอร์เซ็นต์ กับเอสเอเอ็นที่มีปริมาณอะคริโลไนไตรล์ 23.1, 29.3, 32.2 และ 40.7 เปอร์เซ็นต์ พบว่า การกระจายตัวของยางในเอสเอเอ็นมีความคล้ายกัน แต่ในการผสมของเอสเอเอ็นที่มีปริมาณ อะคริโลไนไตรล์ต่างจากปริมาณอะคริโลไนไตรล์ของยางกราฟฟอลิบิวทาไดอีนมากจะมีช่องว่าง ระหว่างการกระจายตัวของยางมากขึ้น

จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา _____
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
ปีการศึกษา 2542

ลายมือชื่อนิสิต Suy K
ลายมือชื่ออาจารย์ที่ปรึกษา Suy K
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม Prist

##4073418923 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEY WORD: SAN / ABS / MECHANICAL PROPERTIES / MORPHOLOGY / PREDICTION.
SUPACHAI RINSOM : EFFECT OF SAN ON THE MECHANICAL PROPERTIES AND
MORPHOLOGY OF ABS. THESIS ADVISOR: ASSO. PROF. SUPAWAN
TANTAYANON, Ph.D. THESIS CO-ADVISOR: MR. PIERRE PRIEST, Ph.D. 64 pp.
ISBN 974-333-155-7

The effects of melt flow index (MFI) and acrylonitrile (AN) content of the styrene-acrylonitrile copolymer (SAN) on the mechanical properties and morphology of acrylonitrile butadiene styrene terpolymer were studied. A series of SAN had been blended with SAN graft polybutadiene rubber. The MFI of SAN matrix was varied from 6.2 to 84.7 gram/10 minutes and the AN content of SAN matrix was varied from 23.5 to 40.7 %, while the AN content of the emulsion-made graft was fixed at 25 %. The rubber content had been varied from 13 to 18 %. The relationships between Izod impact and MFI of ABS with the MFI and AN content of SAN matrix and rubber content were proposed. Transmission electron photomicrographs showed similarity in rubber particle dispersion on 15.5% rubber content and SAN matrix containing 23.1, 29.3, 32.2 and 40.7 % of AN content. However, as the difference in AN content of graft and the matrix increase, the rubber particle appear to be more agglomerated with large area of the matrix free of particles.

จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา _____

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

ปีการศึกษา 2542

ลายมือชื่อนิสิต Supak

ลายมือชื่ออาจารย์ที่ปรึกษา Sup. Tanyan

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม P. Priest

ACKNOWLEDGEMENT



With the assistance of many people, this research work and thesis are finally completed. I would like to express gratitude to my advisor, Associate Professor Dr. Supawan Tantayanon, who has given me important advice during the course of the research. Furthermore, I would like to thank all members of my thesis committee, Dr. Pierre Priest, Professor Dr. Pattarapan Prasassarakich, Associate Professor Dr. Wimonrat Trakampruk and Dr. Vipavee Phuvanartnuruk, who have kindly given their valuable time to comment on my thesis. My sincere thanks are also extended to Dr. Sawitree Bintasan, Mr. John Wong for their kindly support and Bayer Polymers Co., Ltd. for its supply of materials and the incorporate help on the use of the company's excellent testing equipment. The last, I thank all members of my family for their full support and encouragement.

จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

ABSTRACT (in Thai)	iv
ABSTRACT (in English)	v
ACKNOWLEDGEMENT	vi
CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
SUMMARY OF ACRONYM	xii
CHAPTER	
I INTRODUCTION	1
1.1 General introduction	1
1.2 The purpose of the present study	3
II THEORY	5
2.1 ABS manufacturing	5
2.1.1 ABS production techniques.....	5
2.1.2 Characteristics of ABS resins.....	7
2.1.3 ABS processing	8
2.2 Rubber toughening and mechanisms in polymeric material	9
2.2.1 Effect of the dispersed rubber phase.....	10
2.2.2 Interaction between rubber and matrix.....	12
2.2.3 Mechanism of failure	13
2.3 Melt flow of thermoplastics	14
2.4 Morphology	15
2.5 Literature survey	17
III EXPERIMENTAL	19
3.1 Materials	19
3.1.1 Graft polybutadiene.....	19
3.1.2 SAN	19
3.1.3 Ethylene bis-stearamide (EBS) and other additives.....	21
3.2 Machine and apparatus	21

CONTENTS (CONTINUE)

3.3	Mixing and sample preparation	21
3.3.1	Mixing.....	21
3.3.2	Compounding.....	22
3.3.3	Molding.....	23
3.4	Mechanical testing	23
3.4.1	Compounding of Izod impact and tensile specimens.....	23
3.4.2	Izod impact.....	24
3.4.3	Tensile modulus.....	24
3.4.4	Tensile strength and tensile elongation.....	24
3.5	Melt flow index (MFI) or Melt volume flow rate (MVR)	25
3.6	Heat resistance	25
3.7	Morphology by transmission electron microscope	26
IV	RESULTS AND DISCUSSION	27
4.1	Evaluation of reproducibility	27
4.2	The effect of rubber content and type of SAN on Izod impact of ABS	28
4.2.1	Prediction model for Izod impact.....	34
4.2.1.1	Prediction from the effect of rubber content.....	34
4.2.1.2	Prediction from the effect of SAN matrix.....	35
4.3	The effect of SAN on MFI of ABS and the prediction model	38
4.4	The effect of rubber content and type of SAN on the other properties	41
4.4.1	The effect on tensile modulus.....	41
4.4.2	The effect on tensile strength at yield	42
4.4.3	Tensile strength at break	44
4.4.4	Tensile elongation at break.....	44
4.4.5	The effect of SAN matrix in yellowness index (YI).....	44
4.4.6	The effect of rubber content and SAN on gloss.....	45
4.5	The influence of lubricants and colorants in ABS properties.....	46

CONTENTS (CONTINUE)

4.5.1	The effect of lubricants and colorants on the Izod impact of ABS.....	46
4.5.2	The influence on tensile properties.....	48
4.5.3	The influence on MFI.....	48
4.5.4	The influence on yellowness index and gloss.....	48
4.6	Further experiment	49
4.7	Prediction	50
4.8	Morphology	51
V	CONCLUSION AND SUGGESTION	54
5.1	Conclusion	54
5.2	Suggestion for further experiment	55
	REFERENCES	56
	APPENDIX	58
	BIOGRAPHY	65

LIST OF TABLES

Table		
1.1	Typical properties of SAN and ABS	3
2.1	Brittle matrices and their rubber blends	12
2.2	Characterization techniques: size ranges	16
3.1	SAN matrix properties	20
3.2	Mixing formulation for the first set	22
3.3	Mixing formulation for the second set	22
4.1	Properties of ABS blend for checking variation of mixing, sample preparation and testing method	27
4.2	Properties of ABS derived from the blends with different rubber content in SAN	28
4.3	The calculation average 'c' value from Equation 4.1	35
4.4	The comparison between 'c' observed from experiment and 'c' calculated by Equation 4.2	36
4.5	The comparison between experiment and prediction results on Izod impact	37
4.6	The calculate 'x' from the observed result using Equation 4.4	38
4.7	The observed MFI and the calculated MFI by Equation 4.4 using 'x' for easy flow and stiff flow as mentioned	40
4.8	The yellowness index of ABS at different AN contents	44
4.9	The different gloss from the average	46
4.10	Properties of ABS blend in different additives at 15.5 % rubber and SAN 9	47
4.11	The further experiment compared between observed and predicted values	49
4.12	Trend of ABS properties on the effect of SAN, rubber content and additives	50

LIST OF FIGURES

Figure		
1.1	The overview of ABS manufacturing	2
2.1	The alternative blending of ABS manufacturing	6
2.2	Particles of rubber disperse in SAN matrix	7
2.3	Notch impact strength versus percent rubber content for various SAN matrices	10
2.4	Increased toughness versus rubber particle size	11
2.5	Reaction between osmium tetroxide and carbon-carbon double bond	16
3.1	SAN matrix qualities mapping	20
4.1	Izod impact of ABS versus rubber content for various SAN matrices ...	31
4.2	Izod impact of ABS versus rubber content for various SAN matrices ...	32
4.3	Izod impact of ABS versus rubber content for various SAN matrices ...	32
4.4	Notched Izod impact strength versus AN content of SAN matrices	33
4.5	Tensile modulus versus rubber content	42
4.6	Tensile strength at yield versus rubber content	43
4.7	The correlation between An content in SAN versus yellowness index of ABS	45
4.8	Izod impact versus additives at 15.5 % rubber content in SAN 9	47
4.9	Transmission electron photomicrographs (a), (b)	52
4.10	Transmission electron photomicrographs (c), (d)	53

SUMMARY OF ACRONYM

ABS	Acrylonitrile butadiene styrene terpolymer
AN	Acrylonitrile monomer
BD	Butadiene monomer
CB	Carbon black
EBS	Ethylene bis-stearamide
ISO	The International Organization for Standardization
MFI	Melt flow index
NBR	Acrylonitrile butadiene rubber
PETS	Pentaerythriol stearate
PC	Polycarbonate
SAN	Styrene acrylonitrile copolymer
SAN-graft	Styrene acrylonitrile graft on polybutadiene
SBR	Styrene butadiene rubber
Si-oil	Silicone oil, polydimethyl siloxane
SM	Styrene monomer
TE	Tensile elongation
TM	Tensile modulus
TS	Tensile strength
T_g	Glass transition temperature

CHAPTER I INTRODUCTION



1.1 General introduction

Acrylonitrile butadiene styrene terpolymer (ABS) is a well-known commercial polymer. ABS has a wide range of injection molding products consisting of general purpose, high flow, high gloss, paintable and plating grades as well as sheet extrusion products. Key applications are toys, automotive parts, electrical appliances, telephone sets, business machine housings, general consumer durable and refrigeration.

The versatility of ABS is derived from its monomeric building blocks: acrylonitrile, butadiene and styrene. Acrylonitrile primarily offers chemical resistance and heat stability, butadiene delivers toughness and the styrene component provides ABS with rigidity and processability. Figure 1.1 shows the overview of ABS manufacturing. ABS offers a balance of strength, toughness, high gloss, processability, high dimensional accuracy and stability. It has good electrical insulating properties, resistance to many aggressive media, which is partly due to the amorphous structure of the polymer. Finished parts can be made from ABS by injection molding, extrusion, thermoforming and other techniques. In addition, ABS lends itself to secondary processing such as plating, painting and a large number of other secondary processing forms.

ABS is a two-phase system, continuous SAN phase and rubber phase inclusions. It is generally manufactured from graft polymerization of acrylonitrile and styrene onto polybutadiene rubber followed by blending with styrene acrylonitrile copolymer (SAN). Physical properties of ABS are influenced not only by the rubber content, rubber particle size and rubber particle size distribution but also by molecular weight and acrylonitrile (AN) content of matrix SAN¹. Graft polybutadiene has direct influence on properties like impact resistance. SAN provides rigidity, chemical resistance and processability.

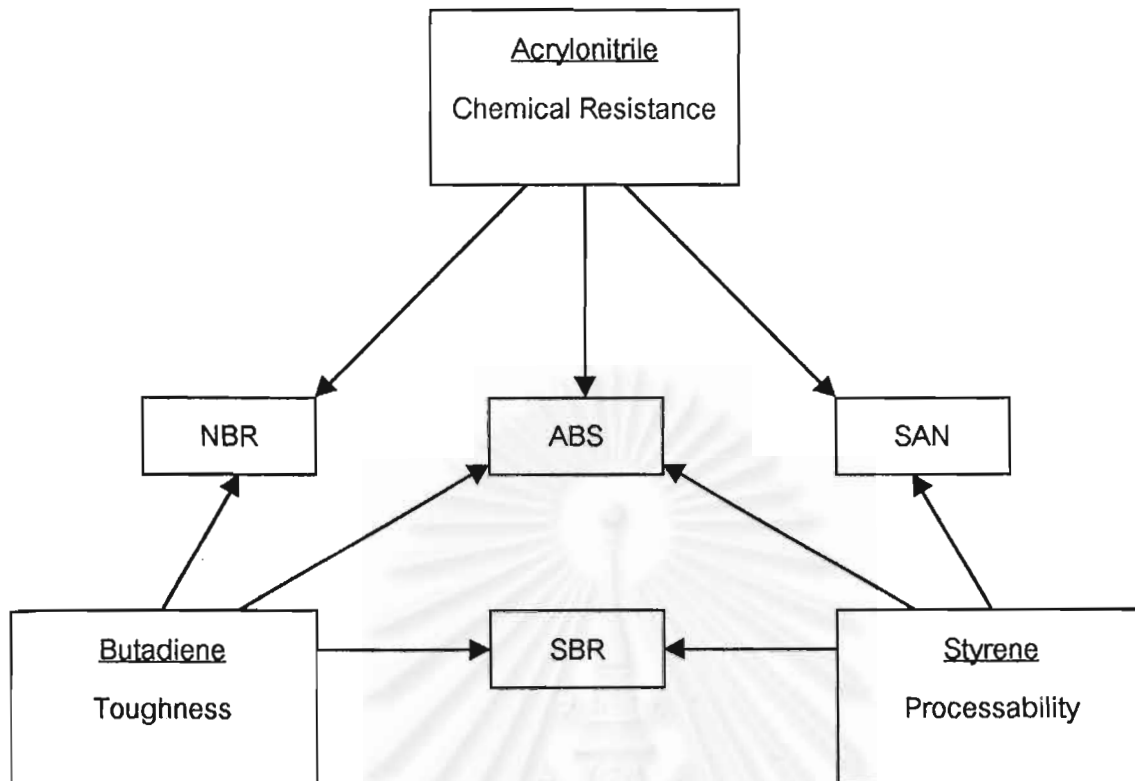


Figure 1.1: The overview of ABS manufacturing

ABS has a wide range of applications. The key properties required in each application are impact, which is designated as standard impact, medium impact and high impact, and flowability designated as high flow. The other properties are plating, paintable, rigidity and chemical resistance. In order to obtain the above properties, rubber content, SAN type, SAN content and additives are varied in many formulations. The critical part for designing the formulation is the balance between impact and flow. Increasing graft polybutadiene rubber content, the impact strength of the polymer is improved, while the other properties, for examples, tensile modulus, tensile strength and melt flow index, are generally lowered. Therefore, type of SAN, which can differ in molecular weight and AN content, is selected for compensation of those tensile and flow properties.

Even though there are many grades available for customer, the development of new ABS product is still necessary. The development of new ABS product aims to meet specific customer requirements and/or application at lower cost and depending on the availability of SAN. The alternative formulations for each grade are also needed in case of shortage of SAN in one formulation. In order to arrive at certain ABS formulation, lab scale blending is prepared then mechanical and flow properties are determined. A large number of experiments may have to be done in order to define the formulation, even when using experimental design techniques. These experiments not only consume materials but also require a lot of time.

Table 1.1: Typical properties of SAN and ABS

Property	SAN	ABS			
		High flow	Medium impact	High impact	High heat
Izod (kJ/m ²)	1-2	15	20	25	19
TM (GPa)	3.7	2.5	2.5	2.2	2.5
TS at yield (MPa)	-	49	48	43	47
TS at break (MPa)	70	35	34	33	33
MFI ^{**} (g/10 min)	20	30	20	16	10
Vicat ^{***} (Celsius)	105	100	98	96	115

* Typical data from Lustran SAN and Lustran ABS, Bayer Polymers 1998

** The MFI condition is at 220 degree Celsius and 10 kilogram.

*** The Vicat condition is at 5 kilogram load.

1.2 The purpose of the present study

The purpose of this research is to study the effect of molecular weight and AN content of SAN on the properties of ABS and using the correlation of this effect to select SAN and estimate the formulation for ABS. Mathematical calculation methods were used to estimate the properties of the new designed formulations. Key properties consisting of Izod impact, tensile modulus, tensile strength at yield, tensile strength at

break, gloss, yellowness index and melt flow index were focused in this experiment. The morphologies of ABS, which contain different SAN, were also examined.



จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER II THEORY

2.1 ABS manufacturing

ABS, one of the oldest commercial polymer blends, is a dispersion of polybutadiene rubber particles in a rigid copolymer of SAN. It was introduced commercially in the 1950s.

ABS resin is a two-phase system having a SAN as a continuous phase with a dispersed elastomeric phase of butadiene-derived rubber. The first ABS resins were made by blending styrene-acrylonitrile (SAN) copolymer with polybutadiene. (The technique was similar to that originally used for blending rubber particles with polystyrene to make high-impact polystyrene.) The acrylonitrile in the matrix contributes to heat stability and chemical resistance. It was later discovered that grafting some of the SAN onto a polybutadiene backbone increases the adhesion between the SAN matrix and the SAN-graft rubber particles and improves the mechanical properties. Grafting refers to the polymerization of one or more monomers onto a preformed polymer of another composition. Impact strength was found much improved when grafting was applied.

2.1.1 ABS production techniques

The properties of ABS are strongly affected by the rubber particle sizes and properties of SAN matrix. ABS materials are normally prepared in one of three manufacturing processes – emulsion, continuous mass, or suspension. Often, more than one of these processes are combined, optimizing the final polymer. The rubber and graft polymer are generally made by emulsion polymerization, when the SAN rigid phase is generally made by continuous mass, or suspension. Figure 2.1 shows the alternative blending procedures of ABS manufacturing.

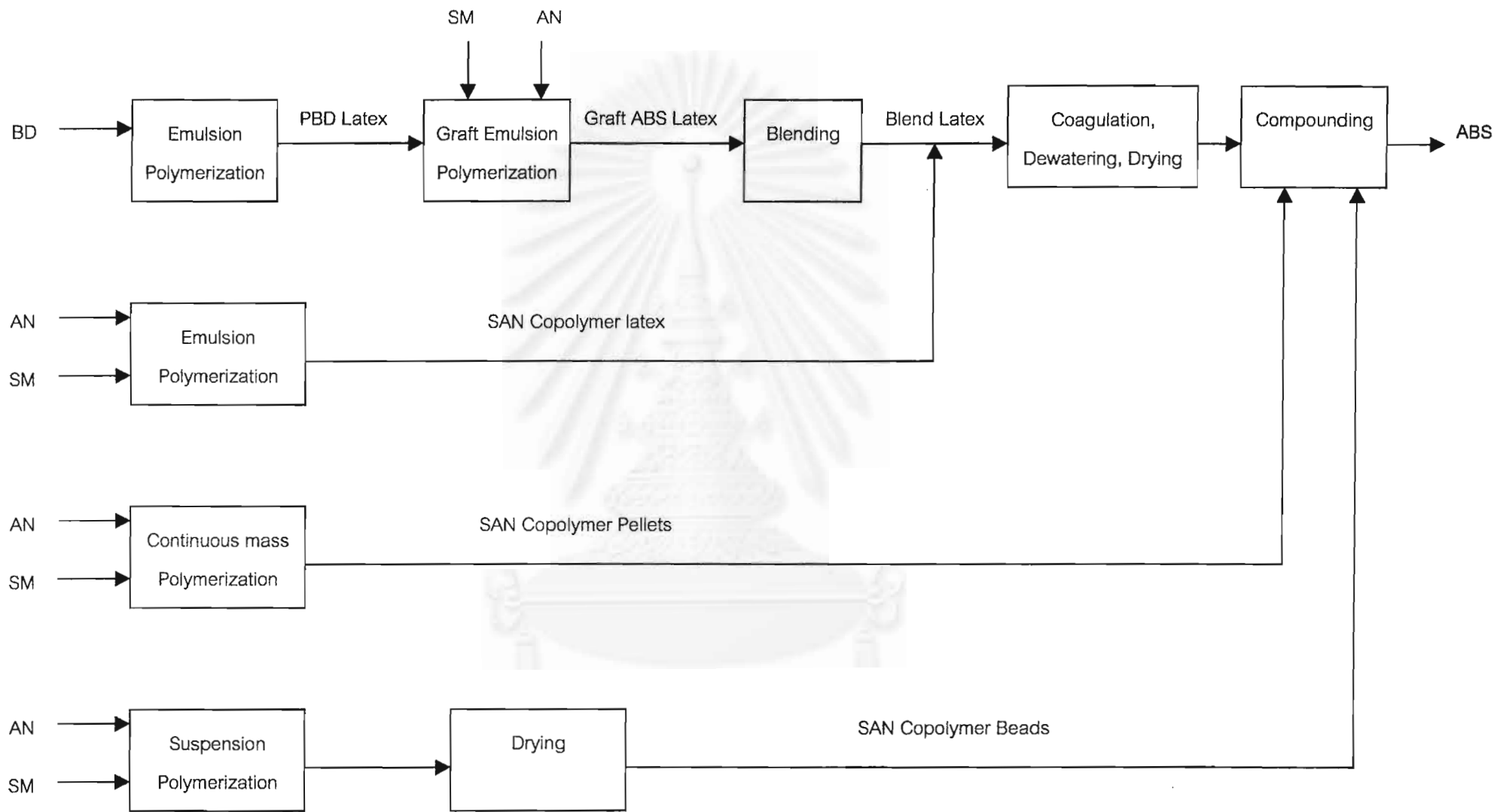


Figure 2.1: The alternative blending of ABS manufacturing

The proportions of the three components in ABS resins can vary widely, as the techniques and order of combining them. Varying the ratio of the three A-B-S monomers, the molecular weight of the polymer, and morphology of the rubber phase provides a limitless number of product options within the ABS family. For example, the particle size of the rubber phase may be varied from less than 0.1 micron to 10 microns.

The average particle size and the particle size distribution within this rubber phase have a significant effect on the overall polymer toughness, and appearance. Large rubber particles typically enhance toughness while lowering gloss. Figure 2.2 shows the particles of rubber phase dispersed in SAN matrix.

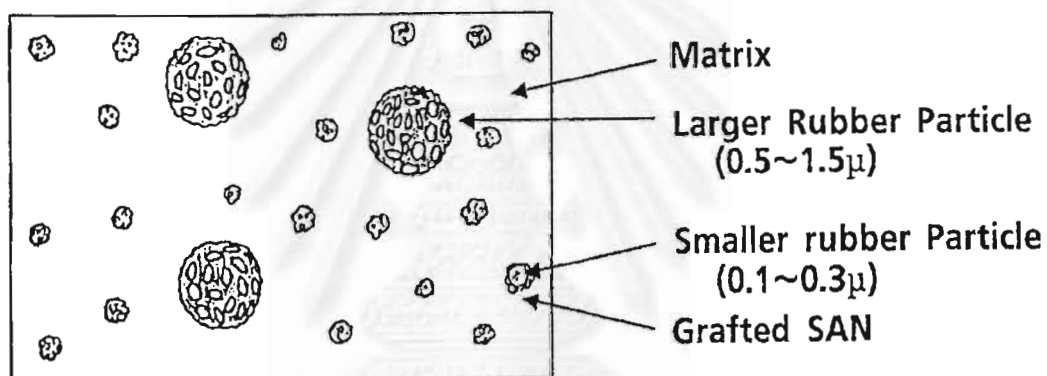


Figure 2.2 Particles of rubber dispersed in SAN matrix.

ABS properties can be modified by blending with other polymers such as polycarbonate or polyamide, replacing styrene monomer with alpha methyl styrene or bromo-styrene, or replacing polybutadiene rubber with acrylic rubber. Additives and fillers including anti-static, glass fiber, flame retardant, are also used to enhance the specific properties.

2.1.2 Characteristics of ABS resins

The physical, chemical, and mechanical properties of ABS resins depend on the structure, as described by these parameters;

- (1) Molecular weight (MW) and MW distribution of the polymer chains and copolymer chains.
- (2) Proportions of acrylonitrile, butadiene and styrene in each of the two phases of the polymer.
- (3) Size and size distribution of rubber particles.
- (4) Degree of grafting of SAN copolymer on the rubber particles
- (5) Degree of adhesion between the rubber particles and the SAN matrix.
- (6) Addition of modifiers to one or both phases.

The rigid SAN phase chain length, as correlated to molecular weight, can also have a significant effect on ABS resin properties. Generally the longer the polymer chains, the higher the strength properties, including impact/ductility, but the lower the flow. The ratio of the rigid SAN phase to the rubber phase will affect the flow/impact balance of the ABS resin. For the example, increases in rubber content will increase the impact/toughness of an ABS material, generally lower the flow. This balance between the flow and impact properties of an ABS material is a basic product characteristic, which distinguishes one general-purpose ABS grade from another.

2.1.3 ABS processing

ABS is an amorphous thermoplastic, which softens over a range of temperatures instead of melting abruptly. It is slightly hygroscopic and should be dried before melt processing. ABS is usually sold as pellets in its natural color or pre-colored. Commonly used secondary operations such as machining, bonding, fastening, plating and painting are easily adapted to a variety of ABS materials.

A basic strength of ABS resin is processability. ABS materials typically have a broad processing window of operating conditions. A large variety of processing options are available including injection molding, extrusion, thermoforming, structural foam, and blow molding.

2.2 Rubber toughening mechanisms in polymeric material

The next paragraphs are a summary of generally accepted recent theories, references are attached.

The method to improve fracture toughness of glassy polymers by adding a small quantity of rubber particles is well known. The toughness improvement is mainly attributed to the presence of rubber particles enhancing energy absorption capacity of the matrix. This can be achieved in several ways. For brittle polymers that on their own failed by crazing, the rubber particle can act like craze initiators, decreasing craze flow stress, hence, effectively increasing the number of crazes in the deformation zone². For pseudo-ductile polymers that under certain test conditions can fail by shear yielding, the presence of rubber particle reduces notch sensitivity of matrix and promotes shear bands to increase the toughness. For polymers that have stresses for initiation of crazes and shear bands, the matrix can fail by crazing, while the rubber-modified counterpart by shear yielding. It was reported that the transition from crazing to shear yielding for this polymer is enhanced by using rubber particles of bimodal size distribution².

The polymers, for example polystyrene (PS) and styrene-acrylonitrile (SAN), failed by crazing, and are brittle at 10-20 C below the glass transition temperature (T_g). They have low crack initiation and low crack dissipation energies during impacts. They have low unnotched and notched impact strengths. When rubber toughened they still tend to fail by crazing³.

In these materials the impact energy is most effectively dissipated by the formation of large craze development. The dispersed impact modifier must arrest these crazes and must be sufficiently large enough so as not to be taken by the approaching craze. The rubber particle size must exceed the craze thickness and the interfacial adhesion must be sufficient to permit the effective transfer of stress to the rubber inclusion to blunt the craze. The size required is of the micron scale.

2.2.1 Effect of the dispersed rubber phase

(a) Rubber content

H. Kim, H. Keskkula and D.R. Paul⁴ studied the effect of rubber content on Izod impact strength. This research has been carried out on graft polybutadiene rubber toughened on SAN. Figure 2.3 shows the variation of notched Izod impact strength with rubber content. At low rubber content from 0 to 10 percent, Izod impact is slightly increased. In the range of 10 to 20 percent rubber contents, Izod impact increases rapidly. The curves are in S-shape. In these results particle size is constant and interfacial adhesion is depended on type of SAN. Increasing the content of the rubber phase decreases the blend modulus and tensile strength irrespective of whether the matrix is brittle or pseudo-ductile³.

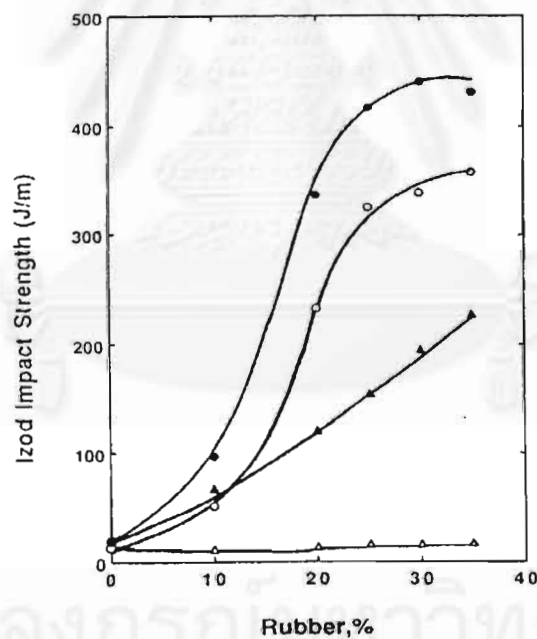


Figure 2.3: Notched impact strength versus percent rubber content for various

SAN matrices; Δ , PS; \circ , SAN 20; \bullet , SAN 34; \blacktriangle , SAN 40

(digits mean AN content of SAN), AN content of SAN-graft is 22.5%⁴

(b) Particle size of rubber

At a fixed rubber concentration and fixed interfacial adhesion, a graph of toughness versus rubber particle size gives a maximum toughness for an optimum particle size, as shown in Figure 2.4. The optimum particle sizes for toughening several brittle matrices are given in Table 2.1, with the Izod impact strength of the matrix and values for the toughened blend.

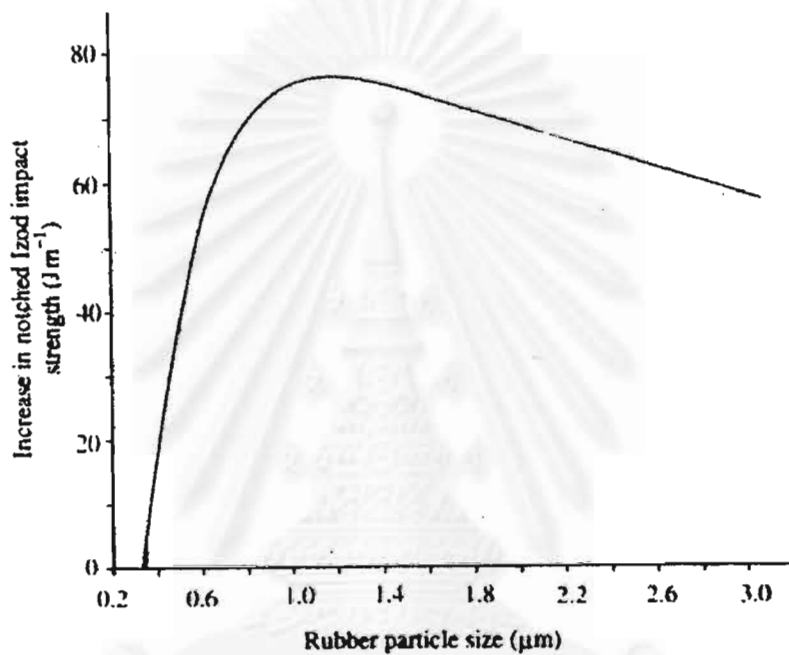


Figure 2.4: Increased toughness versus rubber particle size.

(Adapted from Rubber toughened engineering plastics)³

Bimodal-sized particles are particularly successful in the toughening of SAN, possibly because of the balance of crazing and yielding that occurs in the fracture of this material³.

Table 2.1: Brittle matrices and their rubber blends³

<i>Matrix Polymer</i>	<i>PS</i>	<i>SAN</i>	<i>PMMA</i>
Predominant fracture mechanism	Crazing	Crazing	Crazing
Apparent internal structure of craze	Fibrillar	Mix homogenous and fibrillar	Homogenous
Typical notched Izod impact strength (J m ⁻¹ (ft-lb in ⁻¹))	21 (0.4)	16(0.3)	16(0.3)
Polymer-rubber blend fracture mechanism	Crazing	Crazing and yielding	Yielding and crazing
Optimum rubber diameter (μm)	2.5	0.75 ± 0.15	0.25 ± 0.05
Bimodal size synergism	Marginal	Pronounced	Marginal
Typical notched Izod impact strength (20-25 vol.% rubber) (J m ⁻¹ (ft-lb in ⁻¹))	130(2.5)	780(15)	80(1.5)

2.2.2 Interaction between rubber and matrix

Rubber toughened plastics are composite materials, consisting of a rigid matrix with a relatively high T_g and a rubbery disperse phase with a low T_g . The adhesion between these phases should be strong, and the rubber should be broken down into small particles without becoming too finely dispersed to be effective in toughening the rigid polymer. The problem of polymer-polymer compatibility arises in two ways in the field of rubber toughening. On one hand, it is necessary to produce and maintain phase separation between the rubber and rigid polymer in order to make a product that combines stiffness with toughness. On the other hand, in blending a rubber-toughened thermoplastic with another thermoplastic, it is important to ensure that the two thermoplastics are completely compatible⁵.

Grafting is an important method for obtaining a strong bond between rubber particles and the surrounding resin. For this reason it is an essential feature in the manufacture of ABS. Locatelli and Riess have made an extensive study of ABS polymerization, in which styrene and acrylonitrile are grafted onto polybutadiene, and ungrafted styrene-acrylonitrile is also formed⁵. The graft composition has usually been kept the same as that of the matrix SAN in order to achieve a high degree of compatibility between the SAN grafted to the rubber particles and the matrix⁴.

2.2.3 Mechanism of failure

The first theory of toughening was published in 1956 by Merz et al⁵. The basic idea was that the rubber particles held together the opposite faces of a propagation crack, so that the energy absorbed in impact was the sum of the energy to fracture the glassy matrix and the work to break the rubber particles. The weakness of the theory was that it concentrated attention upon the rubber rather than on the matrix. There were significant differences in fracture behavior between toughened PS and toughened PVC, which could not adequately be explained by the crack theory.

A number of quite different mechanisms for toughening have been proposed but all rely on a dispersion of rubber particles within the glassy matrix. These have included energy absorption by rubber particles, de-bonding at the rubber matrix interface, matrix crazing, shear yielding or combination of shear yielding and crazing³. Both crazing and shear yielding have been observed in ABS. Their dominance in energy absorption for fracture depends on material compositions and testing conditions used for the characterization. Breuer et al. and Donald and Kramer suggested that shear yielding occurs in ABS. Donald and Kramer reported that ABS with rubber particles of bimodal size distribution (0.1 and 1.5 μm in diameter) showed both crazing and shear yielding, depend on the matrix ligament thickness, that is defined as the distance between adjacent particle surfaces².

(a) Matrix crazing

Rubber particles have been shown both to initiate and to control craze growth. Under an applied tensile stress, crazes are initiated at points of maximum principal strain, typically near the equator of rubber particles (maximum concentration of triaxial stress), and propagate outwards normal to the maximum applied stress, although interactions between the particles' stress field can introduce deviations. Craze growth is terminated when a further rubber particle is encountered, preventing the growth of very large crazes. The result is a large number of small crazes in contrast to a small number of large crazes formed in the same polymer in the absence of rubber particles. The dense crazing that occurs throughout a comparatively large volume of the multiphase material accounts for the high energy absorption observed in tensile and impact tests and the extensive stress whitening, which accompanies deformation and failure³.

(b) Shear yielding

Shear deformation is a distortion of shape without significant change in volume. In crystalline materials, shear yielding takes place by slip on specific slip planes, as a result of dislocation slide. In non-crystalline polymers, large-strain deformation requires more movement of molecular segments, and shear processes are therefore much less localized than in crystalline materials. Shear yielding in the matrix phase plays a major role in the mechanism of rubber toughening in polymer blends. Shear yielding, as localized shear bands and diffuse regions of shear yielding, usually occurs in addition to elastic deformation. Shear bands present a barrier to the propagation of crazes and hence crack growth, therefore delaying failure of the material².

2.3 Melt flow of thermoplastics

The flow behavior of polymer melts is of great practical importance in polymer manufacturing and polymer processing. The flow behavior of polymer melts can be characterized by viscosity (ratio of stress and rate of deformation). The viscosity of

polymers depends on the average molecular weight, the molecular weight distribution, the temperature and the pressure or load.

There is a method to determine melt flow index (MFI) or melt volume-flow rate (MVR) of thermoplastics under specified temperature and load. The melt flow index is found useful when comparing between thermoplastics. It indicates the processability of polymer. The apparatus to determine MFI is basically a capillary rheometer, a model for flow of fluid through a capillary die⁶. A pressure flow through a tube may be used to determine the apparent viscosity of a polymer melt.

2.4 Morphology

In polymer science the term morphology generally refers to form and organization on a size scale above the atomic arrangement but smaller than the size and shape of the whole sample. The term 'structure' refers more to the local atomic and molecule details. However, the term 'structure' and 'morphology' are commonly used interchangeably. X-ray, electron and optical scattering techniques and a range of other analytical tools are commonly applied to determine the structure of polymer. X-ray diffraction, for example, permits the determination of interatomic ordering and chain packing on crystalline polymer. The morphology of polymers is determined by a wide range of optical and electron microscopy techniques.

In transmission electron microscopy (TEM), image contrast is the result of variations in electron density among the structures present. TEM of multiphase polymers often do not provide enough contrast to image the phases clearly. Methods which have proven useful in contrast enhancement include shadowing with a heavy metal in a vacuum evaporator and staining, generally by addition of heavy atoms to specific structures. The staining of rubber phases of polymer with osmium tetroxide was introduced by Andrews and Stubbs and Andrew⁷, who stained unsaturated synthetic rubbers, and then further developed by Kato⁷, to show the morphology of rubber modified plastics and unsaturated latex particles. The polybutadiene in ABS polymers is

not apparent in unstained cross sections in the TEM, but staining results in contrast enhancement due to increased density of the unsaturated phase. Osmium tetroxide reacts with the carbon-carbon double bonds in saturated rubber phases enhancing the contrast in TEM by the increased electron scattering of the heavy metal in the rubber compared to the unstained matrix.

Table 2.2: Characterization techniques: size ranges⁷

Wide angle x-ray scattering (WAXS)	0.01 – 1.5 nm
Small angle x-ray scattering (SAXS)	1.5 - 100 nm
Transmission electron microscopy (TEM)	0.2 nm - 0.2 mm
Scanning electron microscopy (SEM)	4 nm - 4 mm
Optical microscopy (OM)	200 nm – 200 μm

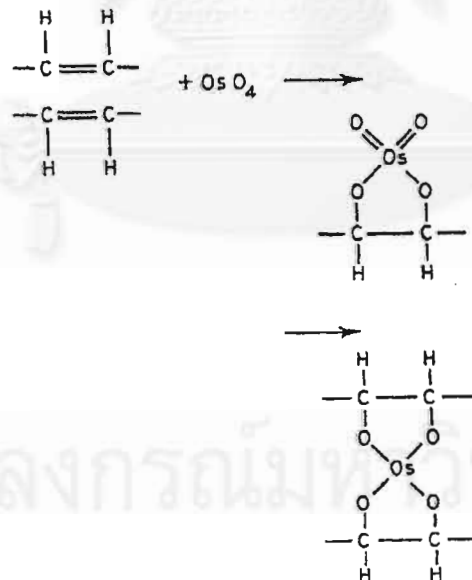


Figure 2.5: Reaction between osmium tetroxide and carbon-carbon double bond

2.5 Literature survey

H. Kim, H. Keskkula and D.R. Paul⁴ studied the effect of composition of the SAN matrix, for a fixed SAN graft, on blended toughness, deformation behavior and morphology. The AN content varied from 0 to 40 % in the matrix copolymers, while the AN content of the emulsion-made graft was fixed at 22.5%. Maximum strength and toughness were observed from composition based on SAN matrices containing 34 % AN. There was no major change in deformation mechanism as the AN content of the matrix changed. Transmission electron photomicrographs showed differences in rubber particle dispersion.

H. Kim, H. Keskkula and D.R. Paul⁸ studied the effect of AN content of SAN graft and AN content of SAN matrix in the mechanical behavior of the blends. The main variables of the study included the AN content of SAN graft (14.2 to 37.5%) and the AN content of the SAN matrix (14.7 to 40 %). Rubber-matrix adhesion, state of rubber particle dispersion and the inherent ductility of matrix polymer were evaluated, and the trends found in the mechanical behavior of the blends are reasonably well explained by these three factors.

C. R. Bernal⁹, et al. investigated the microstructure, deformation, and fracture behavior of commercial ABS resins. Fracture mechanics studies were carried out under both static and dynamic conditions. The ABS resins exhibited different deformation and fracture behavior depending on loading mode, matrix molecular weight, strain rate, temperature, rubber content, and morphologies. The major source of toughness seems to be matrix crazing and rubber cavitation under both static and dynamic experiences, but at low strain rates shear yielding also contributes to toughening.

M. C. O. Chang and R. L. Nemeth¹⁰ studied the effect of molecular structures of ABS fabricated under a severe molding condition of rubber particle agglomeration and molded specular gloss. It was found that as graft level decreased, agglomeration increased. The rubber particle agglomeration also increased when graft molecular

weight was increased. Lowering the particle size also led to a higher degree of agglomeration. Furthermore, increasing the compositional acrylonitrile mismatch between the grafted and matrix SAN increased the rubber particle agglomeration. Molecular structures that increased rubber particle agglomeration decreased the molded gloss.

I. J. Hwang and B.K. Kim¹ studied the effect of the molecular weight and AN content of the SAN on morphology, mechanical, and rheological properties of SAN/chlorinated polyethylene (CPE) blends. The interaction between dispersed particle and matrix is expected to be optimal at the 25 % AN content of SAN. Mechanical properties increased with molecular weight at a constant AN content of SAN. Morphological, mechanical, and rheological properties were more sensitive to the AN content rather than the molecular weight of SAN.

P.Y.B Jar, R. Lee, T. Shinmura, K. Konishi² investigated the toughness and morphology of poly(styrene-N-phenyl-male-imide) (SMI) modified in ABS. SMI is used in ABS to obtain the high thermal resistance. However, the addition of SMI causes a decrease in strength and toughness of the matrix. Three high thermal resistance ABS were evaluated for toughness using stress intensity factor (K_{Ic}). Deformation and fracture behavior were analyzed using an optical microscope and a transmission electron microscope. Matrix deformation of the three ABSs was found to involve particle cavitation, crazing and shear yielding.

จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Graft polybutadiene

Graft polybutadiene rubber is obtained from emulsion polymerization process of Bayer Polymers Co., Ltd. It is in powder form and white color. Polybutadiene is grafted by styrene and acrylonitrile monomers, which bring to the 50 % rubber content, for example 1 kilogram of graft polybutadiene has 0.5 kilogram of rubber. In this work, we used only but one type of graft polybutadiene. The designation of graft polybutadiene is SAN-graft. The rubber particle is bimodal with size 0.4 and 0.6 μm . AN content of SAN-graft is about 25%.

3.1.2 SAN

SAN is obtained from both suspension in bead form and continuous mass processes in pellet form of Bayer Polymers Co., Ltd. They are slightly yellowish color. AN content of SAN is in the range of 23.0 to 40.0 % and MFI is in the range of 6 to 85 gram/ 10 minutes (measured at 220 degree Celsius / 10 kilogram). (See Table 3.1) SAN 1 to SAN 4 were obtained by suspension polymerization, the others by continuous mass. The higher the MFI, the lower the molecular weight is. The correlation, log of MFI versus specific viscosity, is negative and pronounced, as expected.

Even though, SAN obtained from suspension or continuous mass process could be controlled at the same molecular weight and AN content, but their molecular weight distribution (MWD) is different. Suspension SAN has broader MWD than continuous mass SAN. The narrower MWD in continuous mass SAN gives the better balance between impact strength and melt flow index in ABS. However, the advantages of

suspension SAN are flexibility of product change between batches and the ability to make very high molecular weight.

Table 3.1: SAN matrix properties

SAN matrix	Process	MFI	Specific viscosity	AN content
		(220 C/ 10 kg) (g/10 min)	(DMF)	(%)
SAN 1	Suspension	6.2	0.105	28.6
SAN 2	Suspension	9.0	0.092	40.7
SAN 3	Suspension	84.7	0.052	28.7
SAN 4	Suspension	55.8	0.056	29.0
SAN 5	Continuous mass	29.8	0.046	23.1
SAN 6	Continuous mass	24.4	0.067	26.8
SAN 7	Continuous mass	78.7	0.052	29.3
SAN 8	Continuous mass	42.5	0.056	29.4
SAN 9	Continuous mass	15.6	0.066	32.2

Remark: Results are obtained from lot quality control, or if not part of quality control, measured on the actual samples used.

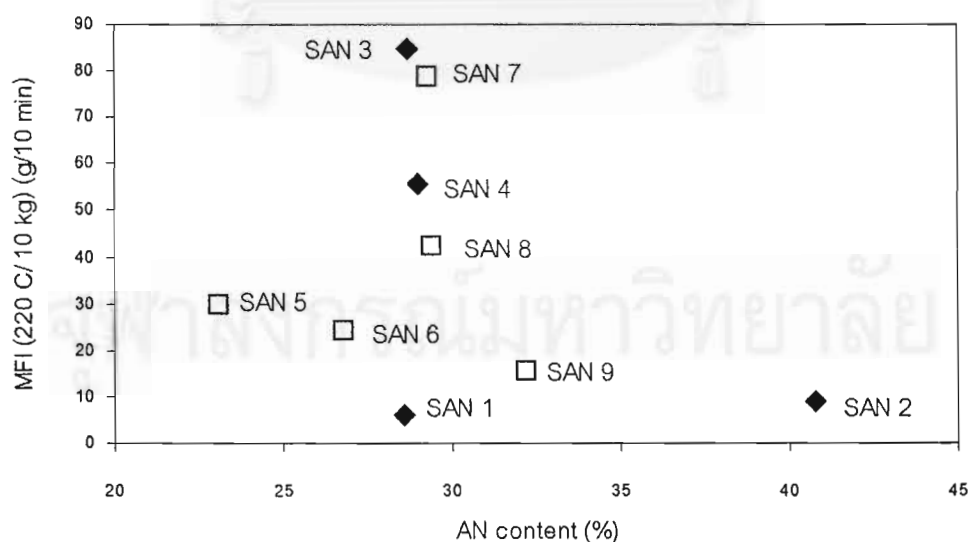


Figure 3.1: SAN matrix qualities mapping

◆, by suspension polymerization; □, by continuous mass polymerization

3.1.3 Ethylene bis-stearamide (EBS) and other additives

EBS is an internal lubricant for ABS to enhance ABS flow property and impact strength. It is in powder form and slightly yellowish color. EBS is commonly used in ABS compounding. Other additives, PETS and silicone oil and basic colorants, titanium dioxide (TiO₂) and carbon black (CB), are also investigated regarding to their influences to mechanical properties of ABS. PETS stands for Pentaerythritol stearate. It is an alternative to EBS, especially used for PC and PC/ABS alloys. Silicone oil, polydimethyl siloxane, is an additive known to reduce friction and has been specified by a German automotive manufacturer as a 'non-squeaking' additive.

3.2 Machine and apparatus

- (a) High speed mixer, Henchel
- (b) Twin screw extruder, Werner & Pfleiderer model ZK-30.
- (c) Molding machine, Arburg model 270 S allrounder 500-150, 50 Tons clamping force.
- (d) Notch machine, Ceast Model Notchvis 684.000.
- (e) Impact tester, Ceast model Resil 25 J 6525.000.
- (f) Tensile testing machine, Instron model 4466.
- (g) Melt flow indexer, Ceast model melt flow matic 6840.000.
- (h) Transmission electron microscope, Jeol, Jem-200CX, 100 kilo-Volt.

3.3 Mixing and sample preparation

3.3.1 Mixing

SAN-graft and SAN were blended in the high-speed mixer. Each batch was prepared in 5 kilogram. Rubber content and type of SAN were varied in different formulations. All ingredients were poured into the mixer and mixed for 1.5 minutes.

Since, SAN-graft is 50 % rubber, the formulations to obtain 13, 15.5% and 18% rubber are shown in Table 3.2. In addition, there are two sets of experiment, first set (See Table 3.2) was a varying between rubber content and type of SAN and second set was a varying of lubricants and colors (See Table 3.3). In the first set, 1 % by weight of EBS was added in every formulation. SAN matrix in Table 3.2 was repeated from SAN 1 to SAN 9, therefore the total of the first set were 27 formulations.

Table 3.2: Mixing formulation for the first set

Rubber content (% wt)	SAN-graft (g)	SAN matrix (g)	EBS (g)
13.0	1,300	3,700	50
15.5	1,550	3,450	50
18.0	1,800	3,200	50

Table 3.3: Mixing formulation for the second set

Additive (% wt)	SAN-graft (g)	SAN matrix (g)	EBS (g)	PETS (g)	Si-oil (g)	TiO ₂ (g)	CB (g)
None	1,550	3,450	-	-	-	-	-
EBS - 1	1,550	3,450	50	-	-	-	-
EBS - 2	1,550	3,450	100	-	-	-	-
PETS - 1	1,550	3,450	-	50	-	-	-
PETS - 2	1,550	3,450	-	100	-	-	-
Si-oil - 0.5	1,550	3,450	-	-	25	-	-
Si-oil - 1	1,550	3,450	-	-	50	-	-
TiO ₂ - 4	1,550	3,450	50	-	-	200	-
CB - 1	1,550	3,450	50	-	-	-	50

3.3.2 Compounding

The mixture from 3.2.1 was compounded in twin screw extruder. The temperature profile from the feeding zone to the die head were set at the same

temperature, 205 degree Celsius in all seven zones. The speed of the extruder was controlled at 320 ± 20 rev. per minute. The melt polymer from die head was pulled into the water bath controlled temperature at about 25-30 degree Celsius. The polymer strands were then pulled into the cutter, which control speed at the suitable rate corresponding to the feed rate and the pellet size.

3.3.3 Molding

The pellets from 3.2.2 were dried in the conventional air draft oven at 80 degree Celsius for two hours in order to remove the moisture. After drying, the pellets were poured into the hopper of the injection-molded machine. Two different types of molding were prepared according to ISO 3167 Plastics – Multipurpose test specimens. They are Izod impact and tensile specimens. (See Appendix 1 and 2) Injection molding temperatures were set at 220, 225, 230 and 240 degree Celsius from hopper to nozzle zone respectively. Mold temperature was controlled at 70 degree Celsius. After rejecting the first five shots, the test specimens were collected for the test. The Izod impact specimens were notched by using the notch machine.

In order to verify the reproducibility of the mixing and sample preparation, four batches of SAN-graft and SAN 7 blend at 15.5 % rubber were prepared, checked and evaluated for their mechanical and melt flow index properties.

3.4 Mechanical Testing

3.4.1 Conditioning of Izod impact and tensile specimens

The Izod impact and tensile specimens were conditioned for at least 16 hours at 23 degree Celsius and 50 % relative humidity according to ISO 291 prior to the tests.

3.4.2 Izod impact test

Izod impact strength was tested according to ISO 180 Plastics – Determination of Izod impact strength standard using notched specimens. Notched Izod impact specimens were tested by using the Izod impact tester. (See Appendix 5) The calculation values were reported in KiloJoules per square meter. (See Appendix 8.1)

3.4.3 Tensile modulus

Test specimens for tensile modulus were made by injection molding machine in dumbbell shape (See Appendix 1) according to ISO 3167. Tensile modulus was tested by tensile testing machine (See Appendix 6), according to ISO 527-1 Plastics – Determination of tensile properties.

Conditioned specimens of each formulation were tested following the procedure. Tensile tester contains microprocessor with the calculation methods. Therefore, with the necessary information including test method, test speed and dimensions of test specimen, it can report the tensile modulus in GigaPascal (GPa) after the test has been done. The average result from the 3 specimens was reported. Standard deviations were calculated. Repeating test with new specimen was done when the standard deviation was larger than the limit. (See Appendix 8.2)

3.4.4 Tensile strength at yield, tensile strength at break and tensile elongation at break

Tensile strength at yield was tested by the same tensile testing machine as Tensile modulus according to ISO 527-1 Plastics – Determination of tensile properties. Test specimen for tensile strength at yield is the same as tensile modulus. The difference is the speed of the test. For the determination of tensile strength at yield, speed was set to the higher rate, 10 millimeter per minute. Using this speed, test specimens were extended until they reached their yield stress and then finally broke.

Tensile strength at break and tensile elongation at break were obtained from the same test of tensile strength. The calculations were done by the machine with the input of test method, test speed and dimension of specimen. Results of each test were evaluated, calculated the average and standard deviation. Repeating test with new specimen was done when the standard deviation was larger than the limit. (See Appendix 8.3)

3.4 Melt flow index (MFI) or Melt volume flow rate (MVR)

MFI was tested according to ISO standard, ISO 1133 Plastics – Determination of the melt mass-flow rate (MFR) and the melt volume-flow rate (MVR) of thermoplastics. There are two factors to be controlled in MFI test consisting of barrel temperature and load. In this experiment, barrel temperature is controlled at 220 degree Celsius and using 10-kilogram load.

Pellets were dried in air draft oven at 80 degree Celsius for 2 hours prior to the test in order to remove moisture. ABS polymer was melted in the barrel at 220 degree Celsius and then pushed by the 10 kilogram load, which lay on top of the barrel, through the capillary die. (See Appendix 7) The results were reported in gram of polymer melt passed through the capillary die in 10 minutes. There are two testing methods, by actual weighing the melt polymer or by the calculation of the volume and then convert to weight by melt density. The second method was used in this experiment. (See Appendix 8.4)

3.5 Heat resistance

This important aspect is not covered, as the different SAN matrices used do not have a very significant effect on heat resistance. Heat resistance of ABS is generally measured in terms of Vicat softening temperature, the temperature that softens polymer at a constant load. Standard grades ABS's, including high flow, medium or high impact, have Vicat (5 kilogram) softening temperature at 95 – 101 degree Celsius.

3.6 Morphology by transmission electron microscope

Morphology of ABS was determined by transmission electron microscope. Sample was taken by cutting the compress thin film into a small piece then stained with osmium tetroxide (OsO_4) by dipped into 2% OsO_4 for 18 hours. Stained samples were coated with epoxy resin, dried in the oven at 70 degree Celsius for 8 hours then sliced into thin film 60-90 nm, and taken picture by transmission electron microscope.



จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Evaluation of reproducibility of mixing, compounding, molding and testing

As many steps (mixing, compounding, molding and testing) are involved before obtaining any result, the preliminary set of experiments was done in order to evaluate the reproducibility of all those steps together.

The formulation of 15.5 % by wt rubber content with SAN 7 was selected for this test. The ingredients were 1,550 gram of SAN-graft, 3,450 gram of SAN 7 and 50 gram of EBS. Four batches of this formulation were prepared at the same time and with the same lot of materials in order to have a guideline to check reproducibility. All properties showed good reproducibility according to their relative standard deviation from 0.4 to 5.6 %, except tensile elongation at break, which had high deviation. Therefore, the reproducibility between these four batches was good and it should be assumed that the following test results have a minimum error in mixing, preparation, compounding, molding and testing steps.

Table 4.1: Properties of ABS blend for checking variation of mixing, sample preparation and testing method

Rubber content (% wt)	Izod impact (kJ/m ²)	TM (GPa)	TS at Yield (MPa)	TS at Break (MPa)	TE at Break (%)	MFI (g/10min)
SAN 7						
15.5	16.5	2.51	49.8	36.2	21.6	29.6
15.5	17.6	2.47	49.5	36.0	33.8	29.9
15.5	17.9	2.46	49.3	36.7	30.5	26.5
15.5	17.2	2.44	49.8	37.3	22.0	28.0
AVG.	17.3	2.47	49.6	36.6	27.0	28.5
SD	0.6	0.03	0.2	0.6	6.1	1.6
Relative SD (%)	3.5	1.2	0.4	1.6	23	5.6

4.2 The effect of rubber content and type of SAN on Izod impact of ABS

The results of Izod impact and other properties of ABS derived from the blends with different rubber content in SAN are shown in Table 4.2. The rubber content range investigated covers high flow, medium impact and high impact grades in commercial ABS (See Table 1.1).

Table 4.2: Properties of ABS derived from the blends with different rubber content in SAN

Rubber content (% wt)	Izod impact (kJ/m ²)	TM (GPa)	TS at Yield (MPa)	TS at Break (MPa)	TE at Break (%)	MFI (g/10min)	YI (-)	Gloss 20° (%)
SAN 1								
13.0	18.8	2.54	55.3	39.0	14.5	2.6	31.9	91.4
15.5	27.7	2.36	50.0	35.4	18.3	2.0	32.3	91.0
18.0	31.3	2.27	48.0	34.6	26.6	1.6	33.0	89.1
SAN 2								
13.0	16.9	2.62	54.7	38.1	19.7	4.7	41.2	91.2
15.5	36.0	2.34	50.3	35.2	22.8	3.7	40.8	90.4
18.0	38.4	2.28	46.4	34.5	22.6	3.1	40.6	89.6
SAN 3								
13.0	10.4	2.59	49.8	37.3	15.5	33.2	32.0	93.1
15.5	17.1	2.35	45.8	34.7	21.2	23.6	33.7	92.7
18.0	23.0	2.33	43.8	32.6	18.8	20.7	33.8	92.4
SAN 4								
13.0	11.5	2.57	50.4	36.4	23.4	23.4	36.6	93.0
15.5	19.1	2.32	46.5	33.2	40.0	19.0	35.7	92.8
18.0	24.7	2.22	44.6	32.0	22.2	14.8	38.5	92.4
SAN 5								
13.0	11.3	2.59	52.4	37.6	13.9	17.5	29.4	95.5
15.5	18.4	2.38	48.0	33.0	18.4	14.1	28.8	94.1
18.0	22.8	2.27	45.4	32.9	16.7	12.1	31.0	93.4

Table 4.2: Properties of ABS blend in different rubber content and SAN (Continue)

Rubber content (% wt)	Izod impact (kJ/m ²)	TM (GPa)	TS at Yield (MPa)	TS at Break (MPa)	TE at Break (%)	MFI (g/10min)	YI (-)	Gloss 20° (%)
SAN 6								
13.0	14.6	2.61	50.8	37.2	23.9	13.7	30.9	93.2
15.5	22.5	2.38	47.2	33.5	26.0	10.6	32.3	93.1
18.0	26.0	2.32	45.7	33.4	20.2	9.2	32.1	92.4
SAN 7								
13.0	11.3	2.70	53.1	35.6	26.5	35.4	33.7	94.1
15.5	17.3	2.47	49.6	36.6	29.9	28.5	34.9	93.2
18.0	24.2	2.27	46.5	33.1	21.9	21.6	36.6	93.0
SAN 8								
13.0	13.8	2.64	53.2	34.7	28.7	23.3	34.1	93.0
15.5	21.7	2.45	48.8	33.8	20.3	18.2	34.9	92.8
18.0	27.5	2.33	46.2	33.4	21.8	15.6	37.1	92.8
SAN 9								
13.0	22.0	2.62	53.4	38.2	19.7	8.3	37.5	90.5
15.5	33.7	2.39	49.4	36.3	20.4	6.3	39.1	90.8
18.0	36.4	2.24	47.1	34.4	18.5	5.5	40.0	90.2

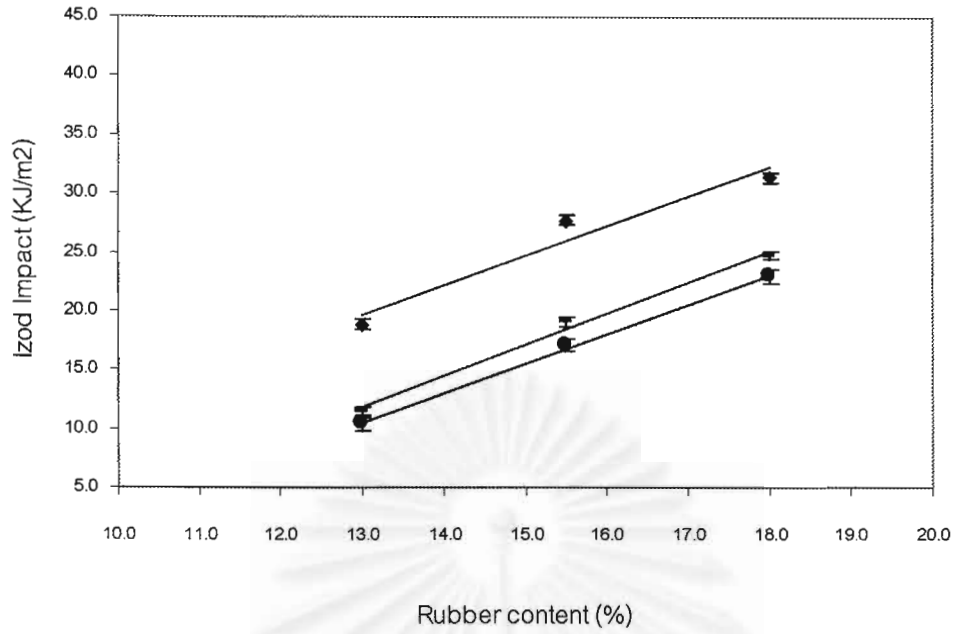
Figure 4.1 (a) and (b) and Figure 4.2 show the relationship between Izod impact and rubber content in ABS blend when using different type of SAN. It is found that at rubber content between 13 to 18 %, Izod impact was increased when the rubber content increased, and this is true for each type of SAN matrix. However, Izod impact of SAN 2 and SAN 9 remains about constant between 15.5 and 18 % rubber.

Those observations are similar to the research by H. Kim⁴, et al. at above 10% of rubber content, ABS showed a significant increase in impact strength. The increase became less at high rubber content. (See Figure 2.3)

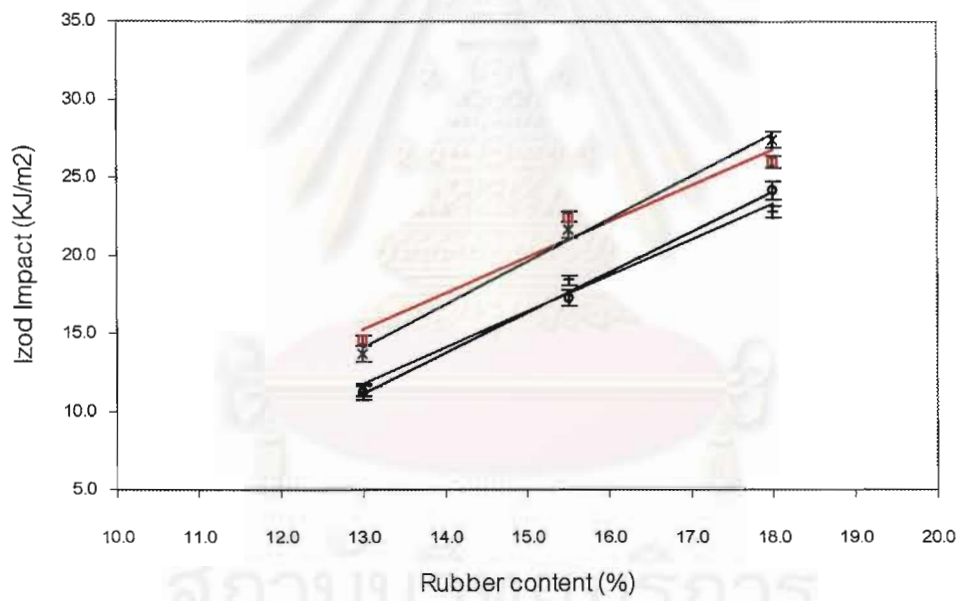
At higher rubber content, above 20 %, Izod impact started slowly increase because the rubber particles dispersed closely to each others and lower the adhesion between rubber and SAN matrix phases.

SAN matrices, which differ in MFI and AN content, influenced the Izod impact, resulting in the different results at the same rubber content. Comparing among SAN, which have the same AN content in Figure 4.1 (a), SAN 1, SAN 3 and SAN 4: SAN 1 which has the lowest MFI shows the highest Izod impact. As mentioned in section 2.3, the flow property or viscosity relates to the polymer molecular weight. The higher the molecular weight, the higher the viscosity and the lower the MFI. Therefore, the low MFI represents high molecular weight and at the high molecular weight of SAN matrix gives better Izod impact resistance. The capability of the matrix to be toughened appears to be related to matrix molecular weight, because the effectiveness in toughening of crazes is highly related to matrix molecular weight. Chain slip is important for low molecular weight SAN matrices, but with higher molecular weight of SAN this mechanism is probably too slow to produce a major contribution⁹.

The second effect from AN content of SAN matrix, when comparing between SAN 1 and SAN 2, at above 13 % rubber, SAN 2, which has higher AN content gave better impact resistance than SAN 1. There has been a discussion on compatibility and interfacial adhesion between SAN-graft and SAN matrix. The effect of the difference in AN content between the SAN-graft and the SAN matrix, the so called 'mismatch' of AN content, is shown in Izod impact results. Even though SAN 2 has higher MFI than SAN 1, Izod impact of SAN 2 blend is higher than SAN 1. There was an observation on the effect of AN content to Izod impact performed by H. Kim⁴, et al., the results showed that Izod impact increased when AN content of SAN matrix increased but decreased after it reached the maximum point. (See Figure 4.4) Above the maximum point, the AN mismatch becomes too large and reduces miscibility between rubber and SAN matrix. The decline in toughness at higher level of matrix AN may result from a failure to achieve a uniform distribution of rubber throughout the systems of phase separation between the added SAN and the free SAN in the SAN-graft.



(a)



(b)

(a) ◆, SAN 1; □, SAN 3; ●, SAN 4;

(b) +, SAN 5; □, SAN 6; ○, SAN 7; *, SAN 8.

Figure 4.1: Izod impact of ABS versus rubber content for various SAN matrices

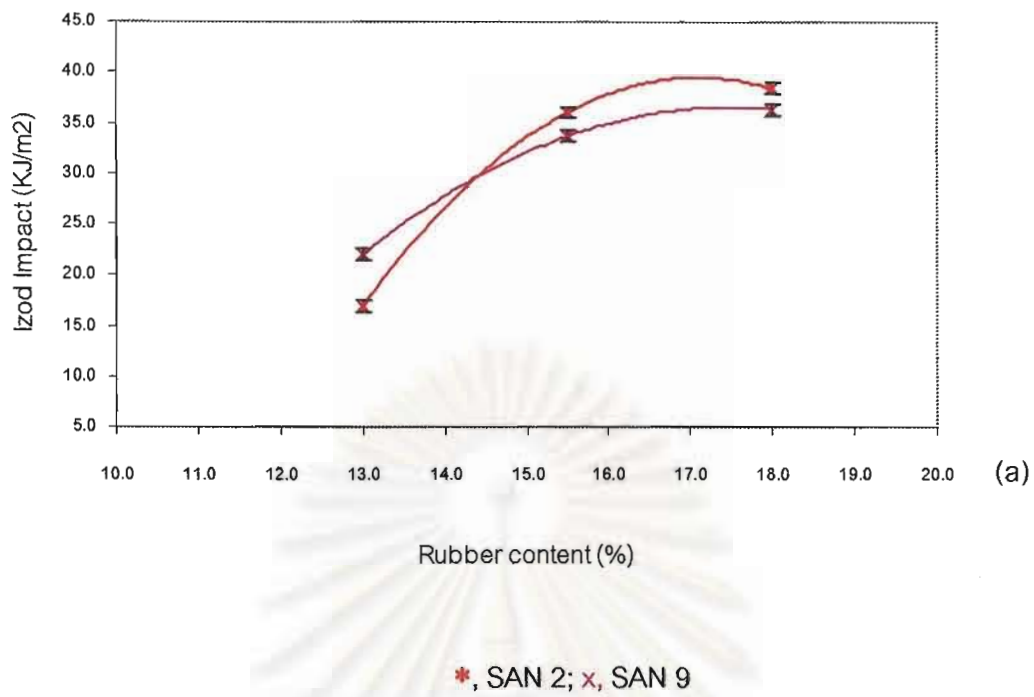


Figure 4.2: Izod impact of ABS versus rubber content for various SAN matrices

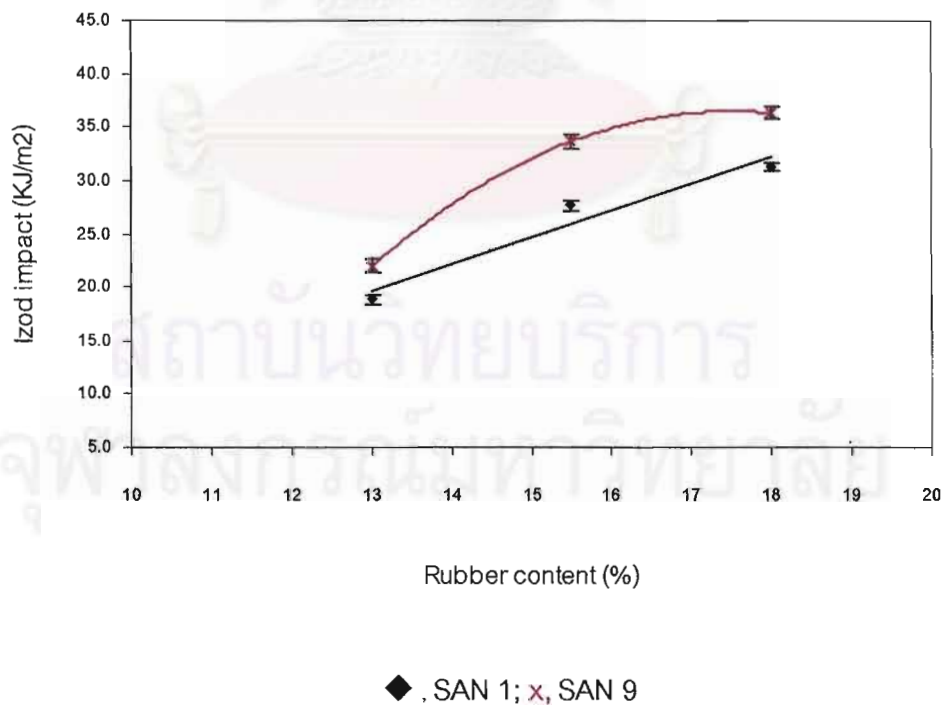


Figure 4.3: Izod impact of ABS versus rubber content for various SAN matrices

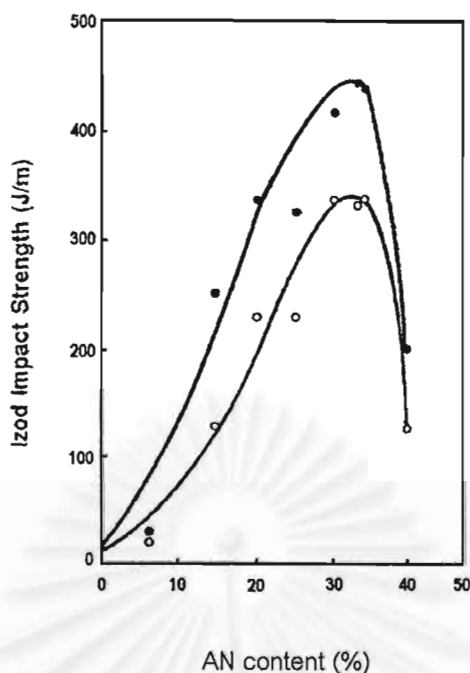


Figure 4.4: Notched Izod impact strength versus AN content of SAN matrices⁴.

20 % rubber (O); 30 % rubber (●),

The different sources of SAN matrix (suspension versus continuous mass) also show an effect in Izod impact. As shown in Figure 4.3, SAN 9, from continuous mass process, which has almost the same AN content and has lower molecular weight than SAN 1 from suspension process but gives higher Izod impact. Since the molecular weight distribution of SAN obtained from continuous mass process is narrower than SAN from suspension process, a narrower distribution may give a better Izod impact result.

The relationship between Izod impact and rubber content is in linear correlation and fairly parallel to each other with slope at about 2.5 kJ/m^2 except in SAN 2 and SAN 9. Both in SAN 2 and SAN 9, their relationship can be fit with a second order polynomial equation. At higher rubber content, the increase of Izod impact was less than at 10 to 15 %. The high AN content in SAN 2 and SAN 9, 40.7 and 32.2 % respectively, increases AN content mismatch from SAN-graft which has 25 % AN content. It is possible to be the cause of lack of linearity in SAN 2 and SAN 9.

The correlation equation of each SAN in Figure 4.1 and 4.2 are shown as follows.

$$\text{SAN 1 : } Y = 2.50 X - 12$$

$$\text{SAN 2 : } Y = -1.34 X^2 + 45 X - 350$$

$$\text{SAN 3 : } Y = 2.52 X - 22$$

$$\text{SAN 4 : } Y = 2.65 X - 22$$

$$\text{SAN 5 : } Y = 2.29 X - 18$$

$$\text{SAN 6 : } Y = 2.29 X - 14$$

$$\text{SAN 7 : } Y = 2.57 X - 21$$

$$\text{SAN 8 : } Y = 2.74 X - 21$$

$$\text{SAN 9 : } Y = -0.72 X^2 + 25 X - 180$$

4.2.1 Prediction model for Izod impact

As already shown, there is one major effect, the rubber content, and three minor ones, MFI, AN content of SAN matrix and type of polymerization of the SAN (suspension or continuous mass polymerization) on Izod impact. In the next sections, the methods that were used in trying to determine the influence of each effect are presented.

4.2.1.1 Prediction from the effect of rubber content

As most of the curves in Figure 4.1, Izod impact of ABS blend versus rubber content, are quite linear and parallel. Even though, there was some lack of linearity on SAN 2 which has the highest AN content, 40.7 % and SAN 9 which has 32.2 % AN content. The equation for the others SAN could be proposed as a linear regression with an average slope at 2.5.

$$\text{Izod impact (kJ/m}^2\text{)} = 2.5 \times \text{rubber content (\%)} - c \quad (4.1)$$

Where, c is assumed to be a constant for each SAN

4.2.1.2 Prediction from the effect of SAN matrix

In order to describe the effect of SAN matrix by the 'c' value on the three minor effects, MFI, AN content and type of polymerization of SAN. The observed values of Izod impact and the rubber content were put into the Equation 4.1 and then calculate 'c'. The Table 4.3 shows the average 'c' value from the 3 results calculated at 13, 15.5 and 18 % rubber contents. The result for SAN 2 at 13 % rubber was discarded because it was deviating from the trend.

Table 4.3 : The calculation average 'c' value from the Equation 4.1

SAN matrix	c values
SAN 1	12.0
SAN 2	3.1
SAN 3	21.1
SAN 4	19.5
SAN 5	20.4
SAN 6	16.9
SAN 7	19.7
SAN 8	16.9
SAN 9	7.2

Remark : Those 'c' values have no direct meaning by themselves as the Izod impact versus rubber content graph is a s-shape. (See Figure 2.3)

(a) Influence of type of polymerization for SAN

When comparing between SAN 3 and SAN 7, and SAN 4 and SAN 8, for each pair, MFI and AN content are quite similar. From the difference of Izod impact to the type of polymerization, the difference of 'c' is 1.4 and 2.6. Therefore, the value '2' was selected as the difference of 'c' between the 2 types of polymerization. Because of the molecular weight distribution of continuous mass SAN is narrower than in suspension SAN, the Izod impact of ABS by continuous mass SAN is higher than by suspension.

(b) Influence of log MFI and AN content of SAN

As described , the differences in each SAN matrix are MFI and AN content, the higher the MFI, the lower the Izod impact, the higher the AN content, the higher the Izod impact. $\log \text{MFI}_{\text{SAN}}$ is fit with the multiplier fraction while AN content is fit with the dividend fraction because the higher the MFI_{SAN} , the lower the Izod impact but the higher the AN content, the higher the Izod impact. The 'c' value is the subtract fraction. The number 310 is fit to the calculation 'c' as a constant to any SAN. Due to ABS produced by suspension SAN had about 2 unit lower than by continuous mass, the factor 2 is added to the equation. Therefore, the Equation 4.2 describes the 'c' calculation and the comparison between 'c' calculation and 'c' observed from the experiment are shown in Table 4.4. The result of calculated 'c' values were close to the 'c' observed from the experiment. The following model gives the best fit with experimental results.

$$c = [(310 \times \log \text{MFI}_{\text{SAN}}) / \text{AN content}] + (2 \text{ if SAN by suspension}) \quad (4.2)$$

Table 4.4: The comparison between 'c' observed from experiment and 'c' calculated by Equation 4.2

SAN matrix	c values	
	observed	calculated
SAN 1	12.0	10.6
SAN 2	3.1	9.2
SAN 3	21.1	22.8
SAN 4	19.5	20.7
SAN 5	20.4	19.7
SAN 6	16.9	16.1
SAN 7	19.7	20.1
SAN 8	16.9	17.2
SAN 9	7.2	11.5

- Remark:
- (i) SAN 1 to SAN 4 were obtained by suspension polymerization.
 - (ii) SAN 5 to SAN 9 were obtained by continuous mass polymerization.

When substitute 'c' from Equation 4.2 in Equation 4.1, resulting in the following equation.

$$\text{Izod impact} = 2.5R - [(310 \times \log \text{MFI}_{\text{SAN}}) / \text{AN}_{\text{SAN}}] + S \quad (4.3)$$

Where:

- Izod impact = Izod impact (kJ/m^2)
- R = rubber content (part)
- MFI_{SAN} = MFI of SAN matrix (g/10 min)
- AN_{SAN} = AN content in SAN matrix (%)
- S = constant, S = 2 if SAN by suspension,
and S = 0 if SAN by continuous mass

Table 4.5: The comparison between experimental and prediction results on Izod impact (kJ/m^2) from Equation 4.3

SAN Matrix	13 wt % rubber			15.5 wt % rubber			18 wt % rubber		
	Exp.	Predict		Exp.	Predict		Exp.	Predict	
	(1)	(2)	(1)/(2)	(1)	(2)	(1)/(2)	(1)	(2)	(1)/(2)
SAN 1	18.8	21.9	0.86	27.7	28.2	0.98	31.3	34.4	0.91
SAN 2	16.9	23.2	0.73	36.0	29.5	1.22	38.4	35.7	1.08
SAN 3	10.4	9.7	1.07	17.1	15.9	1.07	23.0	22.2	1.04
SAN 4	11.5	11.8	0.97	19.1	18.1	1.05	24.7	24.3	1.02
SAN 5	11.3	12.7	0.89	18.4	19.0	0.97	22.8	25.2	0.91
SAN 6	14.6	16.5	0.89	22.5	22.7	0.99	26.0	29.0	0.90
SAN 7	11.3	12.4	0.91	17.3	18.7	1.02	24.2	24.9	0.97
SAN 8	13.8	15.3	0.90	21.7	21.6	1.01	27.5	27.8	0.99
SAN 9	22.0	21.0	1.05	33.7	27.3	1.23	36.4	33.5	1.08

The correlation between observed and predicted results is quite good, especially for SAN 3 to SAN 8. The discrepancies for SAN 2 and SAN 9 are partly due to the lack of linearity.

4.3 The effect of SAN on MFI of ABS and the prediction model

Clearly from results in Table 4.2, and comparing to Figure 3.1 for the pure SAN studied, the higher the MFI of SAN, the higher the MFI of the resulting ABS. The rubber content has less influence on MFI of ABS than MFI of SAN. During the discussion on Izod impact results, it was indicated that MFI, more specifically the log of MFI, was a key parameter.

Therefore, it is valid to propose the following model.

$$\log \text{MFI}_{\text{ABS}} = n \log \text{MFI}_{\text{SAN}} + x \quad (4.4)$$

Where: n = weight fraction of SAN matrix
 x = constant

The following table indicates the observed 'x', averaged between the 3 rubber contents.

Table 4.6: The calculated 'x' from the observed result using Equation 4.4

SAN matrix	$\log \text{MFI}_{\text{SAN}}$	'x'
SAN 1	0.79	-0.24
SAN 2	0.95	-0.08
SAN 3	1.93	+0.07
SAN 4	1.75	+0.06
SAN 5	1.47	+0.14
SAN 6	1.39	+0.08
SAN 7	1.90	+0.14
SAN 8	1.63	+0.15
SAN 9	1.19	0.00

Considering the MFI of the pure SAN's on Table 3.1, it was observed that most of those, the easy flowing ones, have a positive 'x'. The exceptions, SAN 1, SAN 2 and SAN 9 being the stiff flowing ones.

This suggests that 'x' is itself a function of the MFI of the SAN matrix or there are specific interactions between rubber and SAN matrix for SAN 1, SAN 2 and SAN 9. The Izod impact of the formulations containing SAN 2 and SAN 9 showed already a peculiar behavior versus rubber content. In Table 4.7, we compare the observed MFI's to the predicted ones, using specific 'x' for SAN 1, SAN 2 and SAN 9 and an average one of +0.1 for the others.

For the easy flowing, $\log \text{MFI}_{\text{SAN}} 1.39$ to 1.93 , the constant 'x' = +0.1 was fit to the Equation 4.4. However, the stiff flowing, $\log \text{MFI}_{\text{SAN}} < 1.39$, the constant was varied in the range 0.00 to -0.24, depending on the flow of SAN.

Table 4.7: The observed MFI and the calculated MFI by Equation 4.4 using 'x' for easy flow and stiff flow as mentioned.

SAN matrix	MFI _{ABS} observed (1)	MFI _{ABS} calculated		(1)/(2)	
		'x' = 0.10			
SAN 1	2.6	-	'x' = -0.24	2.2	1.18
	2.0	-		2.0	1.00
	1.6	-		1.8	0.89
SAN 2	4.7	-	'x' = -0.08	4.2	1.12
	3.7	-		3.8	0.97
	3.1	-		3.4	0.91
SAN 3	33.2	33.7	-	-	0.98
	23.6	27.0	-	-	0.87
	20.7	21.6	-	-	0.96
SAN 4	23.4	24.8	-	-	0.94
	19.0	20.3	-	-	0.94
	14.8	16.6	-	-	0.89
SAN 5	17.5	15.4	-	-	1.14
	14.1	13.0	-	-	1.08
	12.1	11.0	-	-	1.10
SAN 6	13.7	13.4	-	-	1.02
	10.6	11.5	-	-	0.90
	9.2	9.8	-	-	0.94
SAN 7	35.4	32.1	-	-	1.10
	28.5	25.8	-	-	1.10
	21.6	20.7	-	-	1.04
SAN 8	23.3	20.2	-	-	1.15
	18.2	16.8	-	-	1.08
	15.6	13.8	-	-	1.13
SAN 9	8.3	-	'x' = 0.00	6.0	1.09
	6.3	-		5.3	0.94
	5.5	-		4.6	0.95

4.4 The effect of rubber content and type of SAN on other properties

4.4.1 The effect on tensile modulus

Tensile modulus of SAN matrix is higher than ABS. (See Table 1.1) As expected, tensile modulus decreased with an increase in the rubber content. When comparing between the deviation of reproducibility test of tensile modulus experiment in Table 4.1 and the difference between ABS blend at 15.5 % rubber content in different SAN, it is found that the deviation is almost the same, 0.03 and 0.05. Therefore, it is difficult to determine a significant difference between the different SAN's. SAN 1 and SAN 4 give somewhat lower tensile modulus while SAN 7 and SAN 8 have a higher tensile modulus, about 50 MPa from the average.

Similar results were previously found by K. Kim⁴, et al. that neither matrix composition nor graft composition has a significance on the modulus. Their investigation found that the addition of the first 10% of rubber caused the largest drop in modulus and there was very little change in modulus as the AN content of SAN is changed for any given rubber content

Figure 4.5 shows the tensile modulus as a function of rubber content. There is a linear regression, and the intercept at 0 % rubber content is 3.44 GPa which is nearly the same figure for the tensile modulus of SAN.

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

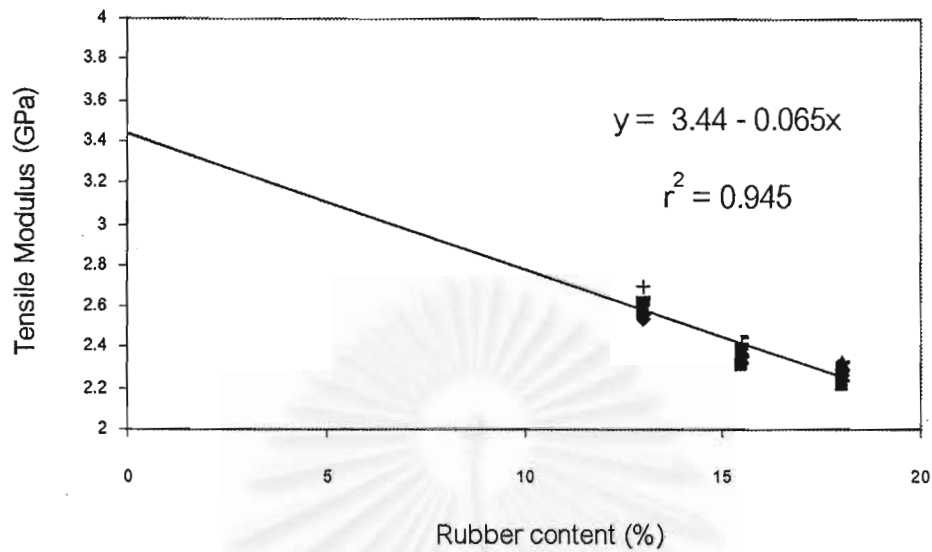
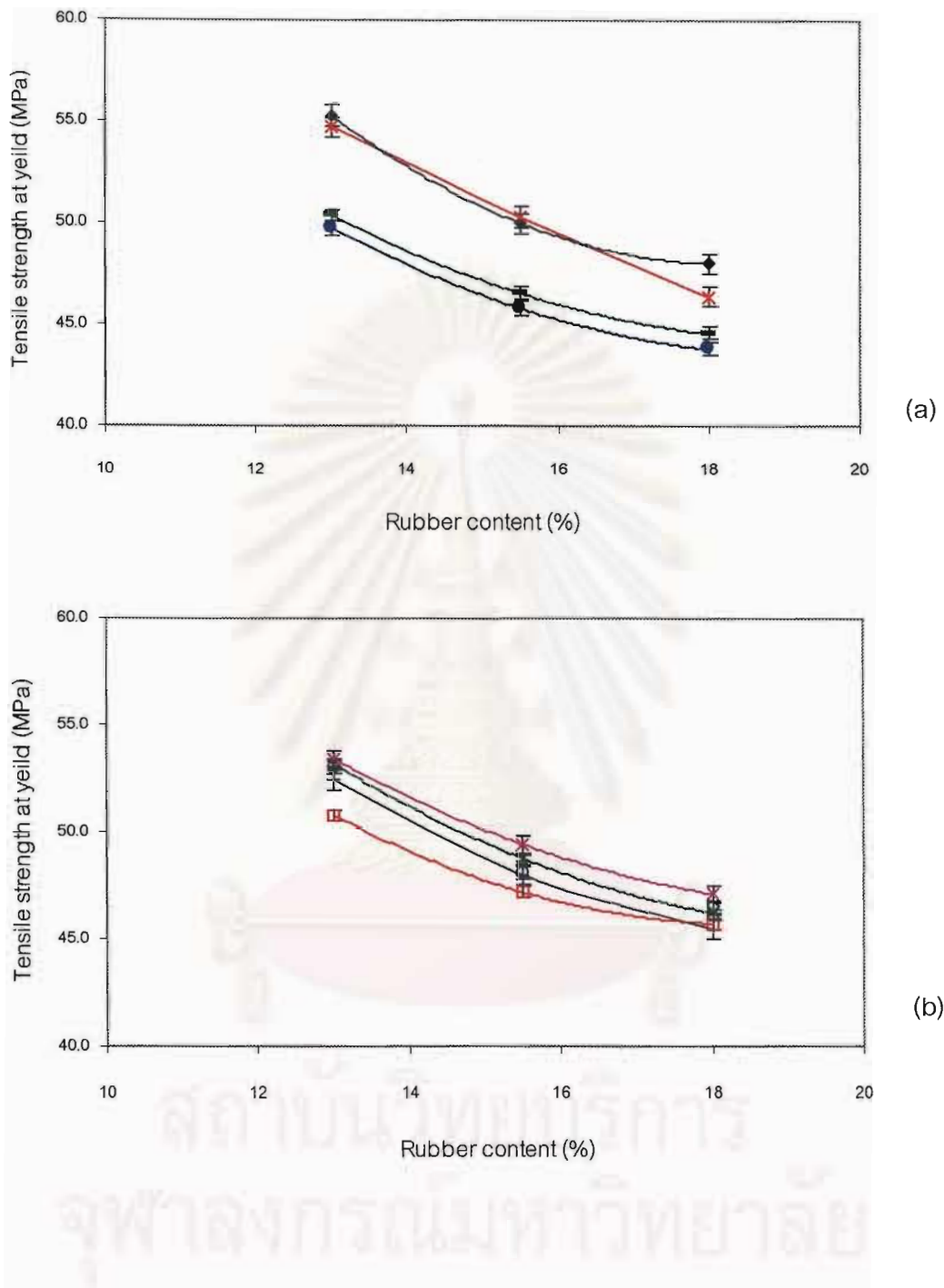


Figure 4.5: Tensile modulus versus rubber content

4.4.2 The effect on tensile strength at yield

The correlation of tensile strength at yield and rubber content is the same as the correlation of tensile modulus. Figure 4.6 shows the tensile strength at yield as a function of rubber content. Expectation of these curves at 0 % rubber, pure SAN, gives a result in the range of 65 to 76 MPa, so similar to the result of pure SAN. (See Table 1.1) The effect of rubber is much more important than the effect of individual SAN matrix. The highest results of tensile strength are obtained with SAN 1 and SAN 2.

While there is a significant increase in yield strength of unmodified SAN copolymers with increasing AN content, rubber modified blends show relatively less sensitivity to AN content, particularly at high rubber concentration⁴. Tensile yield strength is a combined property determined by the strength of each component and the bond between the components⁴.



(a) ◆, SAN 1; *, SAN 2; ■, SAN 3; ●, SAN 4.

(b) +, SAN 5; □, SAN 6; ○, SAN 7; *, SAN 8; ×, SAN 9

Figure 4.6: Tensile strength at yield versus rubber content

4.4.3 Tensile strength at break

Tensile strength at break was reduced according to the increase of rubber content as expected (See Table 4.2). However, the correlation showed lack of linearity. The difference between the different SAN's matrix was less than 3 MPa.

4.4.4 Tensile elongation at break

The results of Table 4.2 are difficult to interpret. There is no clear trend on the influence of the rubber content, nor on specific type of SAN used. All results are between 14 to 30 %, with one unexplained (40% for SAN 4, at 15.5 % rubber content). The poor reproducibility of that property (See Table 4.1) prohibits any conclusion.

4.4.5 The effect of SAN matrix in yellowness index (YI)

Examination of results of Table 4.2 shows a strong influence of the individual SAN and a smaller influence of the rubber content to the YI of ABS. The contribution of each SAN is linked to its' AN content. (See Table 4.8)

Table 4.8 The yellowness index of ABS at different AN content.

SAN matrix	AN content	Yellowness index
SAN 5	23.1	28.8
SAN 6	26.8	32.3
SAN 1	28.6	32.3
SAN 3	28.7	33.7
SAN 4	29.0	35.7
SAN 7	29.3	34.9
SAN 8	29.4	34.9
SAN 9	32.2	39.1
SAN 2	40.7	40.8

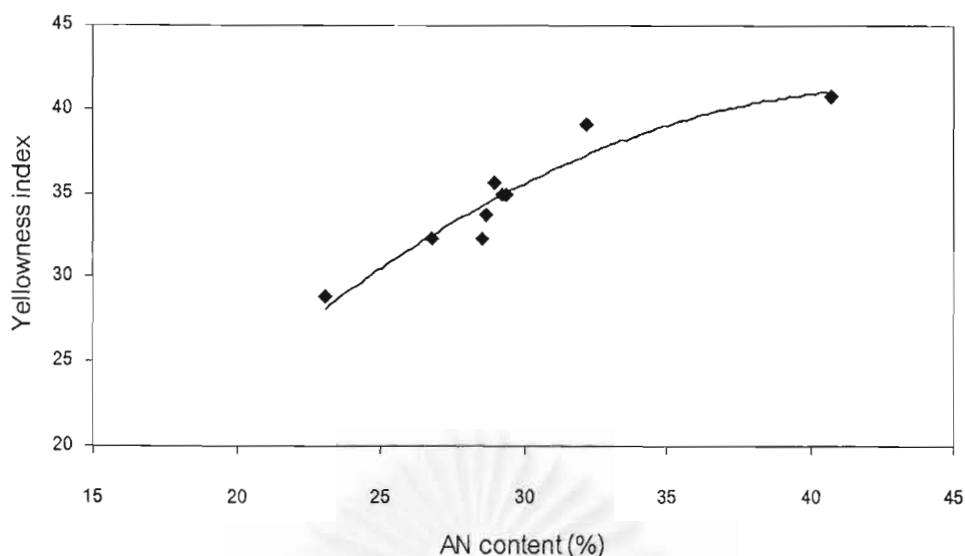


Figure 4.7: The correlation between AN content in SAN versus yellowness index of ABS

It is well known that SAN is yellower than polystyrene due to the AN content. The higher the AN content, the yellower the color. The same trend was observed in ABS. YI was increased slightly with rubber content, about 1 unit per 2.5 % rubber except with SAN 2.

4.4.6 The effect of rubber content and SAN on gloss

As ABS studied in this experiment is a high gloss rubber system, it can be shown that each ABS has high gloss. Overall results are at 92 ± 2 . Generally, gloss would be effected by the rubber particle sizes and their dispersion on the surface of ABS¹⁰. There was a slight effect observed from the rubber content: there was a decrease from 92.8 to 92.3 and 91.7 when rubber content increased from 13, 15.5 and 18 % respectively.

There is also a specific effect from each SAN matrix, compared to the average rubber content. The lowest MFI and the highest AN content, SAN 1 and SAN 2, have gloss 2 percent lower than the average. The low MFI of SAN may effect to the dispersion of the rubber. SAN 2, which has the largest AN mismatch between SAN-graft

and SAN matrix had also gloss 2 % lower than the average. It was observed earlier by M.C.O. Chang and R.L. Nemeth¹⁰ that increasing the compositional AN mismatch between grafted and SAN matrix increased the rubber particle agglomeration. Molecular structures that increased rubber particle agglomeration decreased the molded gloss.

Table 4.9 The different gloss from the average.

SAN matrix	Different from average
SAN 1	-2
SAN 2	-2
SAN 3	Average
SAN 4	Average
SAN 5	+2
SAN 6	Average
SAN 7	+1
SAN 8	Average
SAN 9	-1

4.5 The influence of lubricants and colorants in ABS properties

There were three types of lubricants, EBS, PETS and Silicone oil and two types of basic colorant, white and black, studied in this experiment.

4.5.1 The effect of lubricants and colorants on the Izod impact of ABS

Several types of lubricants are commonly used in ABS manufacturing to enhance processability and mechanical properties. In this experiment, EBS, PETS and Silicone oil were investigated. Even though, these lubricants were normally used to enhance processability, Izod impact was also improved. By addition 1 % by weight of EBS and PETS, Izod impact was increased about 15 %, with a small amount of silicone oil (0.5 % by weight), Izod impact was increased about 20 %.

Table 4.10: Properties of ABS blend in different additives at 15.5 % rubber and SAN 9

Additive (wt %)	Izod impact (kJ/m ²)	TM (GPa)	TS at Yield (MPa)	TS at Break (MPa)	TE at Break (%)	MFI (g/10min)	YI (-)	Gloss 20° (%)
None	29.3	2.49	50.6	36.0	19.0	5.4	39.3	91.9
EBS – 1	33.7	2.39	49.4	36.4	20.4	6.3	39.1	90.8
EBS – 2	33.5	2.44	49.0	35.6	20.3	7.3	38.4	91.6
PETS – 1	33.6	2.45	47.6	35.6	25.1	5.6	39.1	90.3
PETS – 2	35.2	2.34	47.4	35.4	20.9	5.4	37.8	(84.0)
Si-oil – 0.5	35.1	2.45	45.5	35.4	47.9	5.6	36.6	88.8
Si-oil – 1	34.9	2.38	45.4	34.8	38.9	5.7	33.1	88.2
TiO ₂ – 4*	26.9	2.51	48.2	35.9	19.2	6.2	-	91.4
CB – 1*	25.3	2.46	49.3	36.3	18.4	6.3	-	93.0

* Plus 1 % by wt of EBS

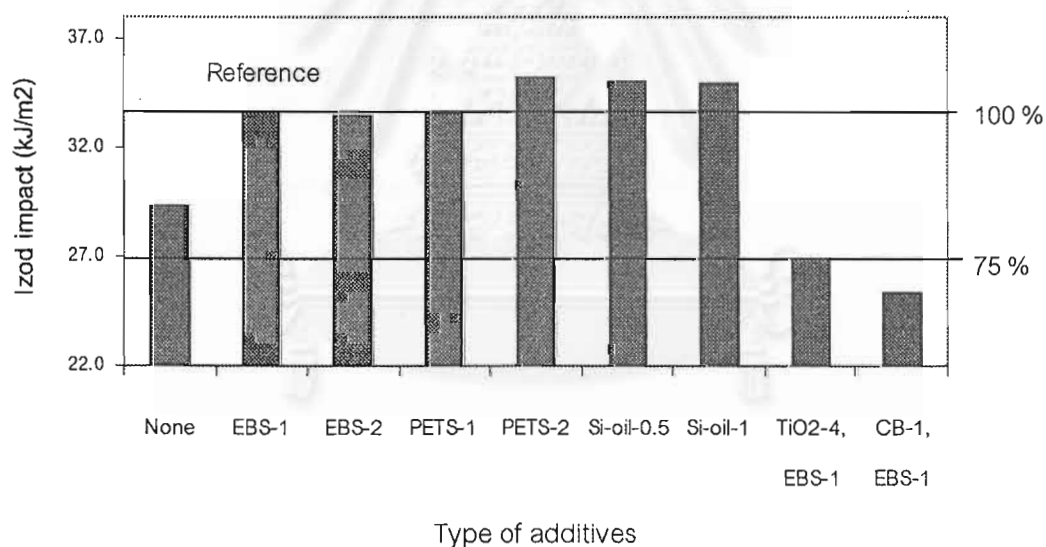


Figure 4.8: Izod impact versus additives at 15.5% rubber content in SAN 9

Colorants play a very important role in ABS manufacturing due to the high demand of color product. Colorants are usually mixed and compounded with SAN-graft and SAN matrix. TiO₂ and carbon black, the basic components of a light and dark color, were compounded in this experiment. EBS was added 1 % by wt. as a normal level of

lubricant, therefore EBS-1 was the reference for comparison. Izod impact was decreased 20 and 25 % when 4 % of TiO_2 and 1 % of carbon black were added respectively.

4.5.2 The influence on tensile properties.

Tensile modulus of ABS was slightly decreased when each of EBS, PETS and Silicone oil was added. Tensile strength at yield of ABS had the same influence from those additives but larger effect in silicone oil. However, tensile strength at break had very small effect. There was a significant increase in tensile elongation at break when silicone oil was added, even considering the poor reproducibility of this test.

Tensile modulus was slightly increased when TiO_2 and CB were added. There was no significant effect on tensile strength or elongation.

4.5.3 The influence on MFI

The MFI is influenced by EBS but has very little influence from PETS and silicone oil. The increase of 1 % to 2 % of EBS did not significantly increase MFI of ABS.

4.5.4 The influence on yellowness index and gloss

There was significant reduction on yellowness index with adding silicone oil, while the other additives did not make any difference. Silicone oil also reduced gloss of ABS significantly.

4.6 Further experiment

Some extra formulations were prepared in order to check the validity of the models, at lower and higher rubber contents, compared to the range so far covered (13-18 %). 1 % of EBS was used like in other experiments. Experimental results are compared to the predicted values as shown in the following table.

Table 4.11: The further experiment compared between observed and predicted values

Rubber content (wt %)	Izod impact (kJ/m ²)	TM (GPa)	MFI (g/10min)	YI (-)	Gloss 20° (%)
Observed					
SAN 9					
8.0	4.8	3.08	11.7	35.2	94.3
10.5	12.6	3.01	10.0	37.7	92.7
20.5	31.1	2.14	4.7	(36.9)	88.8
23.0	36.8	1.99	3.5	40.4	87.6
Predicted					
SAN 9					
8.0	8.5	2.92	10.0	36.1	92.5
10.5	14.7	2.76	8.8	37.1	92.0
20.5	39.7	2.11	5.1	41.1	90.0
23.0	46.0	1.94	4.4	42.4	89.5
Observed					
SAN 7					
8	3.4	3.03	44.7	33.5	95.0
10.5	5.4	2.92	39.3	32.1	93.2
Predicted					
SAN 7					
8	-0.1	2.92	49.7	33.9	94.5
10.5	6.1	2.76	39.9	32.9	94.0

The extrapolation of the model, outside the covered range in rubber content (13 – 18 %) is valid for tensile modulus confirming the linear dependence with rubber content, MFI, YI and gloss.

In the case of Izod impact, those experiments help to define the extent of the linear part of the s-shape, Izod impact versus rubber content. In our case, linearity is not yet obtained at 8 % rubber, but is good at 10.5 %. The linearity is lost above 18 % rubber (at least for SAN 9).

4.7 Prediction

The purpose of this prediction model is to optimize a formulation for a specific requirement by using the existing components, consisting of SAN-graft and SAN 1 to SAN 9 plus the additives. The best balance of Izod impact and flow properties is a compromise with a content of rubber as low as possible but giving a sufficient Izod impact. Therefore, the selection of SAN type is very important. In order to develop a new formulation as requested, it was summarized in following trends. For prediction, first task is to determine the adequate balance between Izod impact and MFI as this is the key compromise.

Table 4.12: Trends of ABS properties on the effect of SAN, rubber content and additives.

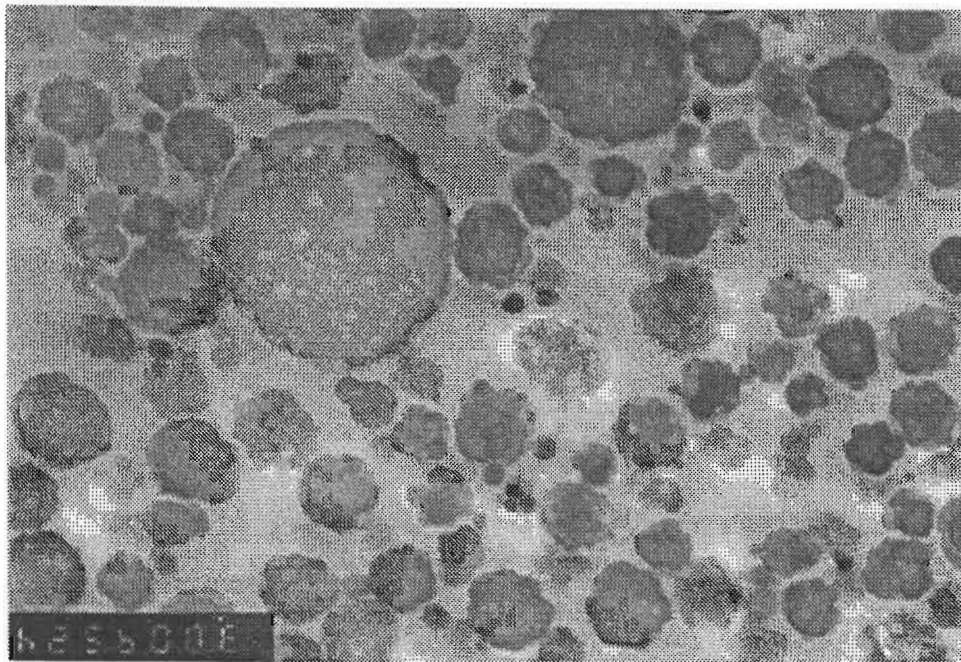
Property to be obtained	Trends and observation	
	Highest	Lowest
Izod impact	SAN 2 > SAN 9 > SAN 1 > SAN 6 = SAN 8 > SAN 4 = SAN 7 > SAN 3 = SAN 5 Plus adequate use of EBS / PETS / Silicone oil.	
MFI	SAN 3 = SAN 7 > SAN 4 = SAN 8 > SAN 5 = SAN 6 > SAN 9 > SAN 1 = SAN 2	
TM	Minimize rubber content	
TS at Yield	Minimize rubber content and do not use silicone oil	
TS at Break	Minimize rubber content	
TE at break	Do use silicone oil	
YI	For low YI, SAN with low AN content and use silicone oil	
Gloss	Minimize rubber content and do not use SAN 1 and SAN 2	

4.8 Morphology

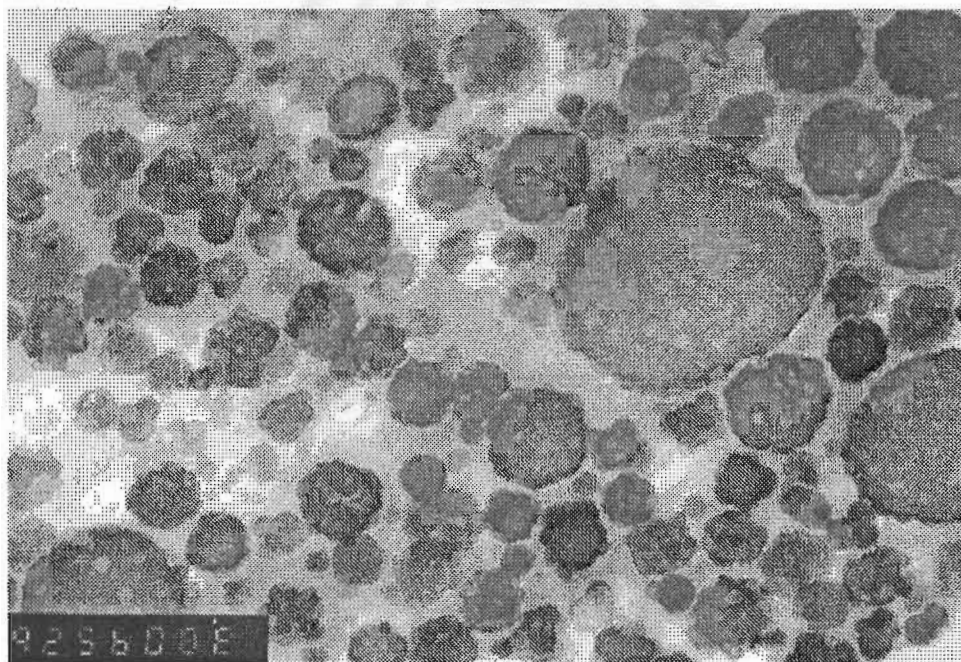
Transmission electron micrographs for SAN 2, SAN 5, SAN 7 and SAN 9 blends are shown in Figure 4.9. AN content of selected SAN varies from minimum 23.1 % in SAN 5, 29.3 % in SAN 7, 32.2 % in SAN 9 and 40.7 % in SAN 2. All blends contain 15.5 % rubber content.

The micrographs show the dispersion of rubber particles in SAN matrix. The SAN matrix is not chemically bound to the rubber particle. In all materials, the dispersed phase consists mainly of small solid particles with a few large particles. The bimodal system of the rubber particle size is confirmed. The micrographs also show the SAN polymer subinclusions on the particles.

The difference in AN content of SAN-graft and SAN matrix influences their miscibility and consequently the dispersion of the rubbery phase. In this work, SAN-graft has 25 % of AN content. The dispersions of SAN 5, SAN 7 and SAN 9, which has the difference in AN content 2.1, 4.3 and 7.2 % respectively, are about the same. Therefore, the difference of AN content in SAN-graft and SAN matrix up to 7 % does not show significant different dispersion. However, the micrograph of SAN 2, which has a 15.7 % difference in AN content, shows less rubber particles and looks different from the others. There might be an effect from the difference in AN content in SAN 2 blend. As the difference in AN content of the graft and the matrix increases, the rubber particle appear to be more agglomerated with large areas of the matrix free of particles.



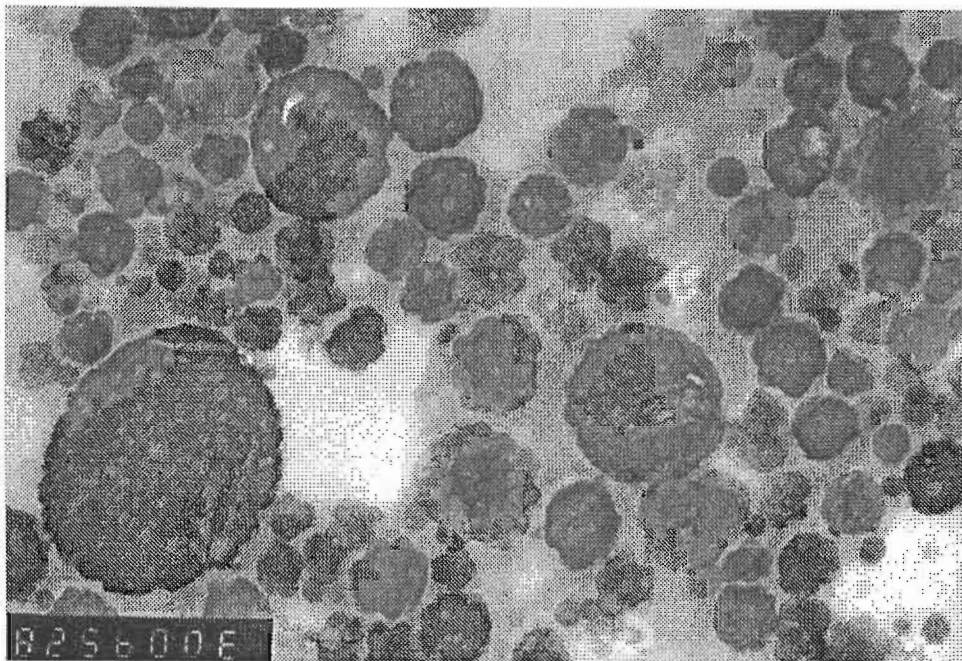
(a)



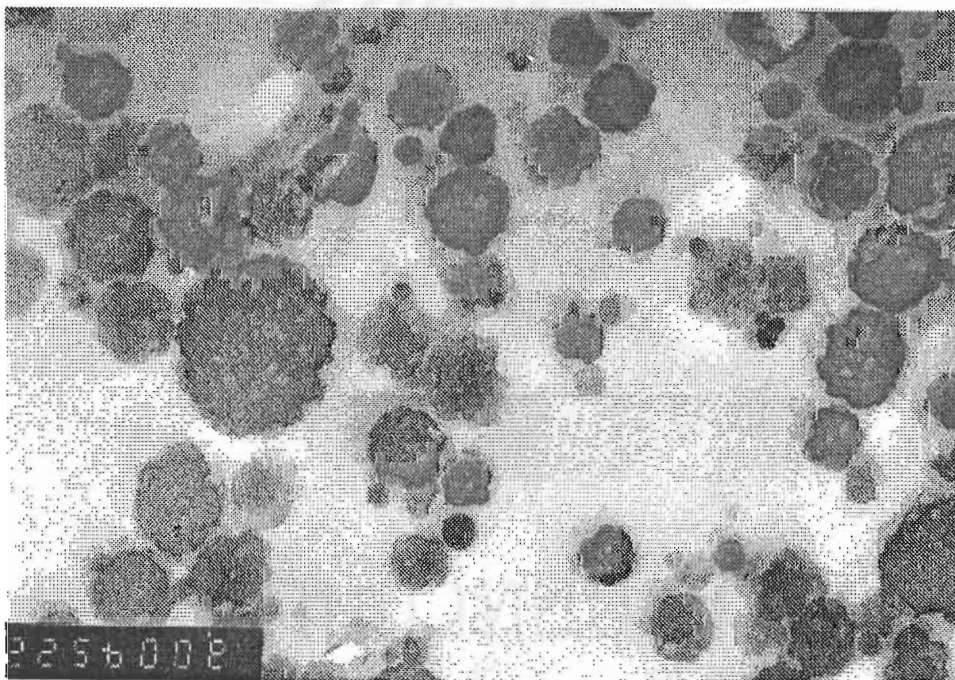
(b)

1 μm

Figure 4.9: Transmission electron micrographs for (a) SAN 5 (2.1%) and (b) SAN 7 (4.3 %). All blends contain 15.5 % rubber. Numbers in parentheses indicate the difference in AN content of the SAN-graft and SAN matrix.



(c)



(d)

1 μm

Figure 4.10: Transmission electron micrographs for (c) SAN 9 (7.2 %) and (d) SAN 2 (15.7 %). All blends contain 15.5 % rubber. Numbers in parentheses indicate the difference in AN content of the SAN-graft and SAN matrix.

CHAPTER V CONCLUSION AND SUGGESTION

5.1 Conclusion

As the rubber toughening material, rubber (SAN-graft polybutadiene rubber) content plays a significant role in improving Izod impact of ABS. Furthermore, there are the influences from SAN matrix. The MFI and AN content of SAN matrix had a significant effect on Izod impact. Low MFI of SAN matrix gives high Izod impact. However, low MFI will cause low MFI ABS which lower the processability. High AN content of SAN matrix not only increases the chemical resistance but also increases Izod impact. At large AN mismatch between AN content of SAN matrix and AN content in SAN-graft, there could be some rubber particle agglomeration with large area of matrix free particle and lower the Izod impact.

Due to rubber content and SAN properties influence to the Izod impact, the correlation between these properties and Izod impact is proposed in the following relationship.

$$\text{Izod impact} = 2.5R - [(310 \times \log \text{MFI}_{\text{SAN}}) / \text{AN}_{\text{SAN}}] + S$$

Where:	Izod impact	=	Izod impact (kJ/m ²)
	R	=	rubber content (part)
	MFI _{SAN}	=	MFI of SAN matrix (g/10 min)
	AN _{SAN}	=	AN content in SAN matrix (%)
	S	=	Constant which S = 2 for SAN by suspension and S = 0 for SAN by continuous mass.

This equation could provide high accuracy results at between 10 to 20 % rubber content. Out of this range, the deviation may be high.

There are no significant effect of MFI and AN content SAN matrix on the tensile properties of ABS but only the rubber content. AN content of SAN matrix has some influence on the YI of ABS, the higher the AN content of SAN matrix, the higher the YI of ABS.

There is the direct effect of MFI of SAN matrix on the MFI of ABS, the higher the MFI of the SAN matrix, the higher the MFI of the ABS. The correlation between MFI of SAN matrix and MFI of ABS is found to be conformed in the log scale as the following relationship.

$$\log \text{MFI}_{\text{ABS}} = n \log \text{MFI}_{\text{SAN}} + x$$

Where 'x' = 0.1 for soft flowing SAN ($\log \text{MFI}_{\text{SAN}}$ in between 1.39 to 1.93)

5.2 Suggestion for further study

The correlation for calculating Izod impact has been benefited of the new designed formulation in ABS manufacturing. More recently, Bayer Polymers started to produce PC-ABS alloy, which has higher Izod impact and heat resistance property. The process for PC-ABS is also mechanical blending which also requires the designed formulations. Therefore the extension of this study would involve PC-ABS systems.

จุฬาลงกรณ์มหาวิทยาลัย

REFERENCES

1. I.J. Hwang and B.K. Kim. Effect of the Type of SAN in SAN/CPE Blend: Morphology, Mechanical, and Rheological Properties. Polymer 67 (1998): 27-36.
2. P.Y.B Jar, R. Lee, T. Shinmura and K. Konishi. Rubber Particle Cavitation on Toughness Enhancement of SMI-Modified Poly(acrylonitrile-butadiene-styrene). Journal of Polymer Science: Part B: Polymer Physics 37 (1999): 1739-1748.
3. I. Walker and A.A. Collyer (ed.), Rubber toughened engineering plastics, London: Chapman & Hall, 1994. pp. 29-56.
4. H. Kim, H. Keskkula and D.R. Paul. Toughening of SAN copolymers by a SAN emulsion grafted rubber. Polymer 31 (1990): 869-876.
5. C.B. Bucknall. Toughened plastics, London: Applied science publishers, 1977. pp.155-179.
6. J. R. Fried. Polymer science and technology, Prentice-Hall international, 1995. p 407.
7. L. D. Sawyer, and D. T. Grubb. Polymer Microscopy. 2nd ed., New York : Chapman & Hall, 1996. pp. 1-15.
8. H. Kim, H. Keskkula and D. R. Paul. Effect of acrylonitrile content on the toughness of ABS materials. Polymer 32 (1991): 1447-1455.
9. C. R. Bernal and P. M. Frontini. Microstructure, Deformation, and Fracture Behavior of Commercial ABS resins. Journal of Applied Polymer Science 58 (1995): 1-10.

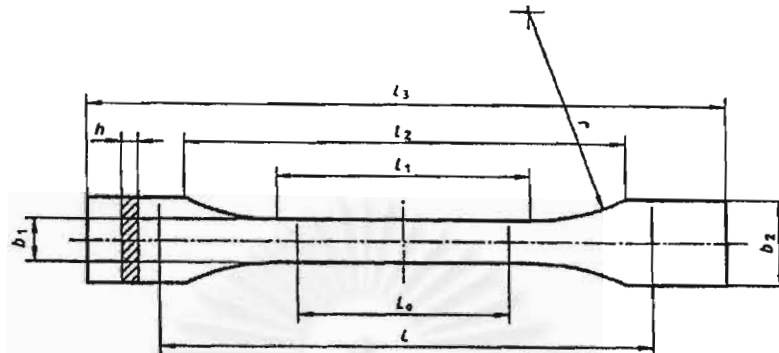
10. M.C.O. Chang and R.L. Nemeth. Rubber particle agglomeration phenomena in acrylonitrile-butadiene-styrene (ABS) polymers. I. structure-property relationship study on rubber particle agglomeration and molded surface appearance. Journal of Applied Polymer Science 61 (1996): 1003-1010.



จุฬาลงกรณ์มหาวิทยาลัย

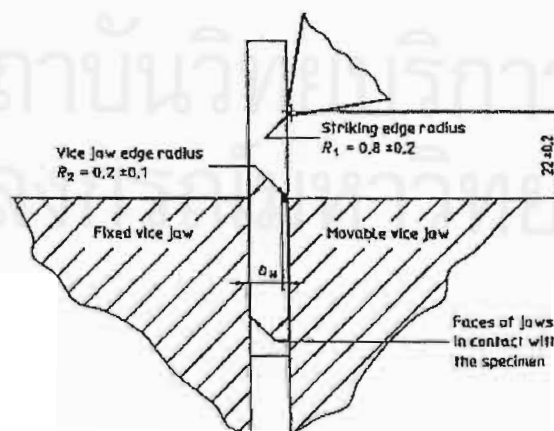
APPENDIX

1. Tensile specimen



l_3 Overall length	170	mm.
l_1 Length of narrow parallel-sided portion	80 ± 2	mm.
r radius, $r = [(l_2 - l_1)^2 + (b_2 - b_1)^2] / 4 (b_2 - b_1)$	20 to 25	mm.
l_2 Distance between broad parallel-sided portions	104 to 113	mm.
b_2 Width at ends	20.0 ± 0.2	mm.
b_1 Width of narrow portion	10.0 ± 0.2	mm.
h Preferred thickness	4.0 ± 0.2	mm.
L_0 Gauge length	50.0 ± 0.5	mm.
L Initial distance between grips	115 ± 1	mm.

2. Notched Izod impact specimen, support and striking edge.



2. Mixer



3. Extruder



4. Injection molding machine



5. Impact tester



บริการ
มหาวิทยาลัย

6. Tensile tester



7. Melt flow indexer



8. Calculation methods

8.1 Izod impact

Calculate the Izod impact strength of notched specimens, a_{IN} , expressed in kilojoules per square meter, using the formulation

$$a_{IN} = (W / H \cdot b_N) \times 10^3$$

where

W is the corrected energy, in joules, absorbed by breaking the test specimen;

H is the thickness, in millimeters, of the test specimen;

b_N is the remaining width, in millimeters, at the notch base of the test specimen.

8.2 Tensile modulus

Calculate the modulus of elasticity (Young's modulus) defined in the following equation on the basis of two specified strain values:

$$E_t = (\sigma_2 - \sigma_1) / (\epsilon_2 - \epsilon_1)$$

Where

E_t is Young's modulus of elasticity, expressed in megapascals;

σ_1 is the stress, in megapascals, measure at the strain value $\epsilon_1 = 0.0005$;

σ_2 is the stress, in megapascals, measure at the strain value $\epsilon_2 = 0.0025$

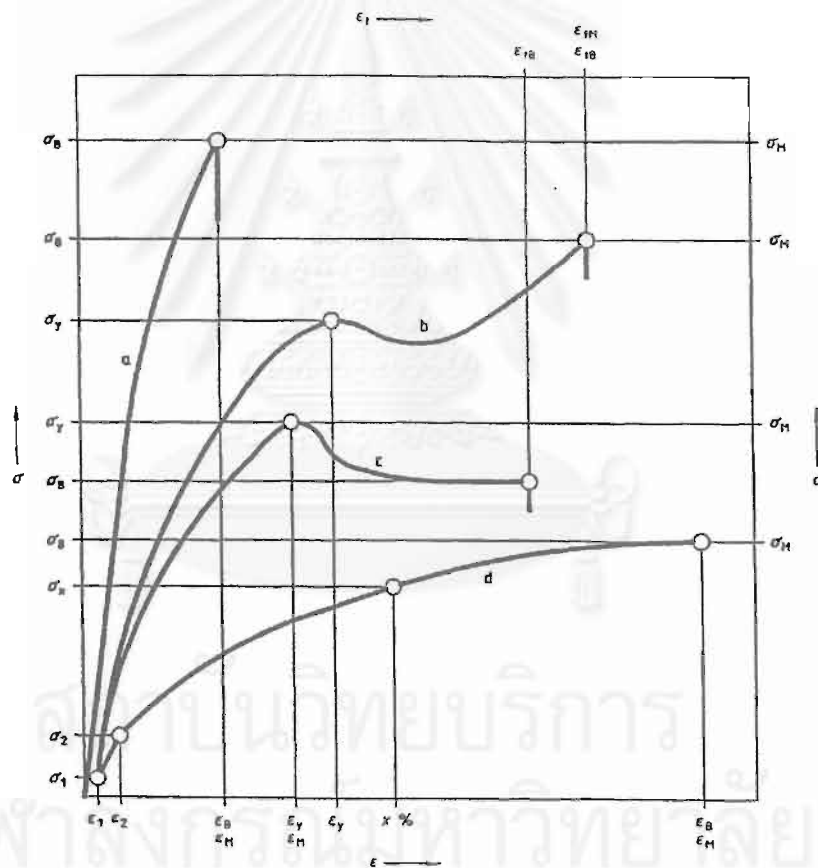
8.3 Tensile strength

Calculate stress values defined in the equation below on the basis of the initial cross-sectional area of the test specimen;

$$\sigma = F/A$$

Where

- σ is the tensile stress value in question, expressed in megapascals;
- F is the measured force concerned, in newtons;
- A is the initial cross-sectional area of the specimen, expressed in square millimeters.



- Curve A Brittle material
- Curve b and c Tough materials with yield point
- Curve d Tough materials without yield point

The points for the calculation of Young's modulus E_1 are indicated by (σ_1, ϵ_1) and (σ_2, ϵ_2) showed only for curved d ($\epsilon_1 = 0.0005$; $\epsilon_2 = 0.0025$).

8.4 Melt flow index

The melt flow index, expressed in grams per 10 minutes is given by the equation

$$\text{MFI}(\theta, m_{\text{nom}}) = (A \cdot t_{\text{ref}} \cdot l) / t$$

Where

- θ is the test temperature, in degrees Celsius;
- m_{nom} is the nominal load, in kilograms;
- A is the mean cross-sectional area, in square centimeters, of the piston and the cylinder ($= 0.711 \text{ cm}^2$)
- t_{ref} is the reference time (10 min), in seconds (600 s)
- t is the predetermined time measurement or the mean value of individual time measurements in seconds
- l is the predetermined distance moved by the piston or the mean value of individual distance measurements, in centimeters.

BIOGRAPHY

Mr. Supachai Rinsom was born on April 25, 1968 in Chiangmai, Thailand. He received Bachelor Degree in Industrial Chemistry from Chiangmai University in 1990. He is working in Bayer Polymers Co.,Ltd. as a production manager in Styrenics Polymerization department. He is pursuing a Master Degree in Petrochemistry and Polymer Science graduate school on 1997.



จุฬาลงกรณ์มหาวิทยาลัย