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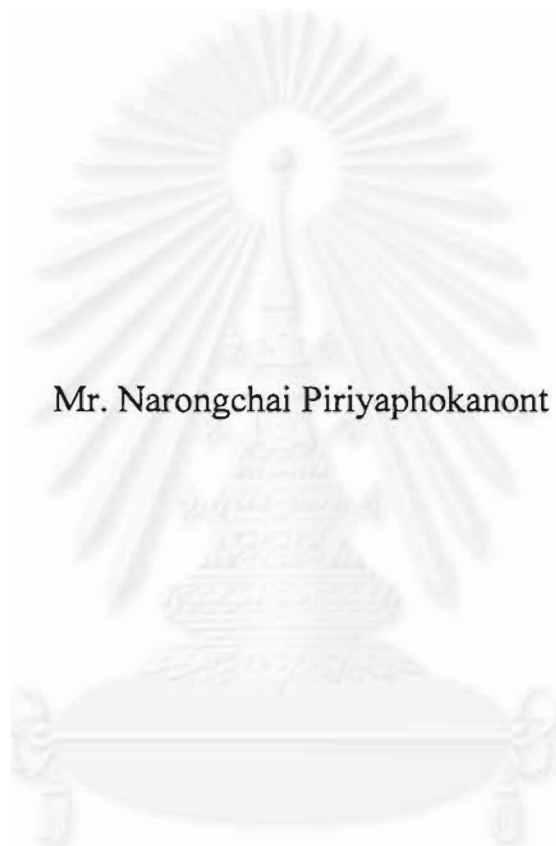
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IMPROVEMENT OF FLEXURAL STRENGTH AND HARDNESS OF
ACRYLONITRILE-BUTADIENE-STYRENE COPOLYMER USING
POLYMETHYLMETHACRYLATE



Mr. Narongchai Piriyaphokanont

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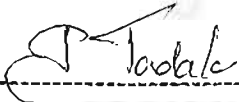
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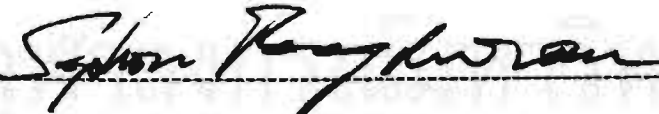

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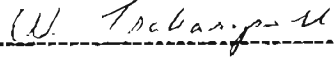
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ณรงค์ชัย พิริยะโกคานนท์ : การปรับปรุงความทนแรงโค้งงอและความแข็งของอะครีโลไนทริล-บิวทาไดอีน-สไตรีนโคพอลิเมอร์ โดยใช้พอลิเมทิลเมทาคริเลต (Improvement of Flexural Strength and Hardness of Acrylonitrile-Butadiene-Styrene Copolymer using Polymethylmethacrylate) อ.ที่ปรึกษา : รศ.ดร.อมร เพชรสม, อ.ที่ปรึกษาร่วม : นายปฏิพล ธาตุการ, 80 หน้า ISBN 974-332-998-6

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NARONGCHAI PIRIYAPHOKANONT : IMPROVEMENT OF FLEXURAL STRENGTH AND HARDNESS OF
ACRYLONITRILE-BUTADIENE-STYRENE COPOLYMER USING POLYMETHYLMETHACRYLATE.
THESIS ADVISOR : ASSOC.PROF.AMORN PETSOM, Ph.D.
THESIS CO-ADVISOR : MR.PATIPOL TADAKORN, M.Sc. 80 pp. ISBN 974-332-998-6

Polymethylmethacrylate (PMMA) was used to improve the mechanical properties especially, Flexural strength (FS) and Hardness (HR) of ABS plastics. The composites were prepared by premixing various amounts of ABS, PMMA and all additives in high speed mixer and kneading all components by single screw extruder. Then, all composites were injected to be test specimens for mechanical property measurement. Differential scanning calorimeter (DSC) and scanning electron microscopy (SEM) were used to study melting temperature and dispersion of the composite, respectively. In the first study, PMMA had been added in different levels and observed that at high level of PMMA, the FS and HR could be increased while the impact property indicated significant loss. For recovery of impact property, the polymer modifier has been added. Unfortunately, it exhibited no improvement. Alternatively, the increasing of the rubber content and acrylonitrile content of the blend could improve the impact properties at the appropriate level. Furthermore, the addition of polyacrylonitrile-styrene polymer (SAN) could improve the miscibility of blended system. This allowed good property balance of the blended. For the best composite comparable in properties to those of the commercial resins composed of 25% wt. ABS, 20% wt. SAN, 55% wt. PMMA and additives at 2.0 phr. ethylene-bis-stearamide, 0.2 phr. calcium stearate and 0.1 phr. silicone oil.

ภาควิชา.....
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
ปีการศึกษา..... 2542
ลายมือชื่อนิสิต.....
ลายมือชื่ออาจารย์ที่ปรึกษา.....
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

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ABBREVIATIONS

ABS	-	Acrylonitrile-Butadiene-Styrene
ACN	-	Acrylonitrile
Ca-st	-	Calcium Stearate
DSC	-	Differential Scanning Calorimeter
EBS	-	Ethylene-Bis-Stearamide
FS	-	Flexural Strength
HR	-	Hardness
MFI	-	Melt Flow Index
Mg-st	-	Magnesium Stearate
NI	-	Notched Izod Impact Strength
PC/ABS	-	Polycarbonate/Acrylonitrile-Butadiene-Styrene
PMMA	-	Polymethylmethacrylate
SAN	-	Styrene-Acrylonitrile
SEM	-	Scanning Electron Microscopy

CHAPTER I

INTRODUCTION



1.1 Statement of problems

Acrylonitrile-Butadiene-Styrene polymer is an opaque thermoplastic polymer, which is formed by copolymerizing of Acrylonitrile-Butadiene-Styrene monomers (ABS). It offers the diversity of the unique combinations of mechanical and chemical properties. In particular, it offers a wide range of impact strength and excellent chemical resistance. Therefore, it could apply to a numerous applications of automotive parts, electrical appliances, etc. However, the limitation of ABS resins usage is examined and the main important reason is the inclusion of rubber in ABS main structure. This limitation caused two weakness points, which are scratch resistance and poor flexural strength when comparing with the other thermoplastics such as modified polyphenylene ether, polycarbonate, etc. So, it cannot be applied to the household product application, especially sanitary ware.

Thus, the major technique to overcome this ABS limitation is considered to be blending technique. The polymethyl methacrylate (PMMA) is the thermoplastic that is chosen due to the advantage in hardness and rigidity characteristic. Furthermore, the price of PMMA is rather cheaper than the other thermoplastics which give similar qualities. In these blends, it is believed that the mechanical properties of ABS resins will be improved by getting higher flexural strength and strong surface hardness characteristics.

Therefore, overall blended product properties can be competed with the existing material, which now available in the markets.

1.2 Household products.

Normally, household product applications are consisted of many finished articles. For example, in sanitaryware which are bathtub, sink, shower trays and other bathroom furnishings etc. The properties required for this application are high rigidity, high scratch resistance and chemical resistance . ABS/PMMA blend shows good combination of mechanical properties of high stiffness and hardness compared to ABS and higher impact resistance than PMMA . Therefore, the material replacement of AS, ABS, PMMA and PC/ABS alloys by ABS/PMMA material should be possible. Users have advantage of using them by lower cost than the other engineering thermoplastics while the other required properties are maintained.

1.3 Purpose of the research.

This research is aimed to study the physical and mechanical properties of ABS/PMMA blends in order to improve the hardness(HR) and the flexural strength (FS) while maintaining the other mechanical properties such as melt flow index (MFI), and notch impact strength (NI). The ABS/PMMA blends are expected to have good physical and chemical properties comparable to those of commercial resins which are now using such as PC/ABS alloys.

1.4 Scope of the research

In this research, the effects of different level of ABS, Bulks SAN and PMMA including additives such as ethylene-bis-stearamide, calcium stearate and silicone oil on mechanical properties of ABS/PMMA blends were investigated.

All compositions were prepared by high speed mixer, single screw extruder and injection molding . The DSC and SEM techniques were used to analyze the blends. Finally, the mechanical properties MFI, NI, HR, and FS were measured and compared to PC/ABS commercial resins.



CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Polymer blends (1)

The blending has become a major technique to overcome many limitations of polymers. The limitations have been resolved to some extent by blending with other resins. So, examining of selected each polymer type to solve the problem is the most importance. It is not only to get the best properties of the blended product but also to reduce the production cost. If the raw material cost of the processes can be reduced and all properties still meet the specifications required, the manufacturer must use it to remain competitive.

There is no doubt that the main reason for blending, compounding and reinforcing is economy. In general the following economy related reasons can be listed:

1. Extending engineering resin performance by diluting it with low cost polymers.
2. Developing materials with a full set of desired properties.
3. Forming a high performance blend from synergistically interacting polymers.
4. Adjusting the composition of the blend to customer specifications.
5. Recycling industrial and/or municipal plastics scrap.

Polymer blend is a mixture of at least two polymers or copolymer. There are two classes of polymer blend depending on the kinetics of phase separation, miscible and immiscible. The immiscible polymers blend which has been modified and/or morphology change, this is called “Polymer Alloy”. The general relation between blends and alloys is shown in Figure 2.1. Polymer alloys constitutes a specific sub-class of polymer blend.

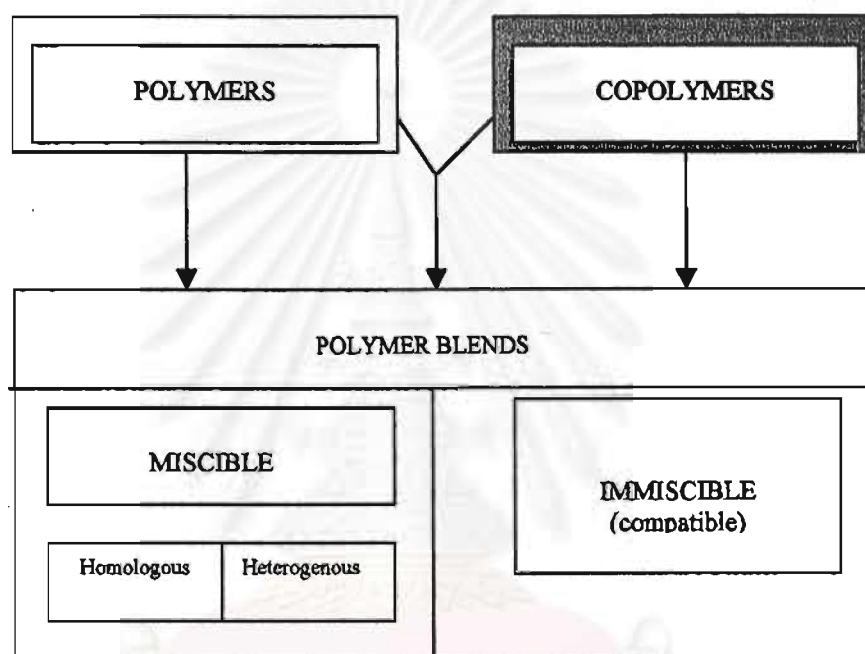


Figure 2.1 Interrelations in polymer blend nomenclature.

2.2 ABS/PMMA blends

Melt blends of ABS and PMMA were prepared by main components of ABS containing ACN content and rubber content. The PMMA is a minor component with regard to ABS blends. The mechanical properties have been investigated. It is believed that blends of ABS with PMMA would improve

the mechanical properties of ABS such as mechanical strength, surface characteristics, etc. Moreover, the properties change should be strongly related to the phase behavior of the migration of rubber particles in to PMMA phase. The disperse phase contains a component of SAN grafted on to poly butadiene rubber which is above its glass transition temperature (T_g), so that chain can be mobile. The other phase is matrix phase. It contains segments of rigidity locked in place because the service temperature is below T_g .(2)

The primary advantage of ABS/PMMA blends is the ease of processing ability, surface characteristics, mechanical strength and it can be reused. Besides, the obvious environmental benefit of recycles is the ability to use raw material, and scrap. In addition, there are many factors that define ABS/PMMA blends properties such as processing technique and morphology which showed as follow.

2.2.1 Main components of ABS/PMMA blends

The main components of ABS/PMMA blends are ABS, PMMA, and additives. All of them will effects the physical and mechanical properties of ABS/PMMA blends.

2.2.1.1 Acrylonitrile – Butadiene – Styrene(ABS).

ABS polymers are a family of opaque thermoplastic resin formed by copolymerization of acrylonitrile- butadiene - styrene. The ABS materials were grafted polymer, formed by polymerization of resin monomers, styrene and acrylonitrile, in the presence of a rubbery polybutadiene. Thus, the

composition of ABS material consists of phase of grafted ABS dispersing in SAN matrix. These are the copolymerization step of acrylonitrile and styrene monomer on the polybutadiene rubber.(3,4)

Mechanism on Emulsion polymerization of ABS

This emulsion polymerization principle is done by adding monomer into aqueous solution contains emulsifier and dispersed stably as emulsion state by agitation, and then polymerization begins by aqueous initiation addition of initiator. When water is used as the medium of polymerization, it can be separated easily from monomers because of the immiscibility between water and oil. Therefore, the emulsifier having hydrophilic group solubilizing water and lipophilic group stabilizing monomer in the same molecule prevents the separation during polymerization.(5)

Function of Emulsifier

Emulsifier solubilizes monomer into water and its structure is shown in Fig 2.2

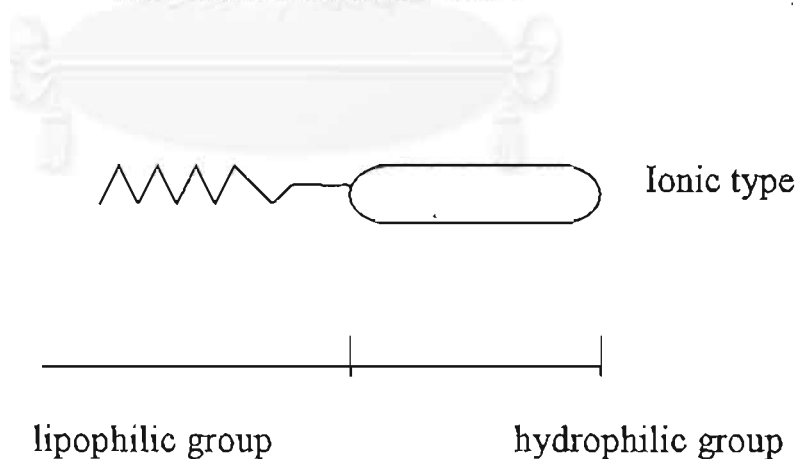


Figure 2.2 Emulsifier structure.

When emulsifier is added into coexistence of water and oil, monomer is not separated from water and becomes a small oil droplet (micelle) surrounded by emulsifier.

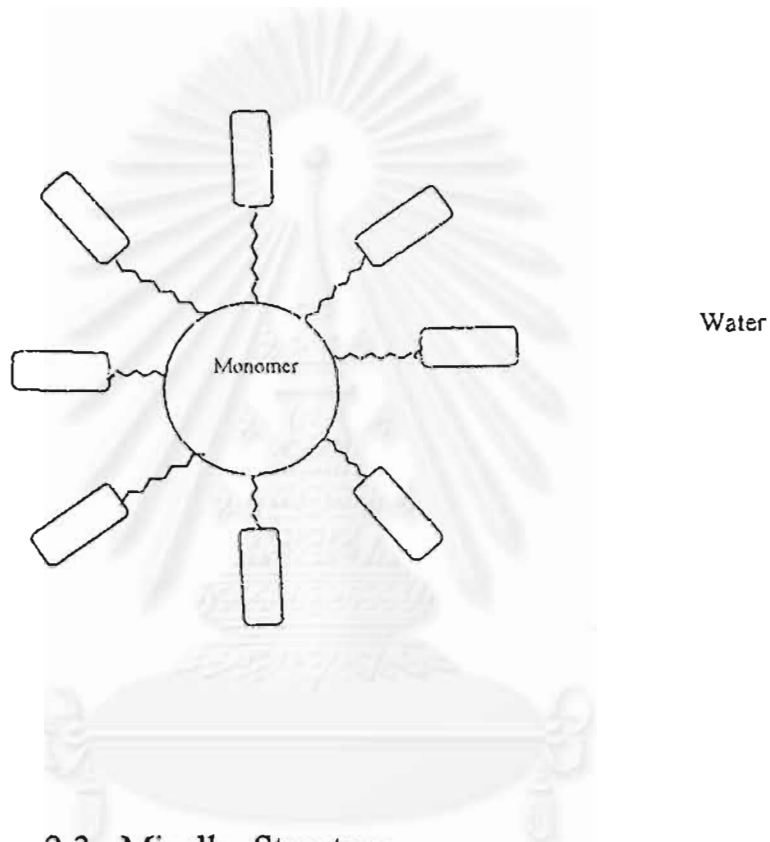


Figure 2.3. Micelle Structure

The radicals born in water system enter into micelle in which they begin polymerization and grow to form polymer particles. The process scheme of emulsion polymerization is shown in Fig 2.4

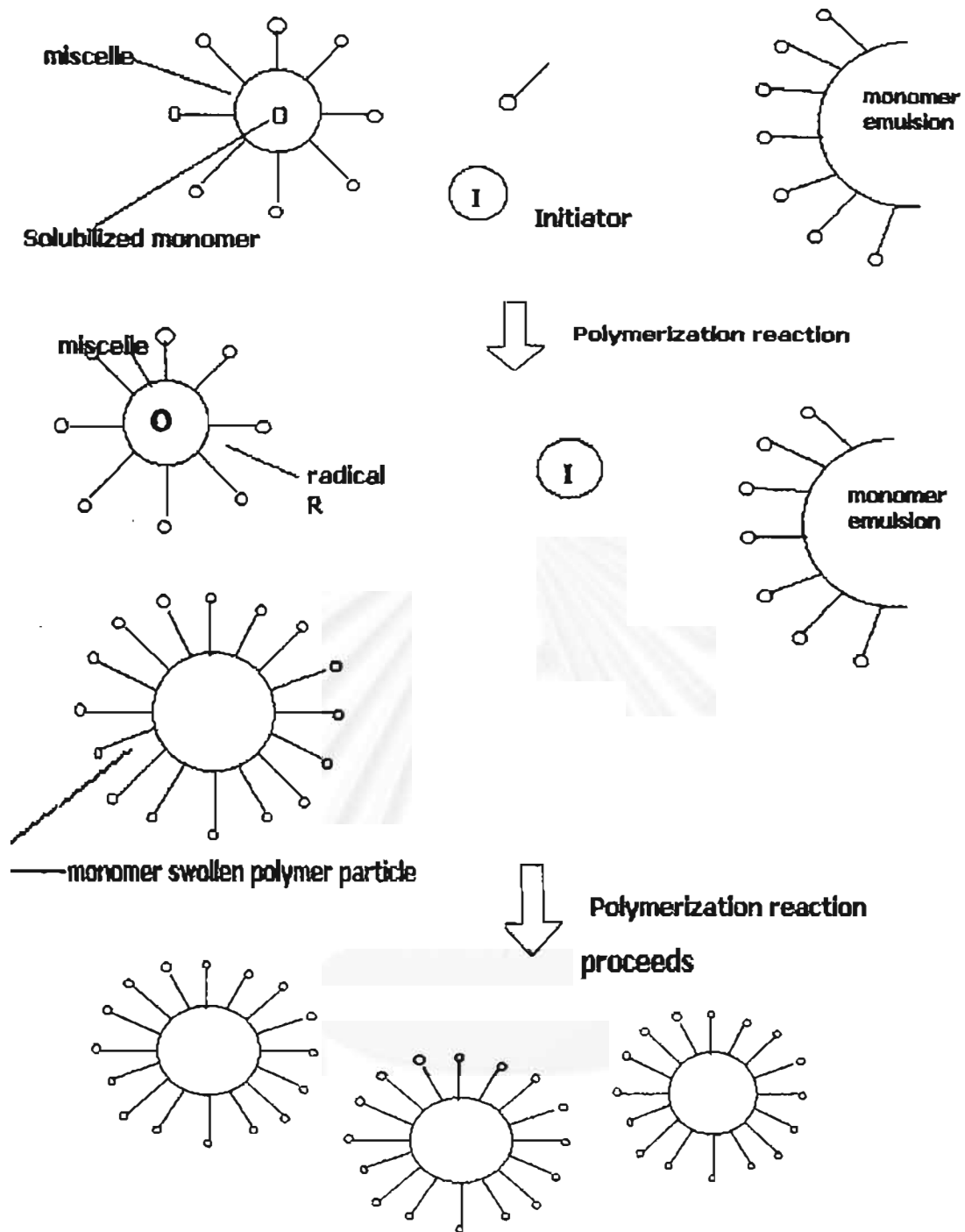
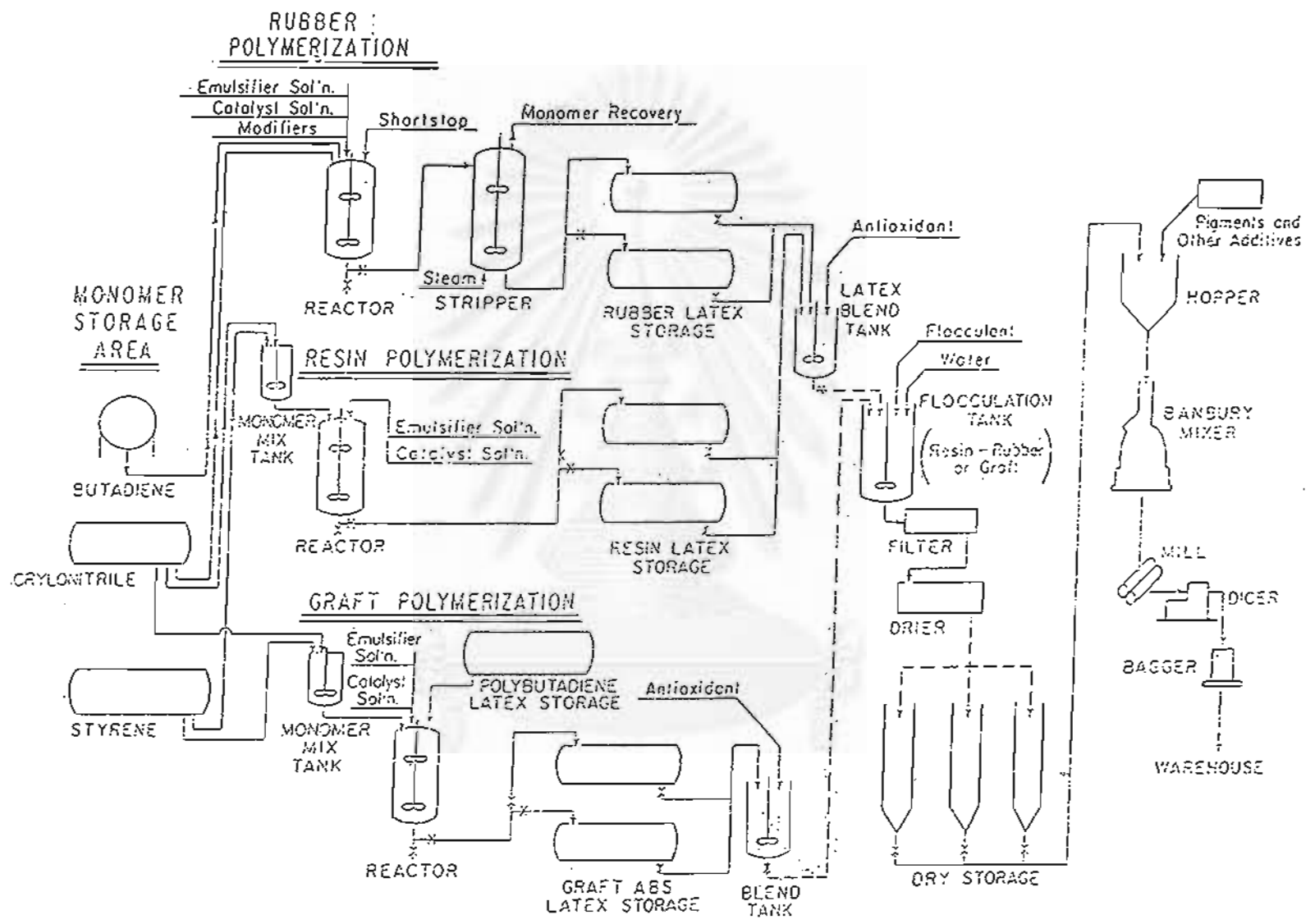


Figure 2.4. Process of emulsion polymerization (6)



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Figure 2.5 ABS Process

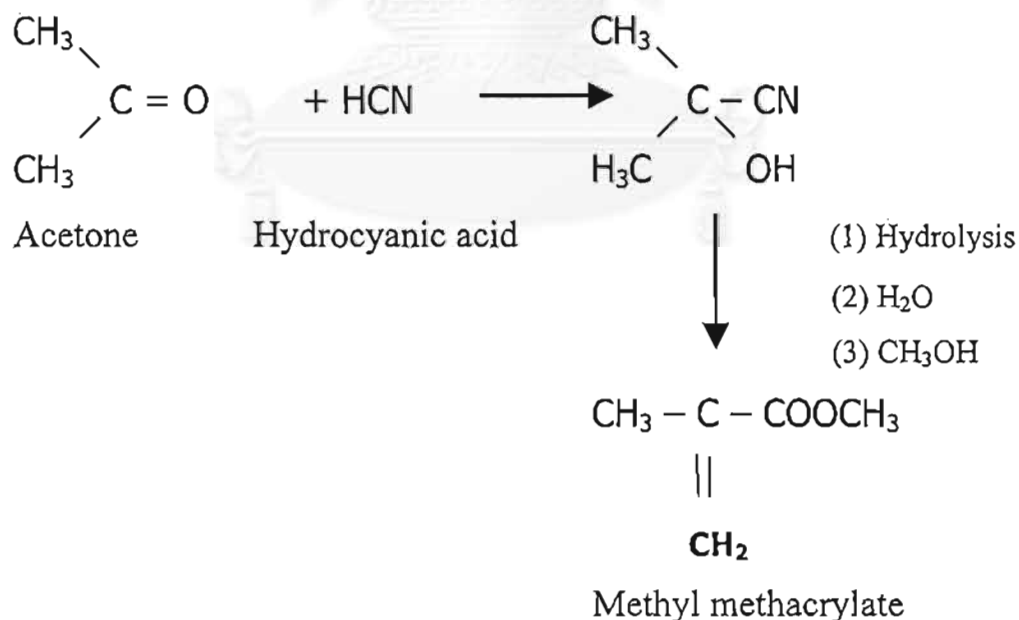
2.2.1.2 Polymethyl Methacrylate (PMMA)

PMMA is a vinyl polymer, made by free radical vinyl polymerization from the monomer methyl methacrylate (MMA). MMA is a glass-like polymer dependent for its strength on stiffness its major use is for sheet and thermoforming as for bathtubs. It also finds important use in surface coatings where it can be used in the form of an emulsion for water base point on as solvent solutions for industrial coating, such as for automobiles.

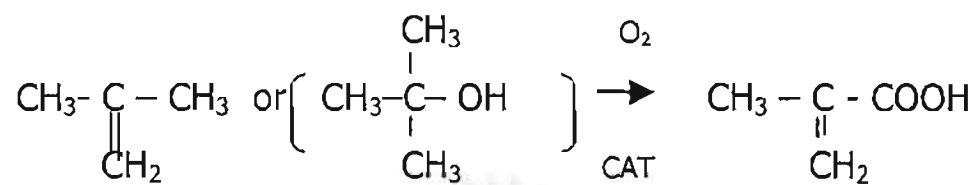
There are three commercial routes for making methyl methacrylate which are shown in Figure 2.6. The acetone cyanohydrin route is the classical one in widest use today. The oxidation of isobutene or t-butyl is being practical. The ethylene hydroformulation route has been announced.

(7)

1. Acetone Cyanohydrin



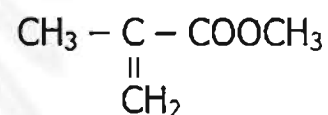
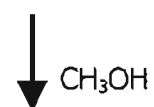
2. Isobutene (t-Butyl alcohol) oxidation



Isobutene

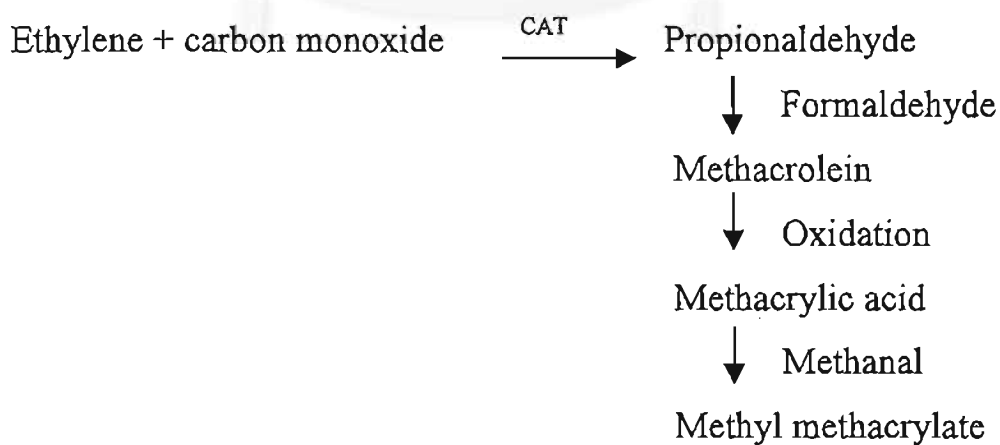
butyl alcohol

methacrylic acid

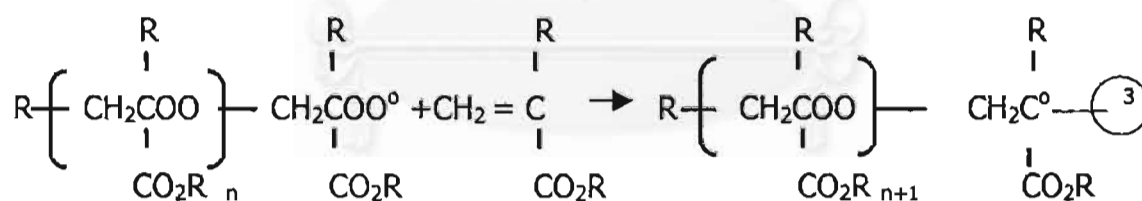
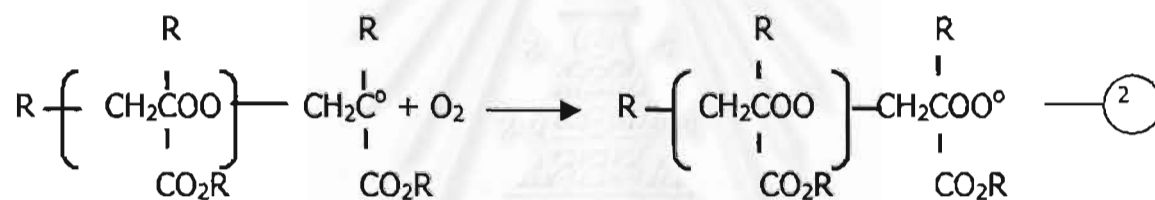
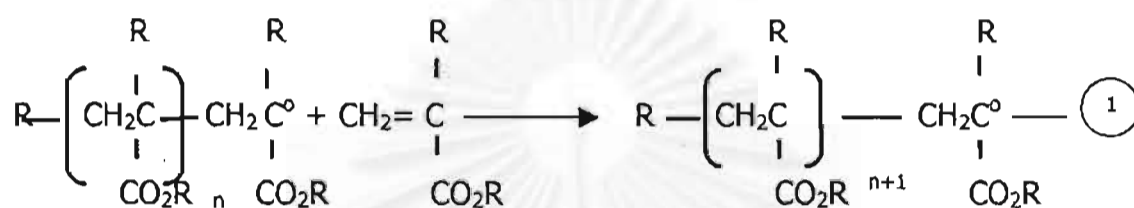


methyl methacrylate

3. Ethylene hydroformulation



Most of the commercial available polymers are prepared by free-radical processes involving initiation, propagation; chain transfer and termination and methacrylate polymerization are inhibited by oxygen .(8)



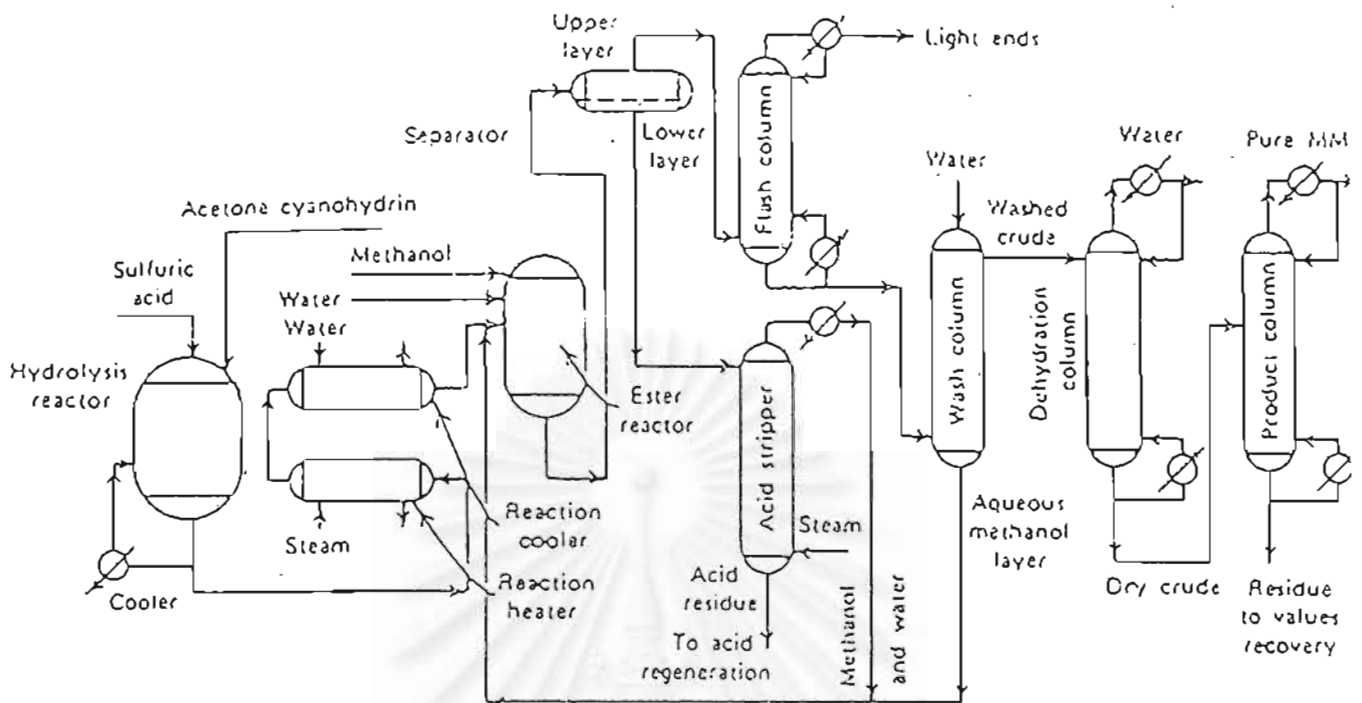


Figure 2.6 PMMA from Acetone cyanohydrin process.(9)

2.2.1.3 Silicone oil fluids additive

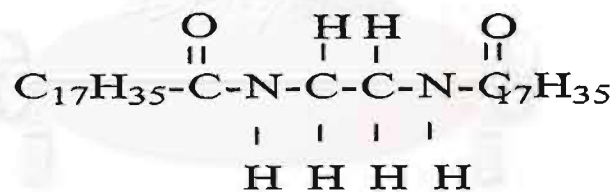
Silicone fluids are dimethylpolysiloxanes. They are available in wide range of viscosities depending on the molecular weight of dimethyl polysiloxane. In plastic and rubber applications it act as mold releasing agent and rubber expansion. These functions are important for improving impact resistance and injection molding process applications.

2.2.1.4 Calcium stearate



Calcium stearate is used as a stabilizer, external lubricant and color dispersing agent for various synthetic resins. It offers the excellent heat stability in combination with zinc or lead soap system for PVC and the other plastic and rubber applications. Furthermore, it can improve the impact resistance of the polymer under the suitable dosage.

2.2.1.5 Ethylene bis-stearamide

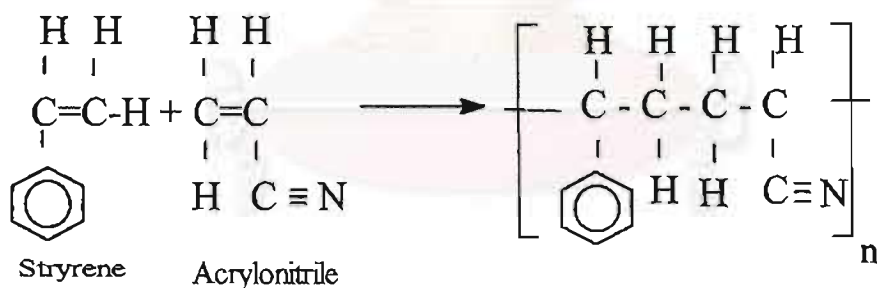


EBS function act as internal and surface lubricant in thermoplastic, As an internal lubricant and processing aid, it plasticizes the resin, thus lowering the power requirements for mixing and extrusion and improving the flow through die or into molds. It also acts as a pigment dispersing, providing faster blending and more uniformity; yet does not discolor white or natural plastics.

As an external lubricant, it migrates to the surface of the plastic, forming a thin film which provides mold release, and antiblock. Furthermore EBS exhibits limited compatibility with polymeric materials such as PS, PVC. This characteristic enhances its performance as a lubricant.

2.2.1.6 Minor components

In this blend SAN copolymer is used as minor component for improving the miscibility of PMMA and ABS. SAN is copolymer of styrene and acrylonitrile, and it offers superior mechanical properties, and chemical resistance.



There are 3 processes of SAN product which are emulsion process, suspension process and bulk process. The bulk polymerization of SAN process is started by styrene monomer copolymerization with acrylonitrile

monomer and initiated by temperature. Ethyl benzene is used as inert solvent for temperature control and reduce viscosity. In commercial route, the continuous bulk polymerization is operated for narrow molecular weight distribution and higher percent yield. The bulk SAN process is shown in Figure 2.7 (10)

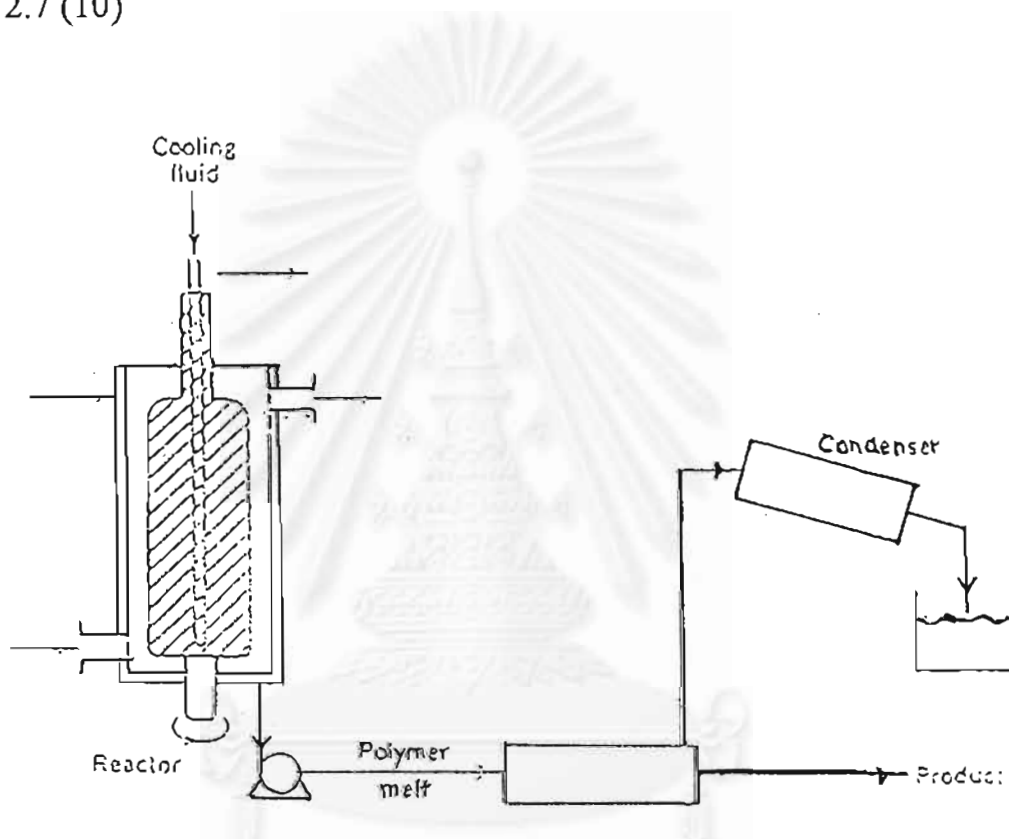


Figure 2.7 Bulk SAN process

2.2.2 Processing technique

ABS and PMMA are obtained different form, in which ABS is a powder form and PMMA is pellet form. In order to blend them together it is necessary to use high speed mixer to pre-mixing all component. The high speed mixer has the function of intensively mixing the main component and additives according to the test formulation. The standard mixer is a cylindrical with vertical axis and shaft passing through the center of the container base to receive and drive the mixing tool in Figure 2.8 (11)

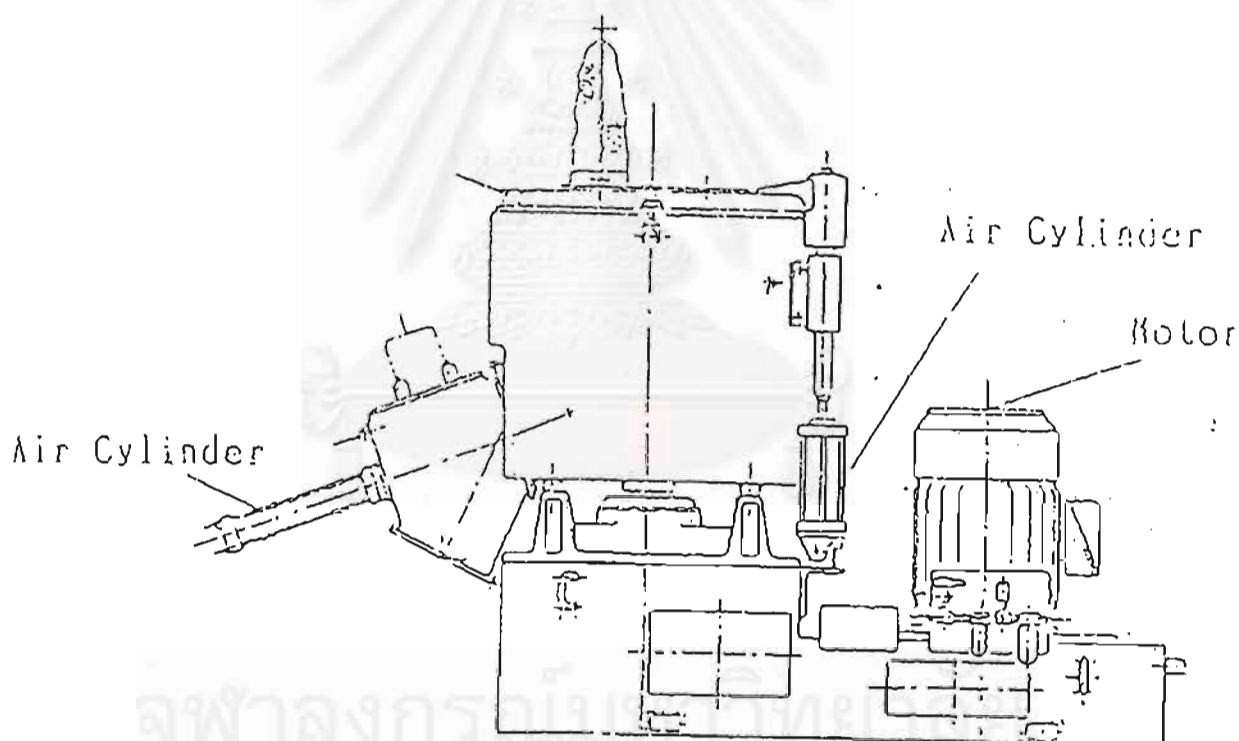


Figure 2.8 The cylindrical mixer

All mixed component are given high shear stress by extrusion process. This study used single screw extruder which generates high shear rate in tip clearance. When the screw turns, a screw flight having a tip clearance forms a thin layer of polymer melt and another flight of screw scrapes the melt film as show in Figure 2.9 and the mixing process continued.

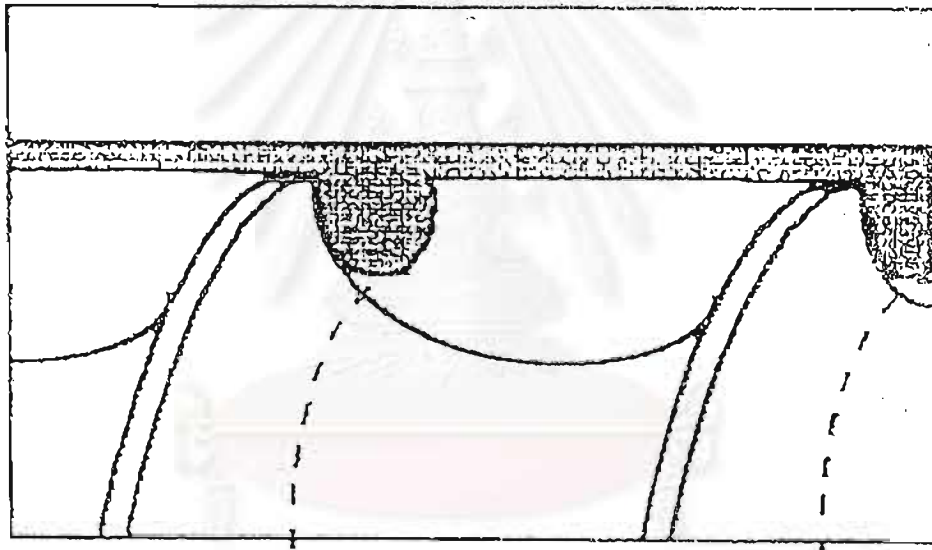


Figure 2.9 Screw flight

2.3 Literature reviews

Nowaday, there are many interesting work in the development of the thermoplastic blending especially ABS/PMMA blend. The blended properties depend on many factors such as blending ratio, rubber content, acrylonitrile content and blending conditions. The work of miscible and immiscible blends of ABS with PMMA are reviewed below.

Kim, B.K, Shin, G.S, Kim, Y.J and Lee, I.T (12) have studied the morphology and Rheology of ABS and PMMA blend with the aim to improve mechanical properties and surface characteristics. They found that ABS containing 24 and 27 wt% AN is miscible but if it contains 35 wt% of AN it will be immiscible with PMMA. The miscibility of ABS with PMMA should depend on the miscibility of SAN with PMMA and the miscibility window exists with AN content of 9-29 wt%. In addition, as the compounding temperature migrates toward the PMMA phases, the migration can also be favored from the reduction of interactions between rubber particles and SAN matrix with the increase of temperature.

Since the rubber particle is a SAN-graft-PB, therefore it gives strong interfacial interaction. These interactions should decrease at higher temperatures. The miscible blends give viscosity lower than additivity would

temperatures. The miscible blends give viscosity lower than additivity would predict, whereas immiscible ones give positive (ABS-rich phase) and negative (PMMA-rich phase) deviations from the additivity.

Kim, B.K, Shin, G.S, Kim, Y.J, and Park, T.S (13) have studied the mechanical and surface properties of injection molded specimens for miscible and immiscible blends of ABS with PMMA. For miscible blend hardness, modulus and strength showed a smooth variation with composition exception that impact strength decreased smoothly with PMMA. It indicated that the property variation with composition is related to the SAN-PMMA miscibility and the migration of rubber particle into the PMMA phase by PMMA is well mixed with the SAN matrix and the rubber particles are evenly spread into SAN-PMMA matrix. In the immiscible blends, it is seen that the hardness, flexural modulus and strength of these blends generally show smooth variation with composition. A significant difference in mechanical property between miscible and immiscible blends is notched impact strength. In miscible blend, impact strength varies smoothly with composition, however in immiscible blends a sharp drop is seen even at 10 wt% PMMA. These are because of the migration of rubber particles. The others factors which affect on the mechanical properties is compounding temperature. As the compounding temperature increases, the flexural

strength and modulus decrease and the impact strength increases. It is less at lower and more at higher temperature and the increase of surface gloss with temperature is due primarily to the improved flow in the mold.

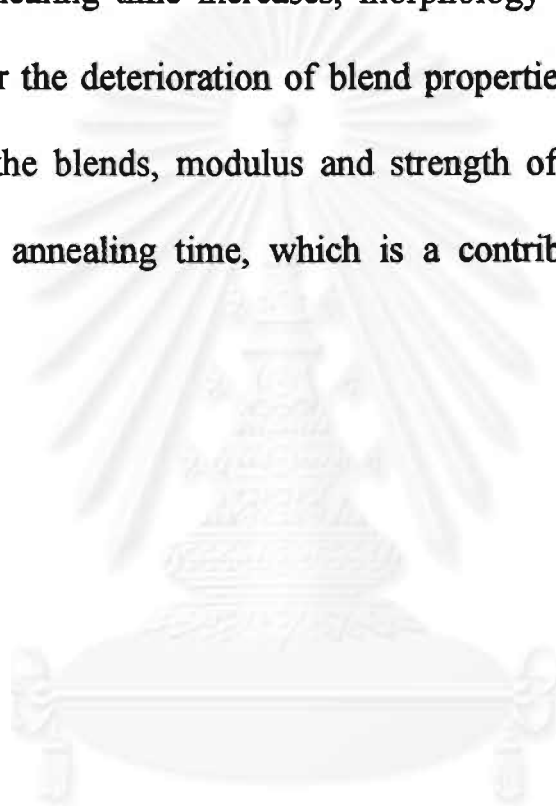
Kim, B.K., Choi, C.H and Xie, X.M (14) studied ABS ternary blends with PMMA and PC (ABS/PMMA/PC) by corotation twin-screw extruder and reported morphologies, surface gloss characteristics and mechanical properties of these blends. The result of TEM micrograph of ABS/PMMA (60/40) binary shows phase separation between SAN and PMMA phases. Most of the rubber particles are retained in the SAN phase. In ABS/PC (60/40), ABS/phenoxy(60/40) blend, the phase-separated structure is also visualized. However, the shape of the dispersed phase is closer to sphere and the domain size is larger in the phenoxy blend than in either PMMA or PC blends. In ternary blend it is seen that PMMA phases is preferentially interposed between SAN and PC and encapsulated the dispersed PC phases. In mechanical properties, tensile modulus shows a synergism for PC blends and a linearity for phenoxy blends these should be closely related to the inter position of the PMMA phases between PC and SAN phases. On the other hand, the tensile properties with phenoxy in ABS/PMMA/phenoxy blends are decreased due to the miscibility of PMMA with phenoxy. The impact strength of the blend shows large positive deviation in PC ternary blend (PC-

rich blend) and does not change in PMMA-rich blends. It seems that the higher loading of PMMA may embrittle the ABS owing to dilution of the rubber particles in the continuous phases at low PC content. At higher PC content ($\geq 20\%$) migration of rubber particles into PMMA phase becomes insignificant, and interposition of PMMA becomes more significant to the interfacial adhesions. In gloss characteristic, it shows relatively large difference in refractive indices by ABS/PMMA blend. The decreasing of gloss with the addition of PC is due to the decreasing of Δn between SAN and PC

Kim, B.K, Yoon, J.K and Xie, X.M (15) have studied the influence of annealing on the phase morphology and mechanical properties of ABS/PMMA binary and ABS/PMMA/PC ternary blends. Samples were annealed up to 85 min at 215 and 225 °C. Coalescence was visualized by transmission electron microscopy (TEM). Changes in mechanical properties were measured as a function of annealing time. In ABS/PMMA (70/30 by weight) blends which annealed at 225 °C for various periods of time, it indicates that most of the rubber are retained in SAN due to the greater miscibility of rubber with SAN than with PMMA. The quantitative analysis of the TEM micrograph indicates the changes in the number of domains and average domain sizes from the image analyses. The domain size is increased

becomes narrower with annealing time. The coarsening process occurs faster at higher temperature. In the stress-strain curves of ABS/PMMA blends annealed at various times, the decrease in modulus, strength and elongation at break with annealing time are obvious. At higher temperature (225 °C), these properties deteriorate faster.

Thus, as annealing time increases, morphology coarsening becomes the prime cause for the deterioration of blend properties. With the addition of PC content in the blends, modulus and strength of the blend increase, especially at long annealing time, which is a contribution of PC to the thermal stability.



CHAPTER III

EXPERIMENTAL

3.1 Materials

There are many materials which are used in this research and obtained from various sources as shown in Table 3.1. Their physical and chemical properties are shown in Appendix A.

Table 3.1 Materials and sources of supplier used in the ABS/PMMA composition.

Material	Trade name	Source of Suppliers
ABS	PORENE	Thai Petrochemical Industry (Public) Co.,Ltd.
PMMA	CRYSTALITE	TPI : Polyacrylate Co.,Ltd.
bulk SAN	PORENE	Thai Petrochemical Industry (Public) Co.,Ltd.
Ethylene-bis-Stearamide	KAO WAX EB-P	KAO CORPORATION

Material	Trade name	Source of Suppliers
Silicone oil	TSF451	TOSHIBA SILICONE
M a g n e s i u m Stearate	Magnesium Stearate	NIPPON OIL & FAT CO.,LTD.
Polymer modifier	MODIPER A4200	KURARAY Co.,LTD.

3.2 Apparatus

1. High speed mixer : KAWATA MFG CO.,LTD.
Model SMG100
2. Vented single screw extruder: ISHINAKA : Model HS-50
3. Balance weigher : METLERR TOLEDO
Type SB32000
4. Injection molding machine : NESEI: Model FS80S12 ASE
5. Melt flow rate tester : TOYO SEIKI: Type C-5059D2
6. Izod impact tester : ZWICK :Type 5102,100/100
7. Flexural strength testing : ZWICK : Model 1435.01
8. Hardness tester : MATSUZAWSEIKI
: Model DXT-1
9. Differential scanning calorimeter: PERKIN ELMER DSC7
10. Scanning electron microscopy : JEOL : Type JSM-6400

3.3 Experimental procedure

All of ABS/PMMA blends were prepared by varying the weight amounts of ABS, PMMA, bulk SAN and additives. Such as, ethylene-bis-stearamide, calcium stearate and silicone oil fluids etc. (Table 3.1). The mechanical properties, MFI, NI, HR and FS of the polymer blends were measured and compared to those of the commercial resin PC/ABS alloy.

3.3.1 Mixing procedure

The compositions were dry blending in the high speed mixer at room temperature including all additives and then the blended compositions were melted and kneaded in order to make a homogeneous samples by vented single screw extruder as the compounding conditions in Table 3.2.

Table 3.2 : Compounding Condition.

Cylinder temperature	
C1	180 °C
C2	190 °C
C3	200 °C
C4	200 °C
C5	200 °C
D	240 °C
Main screw speed	250 rpm
Feeder screw speed	10 rpm
Vacuum pressure	-18 mbar
Resin temperature	250 °C

3.3.2 Molding procedure.

The sample was preheated in an oven chamber at 80 °C for 2 hours before injected to be test specimens. In molding process, cylinder temperature was set up at nozzle at about 230 °C and mold temperature at 70 °C. Then the test specimens were conditioned in conditioning room which

control temperature at 23 °C and 50% humidity before mechanical properties were measured.

Table 3.3 Formulation of ABS/PMMA blends

Sample no.	Ingredients (wt %)							
	ABS	PMMA	bulk SAN	EBS	Ca-st	Si-oil	Mg-st	Polymer modifier
1	35	-	65	2.0	0.2	0.1	-	-
2	35	-	65	2.0	0.2	0.1	-	-
3	35	32.5	32.5	2.0	0.2	0.1	-	-
4	35	32.5	32.5	2.0	0.2	0.1	-	-
5	35	65	-	2.0	0.2	0.1	-	-
6	100	-	-	1.8	-	-	1.0	-
7	75	25	-	1.8	-	-	1.0	-
8	50	50	-	1.8	-	-	1.0	-
9	25	75	-	1.8	-	-	1.0	-
10	75	25	-	1.8	-	-	1.0	5
11	50	50	-	1.8	-	-	1.0	10
12	70	20	10	1.8	-	-	1.0	-
13	65	25	10	1.8	-	-	1.0	-
14	60	30	10	1.8	-	-	1.0	-
15	55	35	10	1.8	-	-	1.0	-
16	30	-	70	1.5	-	0.05	-	-
17	30	70	-	1.5	-	0.05	-	-
18	30	65	5	1.5	-	0.05	-	-
19	30	60	10	1.5	-	0.05	-	-
20	25	75	-	1.5	-	0.05	-	-
21	25	65	10	1.5	-	0.05	-	-
22	25	75	-	2.0	0.2	0.1	-	-
23	25	55	20	2.0	0.2	0.1	-	-
24	28	72	-	2.0	0.2	0.1	-	-
25	28	52	20	2.0	0.2	0.1	-	-

3.3.3 Effect of PMMA content.

Various amounts of PMMA at 0, 25, 50 and 75% were mixed together with ABS. The mechanical properties of each composition were measured and compared to those of commercial resin PC/ABS alloys.

3.3.4 Effect of polymer modifier.

Polymer modifier used is a graft copolymer consisting of a polyolefin as a backbone and vinyl polymer as a branch. In this research, polymer modifier was used at 5 and 10 %. The mechanical properties were measured and compared to those of the formulation without polymer modifier.

3.3.5 Effect of rubber content.

Various amounts of ABS at 30, 35, 55, 70 and 100 % were mixed together with Bulk SAN and PMMA. These amounts of ABS contain the rubber content about 6, 9, 12, 14 and 17 % respectively. The mechanical properties of each composition were measured and compared to those of commercial resin PC/ABS alloys.

3.3.6 Effect of bulk SAN content.

The bulk SAN resin at 0, 5, 10% were mixed together with ABS/PMMA. Then, the mechanical properties of each composition were measured and compared to those of commercial resin PC/ABS alloys.

3.3.7 Effect of acrylonitrile content.

Various amounts of ABS and bulk SAN at 20, 25, and 28% mixed together with PMMA. These amounts of ABS and bulk SAN contain the acrylonitrile content about 3.5-9.7%. Then, the mechanical properties were measured and compared to those of PC/ABS alloys.

Each composition of this experiment was prepared twice and the mechanical properties, MFI, NI, HR and FS were obtained three times. The results of all experiment are shown in Appendix A.

3.3.8 Mechanical measurement.

The mechanical properties, MFI, NI, HR and FS were obtained by using standard size and shape under standard test methods of the American Society for Testing and Materials (ASTM) which subjected to the following measurement.

Melt flow index	: Testing method of ASTM D1238
Impact strength	: Testing method of ASTM D256
Flexural strength	: Testing method of ASTM D790
Hardness	: Testing method of ASTM D785

3.3.9 Differential scanning calorimeter.

The Differential scanning calorimeter was used to study the thermal behavior of samples. The experiment was carried out on 4-5 mg sample

using nitrogen as purge gas to control atmosphere in the sample cells. The temperature range of analysis was from 40 to 180 °C at heating rate at 20 °C min⁻¹



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of the composites.

The ABS/PMMA blends were prepared according to the procedure outline in 3.3. The DSC curves illustrating melting behavior of the pure ABS, PMMA, commercial PC/ABS alloys and the prepared ABS/PMMA blends are shown in Appendix B, Figure B5. From the curves the glass temperatures of ABS/PMMA blends occur at about 103.7 °C and those of PC/ABS alloys shown in Appendix B, Figure B1 is about 98.9 °C. It is difficult to compare the two sets of data because of the difference base polymer composition. However, these curves show that glass transition temperatures of the prepared ABS/PMMA occur at the same point. These indicate the miscible blends system.(16)

4.2 Mechanical properties of commercial resins PC/ABS alloys.

In this research, the PMMA have been used for improving flexural strength and hardness properties of the ABS resins in order to compete with the existing PC/ABS alloys. At present, some of PC/ ABS alloys have been used in the household applications. Thus, their mechanical properties were measured and compared with those of the composites of this study. Commercial PC/ABS alloys illustrate very high FS and HR as shown in Table 4.1.(17)

Table 4.1 Mechanical properties of PC/ABS alloys.

Resin	MFI (g/10 min)	NI (g-cm/cm ²)	FS (kg/cm ²)	HR (R-scale)
PC/ABS	11.3	13.8	792	120

4.3 Effect of PMMA content.

The effect of PMMA content on mechanical properties is presented in Figure 4.1. It was observed that the addition of PMMA from 0 to 75 Wt % decreased NI to approximately 35% to 45% related to SAN-PMMA miscibility and the migration of rubber particles into the PMMA phases. For 25% PMMA, PMMA is well mixed with SAN matrix and rubber particles are dispersed in the SAN-PMMA matrix. When PMMA content was increased to 50 and 75%, it became an immiscible blend. The rubber particles, especially the large ones migrate into the PMMA phase, the SAN phase cannot thus absorb sufficient fracture energy. While the PMMA phase may not be enough toughen due to its lower concentration of rubber. This results in significant drop in NI. On the other hand, FS and HR are increased to approximate 15% and 5% respectively because of the migration of rubber particle to the PMMA phase. It allows the SAN to exhibit its good mechanical strength due to the lower rubber level in SAN. In MFI property, at 0-50 % wt PMMA content, MFI was not significantly changed. However at 75% wt PMMA, MFI was decreased. At this composition the complex viscosity was increased because of the phase inversion of the blends. (18)

From this result, ABS/PMMA blend at 50%wt PMMA gives the similar HR and FS values to those of the commercial resin PC/ABS alloy. However, the NI is expected to be improved by increasing the ABS rubber content or the other polymer modifier.

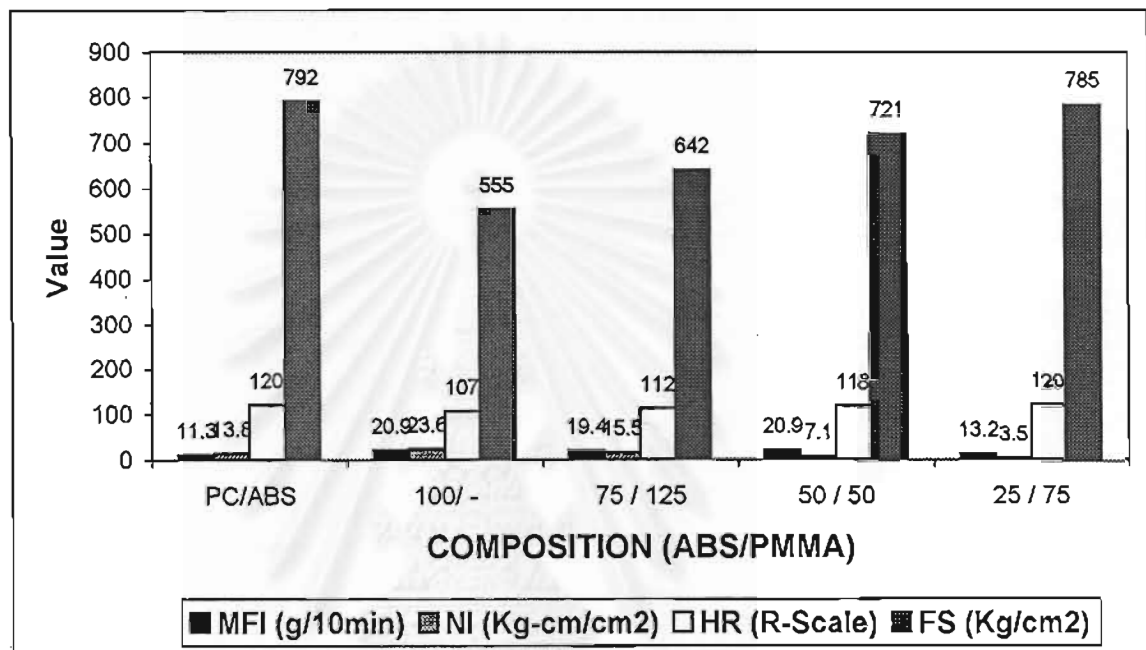


Figure 4.1 Effect of PMMA content on mechanical properties of ABS/PMMA blends compared to commercial resin PC/ABS.

4.4 Effect of polymer modifier.

Figure 4.2 shows the effect of polymer modifier incorporated into ABS/PMMA/modifier at 75/25/5 and 50/50/10, respectively. It was observed that NI value did not show any improvement compared to blank formulations. On the other hand, FS and HR properties exhibit a little lost while MFI exhibits an insignificant change.

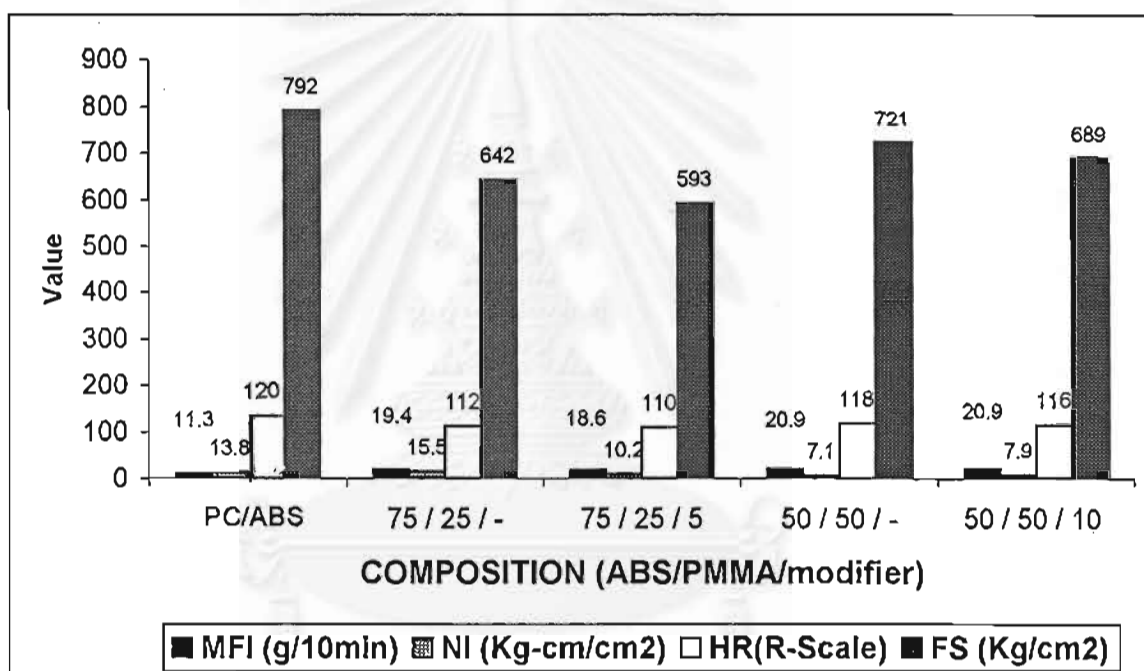


Figure 4.2 Effect of polymer modifier level on physical properties of ABS/PMMA blends.

4.5 Effect of rubber content.

The impact strength of ABS is obtained mainly from its rubber content. From Figure 4.3, there was a increase twice of NI when rubber content increased about 3%. This improvement is probably due to both the rubber particle size and the crosslink level in the rubber phase. As it would be expected when rubber content is increased, the FS and HR would be lost. The FS was decreased to about 8-10 % and HR was decreased to about 3-5 % when 3% of rubber content was increased.

From this result, the expected rubber content of ABS/PMMA blends at around 10-12% would give similar values of NI to the commercial resin PC/ABS alloys. However, the FS and HR could be improved by using bulk SAN resin.



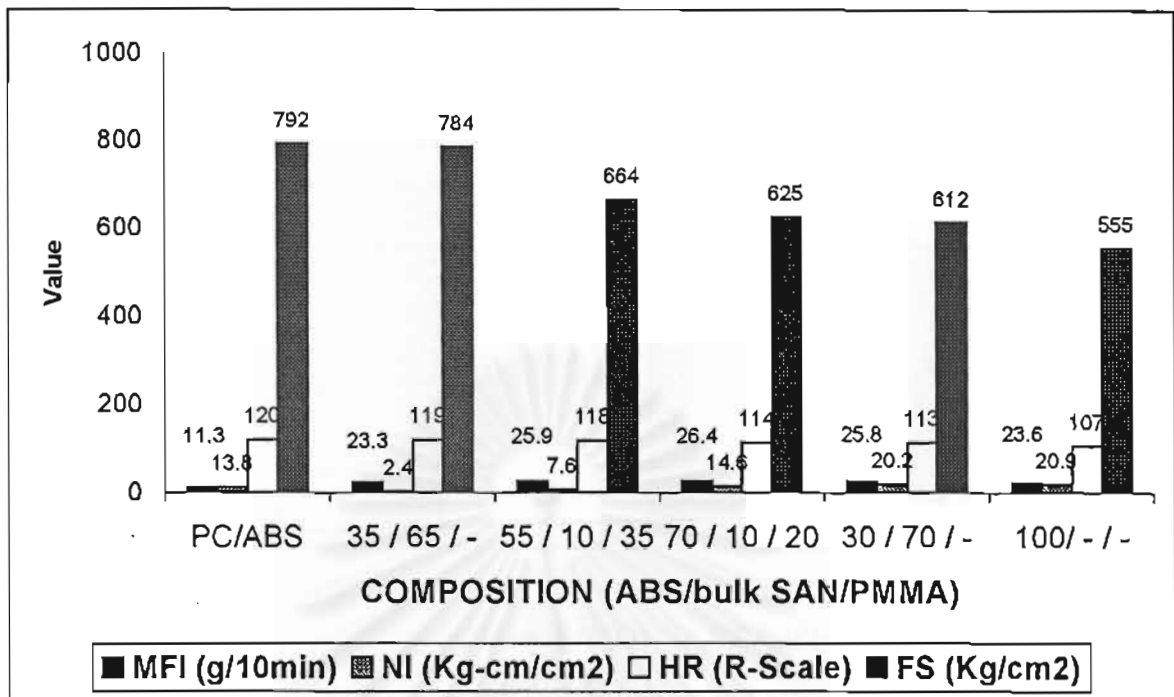


Figure 4.3 Effect of rubber content on mechanical properties of ABS/PMMA blend.

4.6 Effect of bulk SAN.

Typically, the property variation with composition is related to the SAN-PMMA miscibility. The results in Figure 4.4 exhibit the achievement of NI and MFI by using bulk SAN. There is only a little or no loss of hardness and flexural strength. It is because of the well mix of PMMA and SAN matrix. Consequently, the rubber particles will be easier to spread in the SAN-PMMA matrix. Therefore, the bulk SAN combination with PMMA can boost the impact strength with no loss of flexural strength and hardness properties.(19)

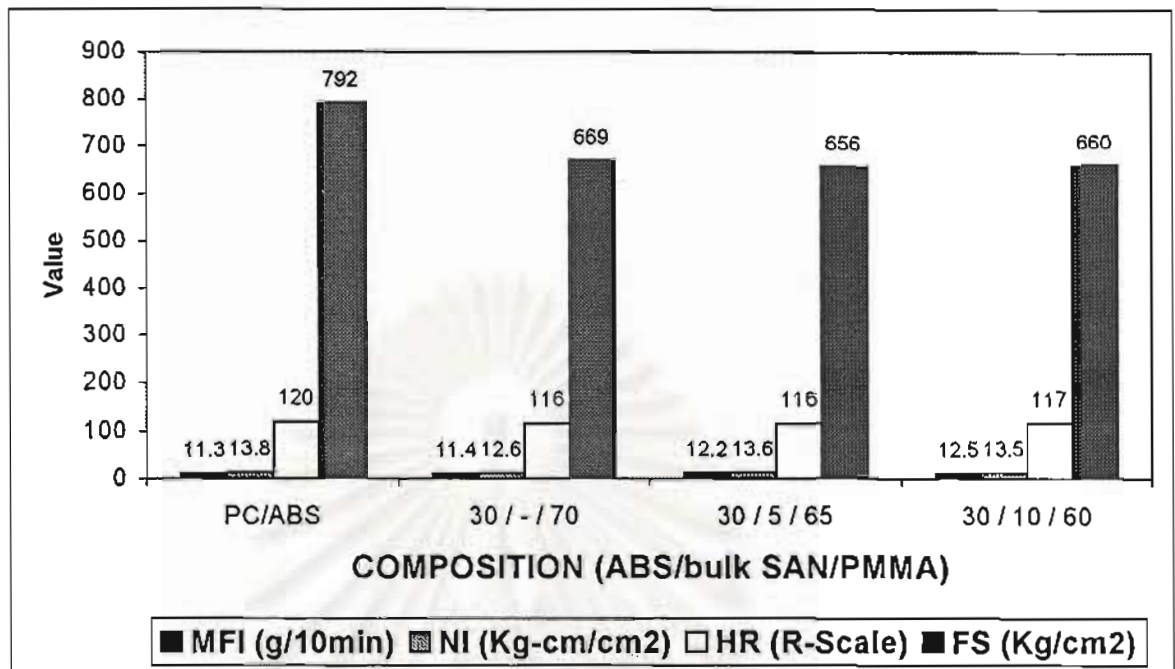


Figure 4.4 Effect of bulk SAN level on mechanical properties of ABS/PMMA blends.

4.7 Effect of acrylonitrile content.

Figure 4.5 shows the effect of ACN content on impact strength and melt flow index properties which were increased with higher ACN content. The flexural strength and hardness still remained the same or slightly decreased. These are because the miscibility window exists with ACN content at 9-29 % wt. The ACN content that fell inside the miscibility window gave a good mechanical properties.(20)

Finally, the best balance composition in this work is ABS/bulk SAN/PMMA at 25/20/55, and using additive of EBS/ca-st/Si-oil at 2.0/0.2/0.1 which gives comparatively NI, MFI, FS and HR to those of the PC/ABS alloy.

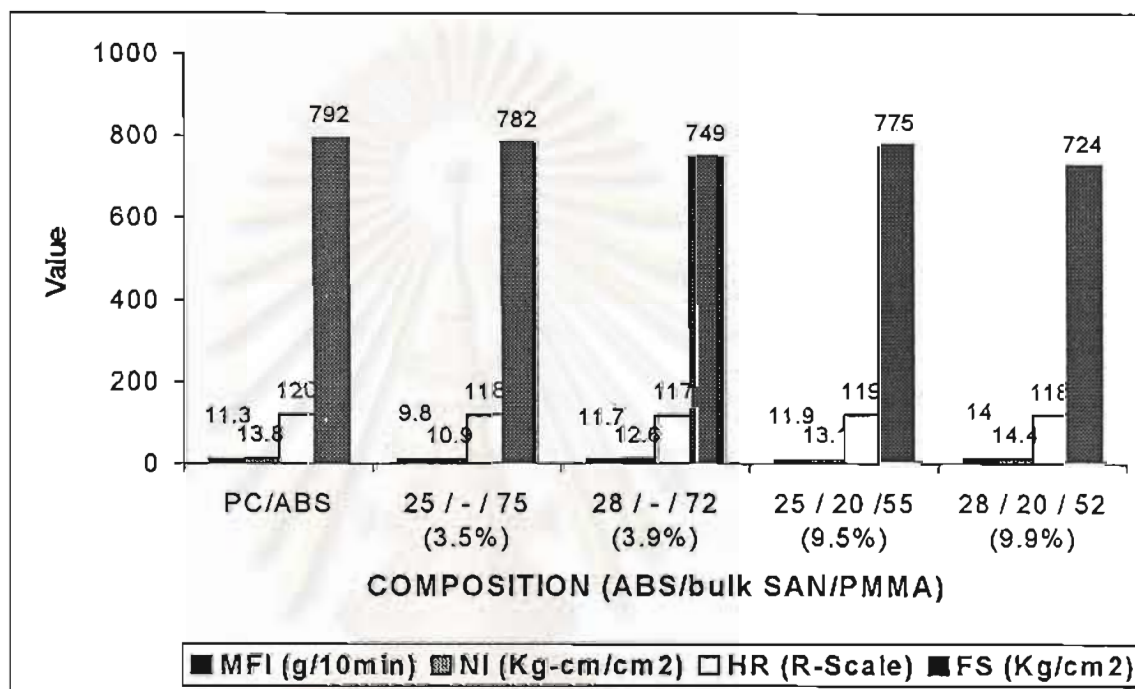


Figure 4.5 Effect of acrylonitrile content on mechanical properties of ABS/PMMA blends.

4.8 The state of dispersion of the blends.

Morphology of the blends was observed by SEM (Scanning Electron Microscopy). It is a well-established fact that the state of the blend influences its rheological behavior. The SEM micrographs of commercial PC/ABS alloys and the prepared ABS/PMMA blend are shown in Appendix

B (Figures B1 to B5). The micrographs reveal that in ABS resin rubber particles are embedded in the SAN matrix. In the immiscible blend, SAN and PMMA form separated domains. Most of rubber particles are retained in the SAN phase, but in the miscible blends rubber particle especially the large ones are migrated to PMMA phase continuously. The SEM micrograph of the prepared ABS/PMMA blends is similar to the micrograph of commercial PC/ABS alloys.

4.9 Economic consideration

From this research, the **best composition** is ABS/bulk SAN/PMMA/EBS/ca-st/Si-oil at 25/20/55/2.0/0.2/0.1 **respectively**, which its mechanical properties approach to those of **the PC/ABS alloy**. The cost of this composite is calculated base on the cost **of main** raw materials, ABS, PMMA, bulk SAN and additives. The cost of **ABS**, bulk SAN, PMMA, EBS, Ca-St and Si-oil in July 1999 are approximately 23,17,40,35,45 and 90 Bath/Kg, respectively. The price **of commercial PC/ABS alloy is** about 90 Bath/Kg. Therefore, the cost of prepared **composite** per kilogram is relatively lower than PC/ABS alloy. (See Table 4.2) Thus, the price of this composite will be attractive and competitive as an alternative to replace the PC/ABS alloy in the household applications. However, it is noteworthy that this calculation excluding the operating cost.

Table 4.2 Cost analysis of the prepared composite.

ABS/PMMA Composite	Material Cost in July 1999						Cost of composite (Baht/Kg)
	ABS	bulk SAN	PMMA	EBS	ca-st	Si-oil	
25/20/55/2.0 /0.2/0.1	5.75	3.40	22.00	0.70	0.09	0.09	32.03

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

From this research, it is concluded that the flexural strength and hardness properties of the modified ABS can be improved by PMMA blending in the appropriate composition. However, by this modification the impact property of the blends was dropped significantly. In this work, there are three methods for recover this loss. The increasing of the rubber content of ABS materials is one effective method because of the rubber particle size and cross-linking of rubber can improve the impact property. The other method is by using bulk SAN polymer to improve efficiency of dispersity between ABS phase and PMMA matrix. Moreover, the appropriate level of acrylonitrile content in blends system is also important. By about 9-29% acrylonitrile content is appropriate to make the blend miscible and homogeneous system. The combination of these factors should be useful to improve flexural strength and hardness with a little change in other properties.

In this work, the composition that performed a good balance of mechanical properties consists of 25% of ABS, 20 wt% of bulk SAN and 55 wt% of PMMA. This composite gave NI at 13.1 kg.cm/cm², MFI at 11.9 g/10 min, FS at 775 kg./cm² and HR at 119 R-scale.

Consequently, this composite is a potential material for replacing PC/ABS in household application due to a good balance of mechanical properties and total cost advantage.

5.2 Suggestion

According to this research, the main application is the household product. It does not require the high impact strength and high melt flow. Therefore, in order to expand to other applications, for example, electrical appliance, it is necessary to improve impact strength and melt flow ability. The following studies are suggested.

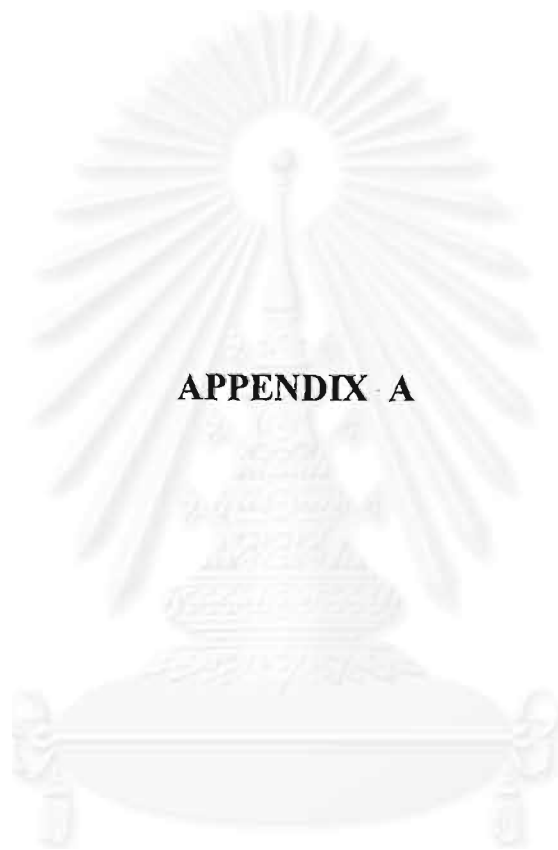
1. The effect of high rubber content of ABS on mechanical properties should be investigated.
2. The effect of rubber particle size on mechanical properties should be investigated.
3. The effect of molecular weight of PMMA on mechanical properties.
4. The effect of processing condition on the mechanical properties should be investigated.
5. The twin screw extruder may be investigated to improve the mixing efficiency.
6. The new types of polymer modifier should be considered for using in ABS/PMMA blended system.

Furthermore, the important items of the polymer blends to be considered are the cost performance, recyclability and environmental impact.

REFERENCES

1. Utracki, L.A. Polymer Alloys and Blends. Munich, 1989, pp.3-27.
2. Freid, J.R. Polymer Science and Technology. Cincinnati : Prentice-Hall International, pp. 137-143.
3. Nelb, R.G. Manufacture of Plastics. Connecticut, 1964, vol. 1 pp. 437-454.
4. Carrock, F.E , Paramus and Doak, R.W. Process for preparation of Acrylonitrile-Butadiene-Styrene graft Copolymers. U.S Patent 3,515,692 (June 2, 1970).
5. Mechanism on Emulsion Polymerization of ABS. JAPAN: Sumitomo Naughtuck: Ehime Research Division, 1989. pp 1-5.
6. Odian, G. Principals of Polymerization . 3rd ed.NewYork : John Wiley & Sons, 1991. pp 335-341.
7. Wiseman, P. Petrochemicals. West Sussex,1986. pp 119,63-68.
8. Acrylic Polymers. Philadelphia : Rohm and Haas company, 1969. pp 1-15.
9. Methacrylic Compounds . 2nd ed., vol 13. Philadelphia : Rohm and Haas company, 1970. pp 331-363.
- 10.Moriyama, K. and Takahashi, S. Process for production of Styrene / Acrylonitrile Copolymer. U.S Patent 3,738,972(Jun 12,1973).
- 11.Langenberg, H. Design of Heating Mixers for Compounding of Plastics. Munich, 1986. pp 7-14.
- 12.Kim, B.K , Shin, G.S , Kim, Y.J and Lee, I.T Miscible and Immiscible Blend of ABS with PMMA I. Morphology and Rheology. Journal of Applied Polymer Science. 47 (1993) : 295-304.

13. Kim, B.K , Shin, G.S ,Kim, Y.J and Park, T.S Miscible and Immiscible Blends of ABS with PMMA II. Mechanical and surface properties. Journal of Applied Polymer Science 47(1993) : 1581-1587.
14. Kim, B.K ,Choi, C.H ,and Xie, X.M ABS Ternary Blends : Morphology, Surface Gloss And Mechanical Properties. Journal of Macromolecul Science-Physics B35(1996) :829-841.
15. Kim, B.K , Yoon, L.K and Xie, X.M Effects of Annealing in ABS Ternary Blends. Journal of Applied Polymer Science. 66(1997):1531-1542.
16. Parsons, C.F Polymer blends of Polycarbonate Styrene terpolymer and ABS resin U.S Patent 4,886,855(Dec 12,1989).
17. Lombardo, B.S , Keskkula, H. and Paul, D.R Influence of ABS Type on Morphology and Mechanical Properties of PC/ABS Blends. Journal of Applied Polymer Science. 54 (1994) : 1697-1720.
18. Mijovic, J. , Ho, T. and Kwei, T.K Physical Aging in Poly(Methyl Methacrylate) / Poly(Styrene-co-Acrylonitrile)Blend. Part II : Enthalpy Relaxation. Polymer Engineering and Science. 29(1989):1604-1610.
19. Ho, T. and Mijovic, J. Physical Aging in Poly(Methyl Methacrylate) / Poly(Styrene-co-Acrylonitrile)Blend. 3. Simulation of Enthalpy Relaxation. Using the Moynihan Model. Macromolecules 23 (1990) : 1411-1419.
20. Mijovic, J., Devine, S.T and Ho, T. Physical Aging in Poly(Methyl Methacrylate) / Poly(Styrene-co-Acrylonitrile)Blend. I. Stress Relaxation. Journal of Polymer Science 39(1990) :1133-1151.



APPENDIX A

Table A1 Properties of ABS monomers.

Typical Data	Unit	Acrylonitrile	Butadiene	Styrene
Autoignition Temperature	°C	-	414	490
Boiling point	°C	77	-44	145.2
Flash point	°C	0	-76	31.1
Density	g/cm ³	0.8004 (25 °C)	0.6211 (20 °C)	0.9045 (25 °C)
Explosive limit	%in air	3-17	2-11	1.1-6.1
TLV	ppm	2	10	50

Table A2 Properties of MMA monomer.

Typical Data	Unit	Methyl methacrylate
Autoignition Temperature	°C	421
Boiling point	°C	101
Flash point	°C	10
Density	g/cm ³	0.940 (25 °C)
Explosive limits	% in air	2.1-12.5
TLV	ppm	100

Table A3 Typical data of polymethyl methacrylate.

Typical Data	Unit	Value	Test Method
Property MFI 3.8 kg/23 °C	g/10 min	5.8	ASTM D1238
Heat distortion temperature	°C	89.8	ASTM D648
Tensile strength	kg/cm ²	713	ASTM D638
Elongation	%	5.6	ASTM D638
Izod impact strength	kg- cm/cm ²	2.5	ASTM D256
Rockwell hardness	M-scale	98	ASTM D785
Flexural strength	kg/cm ²	1213	ASTM D638
Flexural modules	kg/cm ²	3.36 x 10 ⁴	ASTM D638

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Table A4 Product specification of ethylene-bis-stearamide.

Item	Unit	Specification	Test Method
Color (Gardner)	-	5 maximum	Gardner method
Acid value	mg-KOH/g	10 maximum	Titration
Total amine value	mg-KOH/g	2.5 maximum	Titration
Melting point	°C	140 minimum	JIS K-0064
Volatile matter	%	0.5 maximum	Dried at 105 °C, 1H

Table A5 Product specification of magnesium stearate.

Item	Unit	Specification	Test Method
Metal content (as Mg)	%	3.9 – 5.1	Titration
Heavy metals	ppm	20 maximum	-
Arsenic	ppm	2 maximum	-
Heat loss	%	4.0 minimum	1g, 90 °C, 4H vacuum drying

Table A6 Product specification of calcium stearate.

Item	Unit	Specification	Test Method
Metal contents(as mg)	%	6.5 – 7.0	Titration
Water content	%	3.0 maximum	JIS K-0067
Melting point (clar)	°C	150 – 165	JIS K-0064
Particle size - 325 megh screen under size	%	99 minimum	JIS K-0069
Free fatty acid	%	0.5 maximum	Titration

Table A7 Product specification of silicone oil.

Item	Unit	Specification	Test Method
Odor	-	Odorless	-
Viscosity (25 °C)	cst	95 – 105	JIS K-2283
Heat loss	%	2 maximum	JIS K-0067

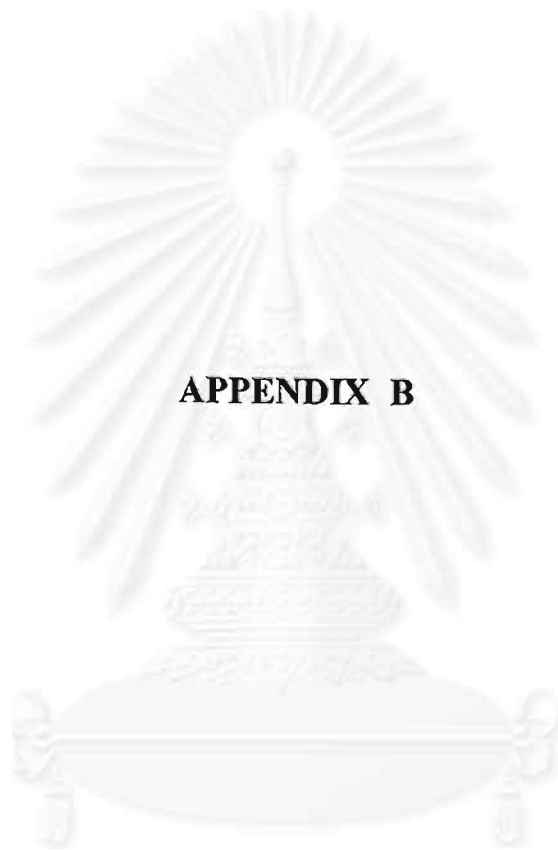
Table A8 Typical data of polymer modifier.

Typical Data	Unit	Value
Melt flow rate	g/10 min	0.6
Tensile strength	kg/cm ²	150
Elongation at break	%	100
Tensile modulus	kg/cm ²	900
Notched izod impact strength	Kg-cm/cm ²	No break
Vicat softening temperature	°C	80

Table A9 Typical data of Bulk SAN.

Typical Data	Unit	Value	Test Method
Melt flow index	g/10 min	2.0	ASTM D1238
ACN content	%	31.5	-
Yellowness index	-	4.1	-
Notched izod impact strength	kg-cm/cm ²	2.3	ASTM D256
Hardness	R-scale	95	ASTM D785
Tensile strength	Kg/cm ²	756	ASTM D638
Elongation	%	3.4	ASTM D638
Heat distortion temperature	°C	85.2	ASTM D648
Flexural strength	Kg/cm ²	1269	ASTM D790
Flexural modulus	Kg/cm ²	3.76 x 10 ⁴	ASTM D790

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APPENDIX B

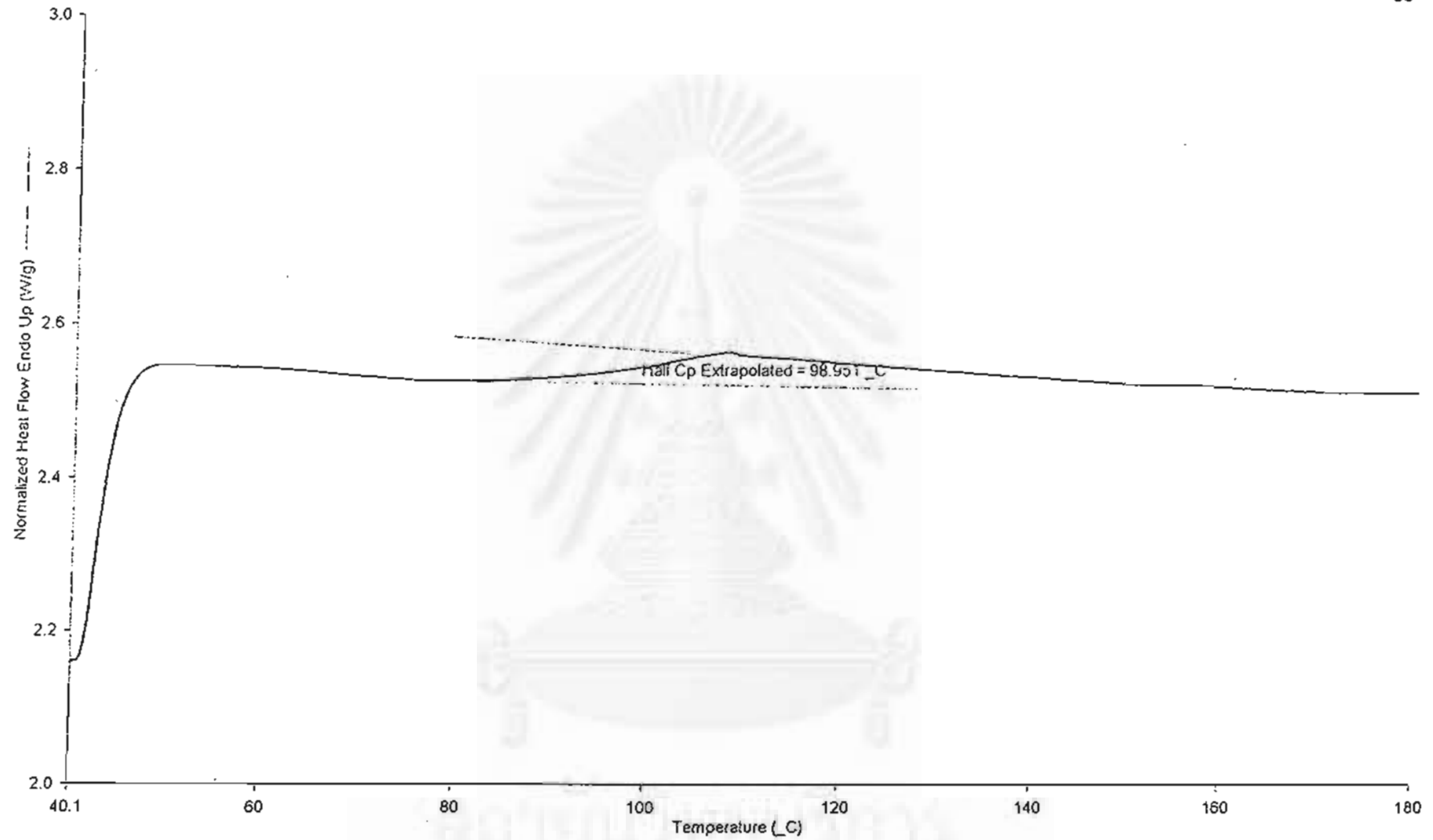


Figure B1. DSC curve of commercial PC/ABS Alloy

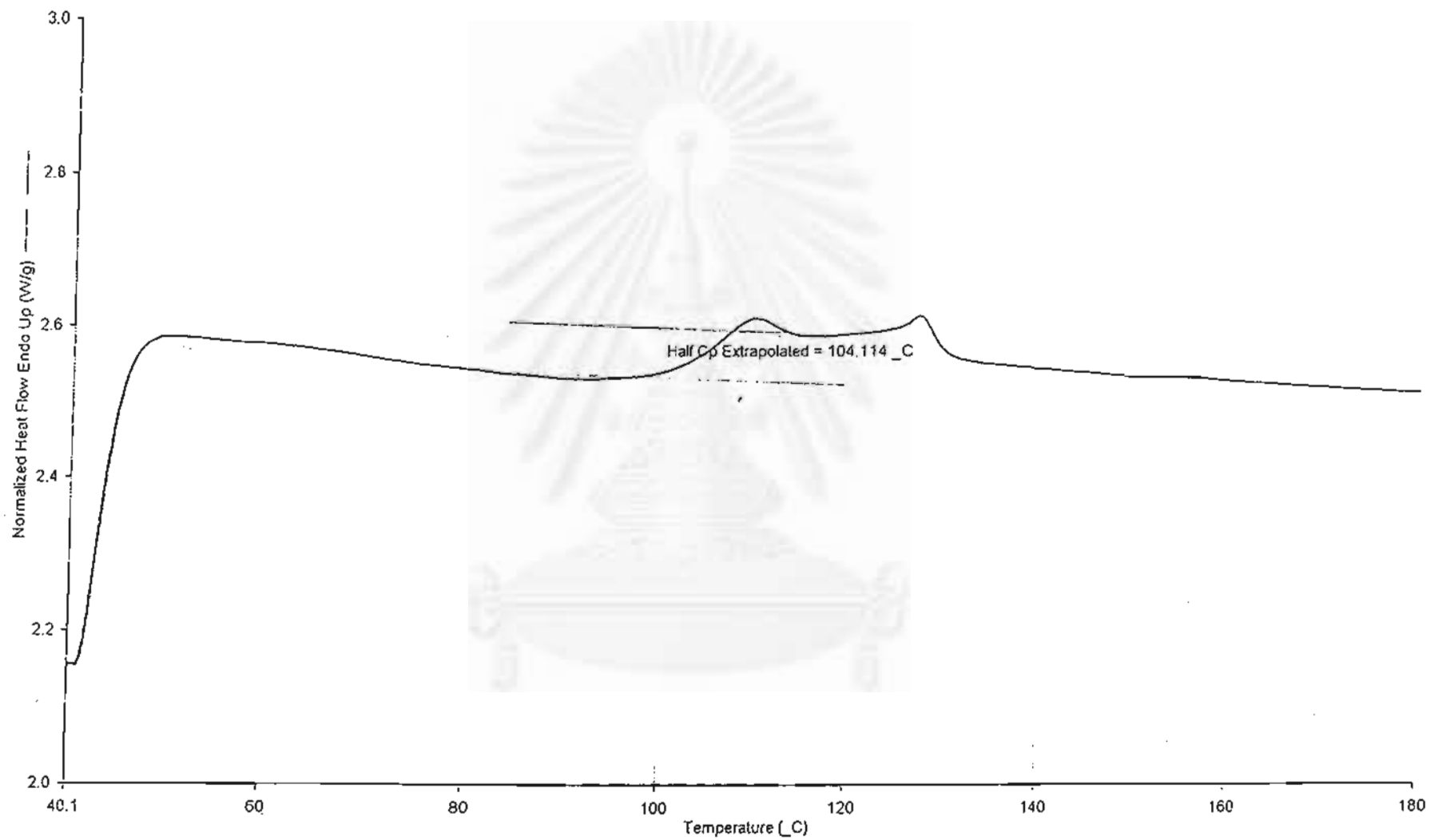
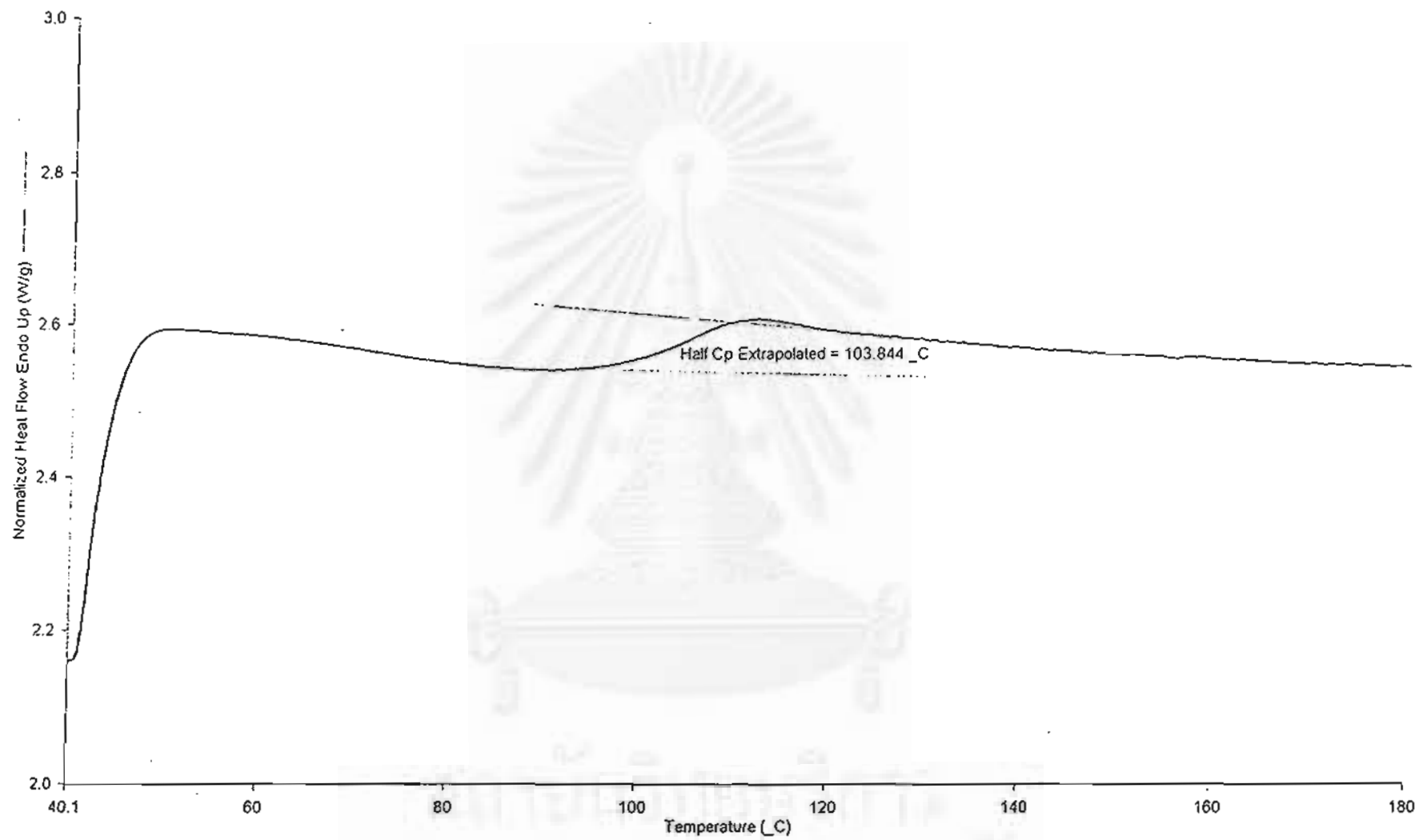


Figure B2 DSC curve of ABS



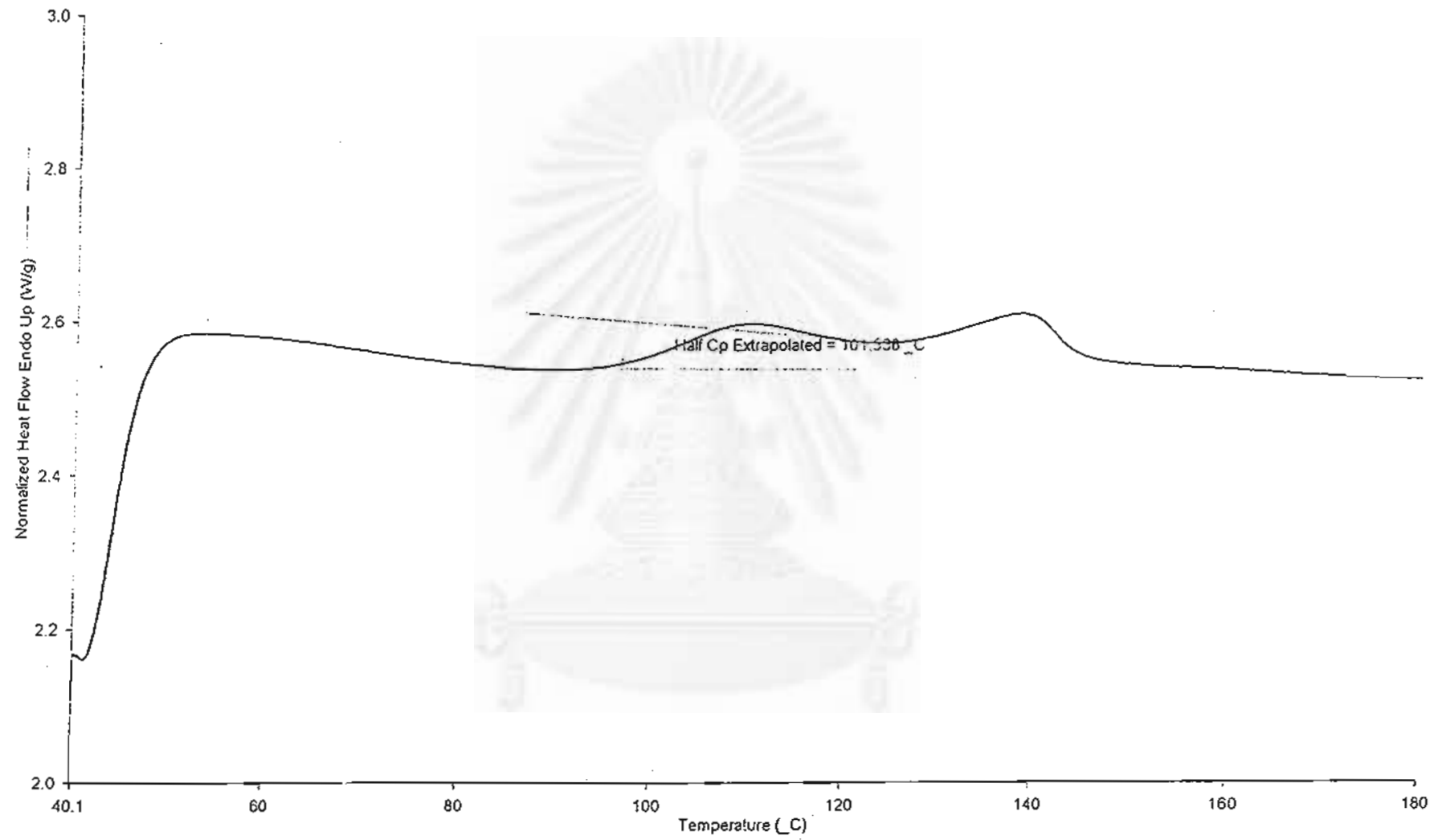


Figure B4. DSC curve of ABS/PMMA blend.

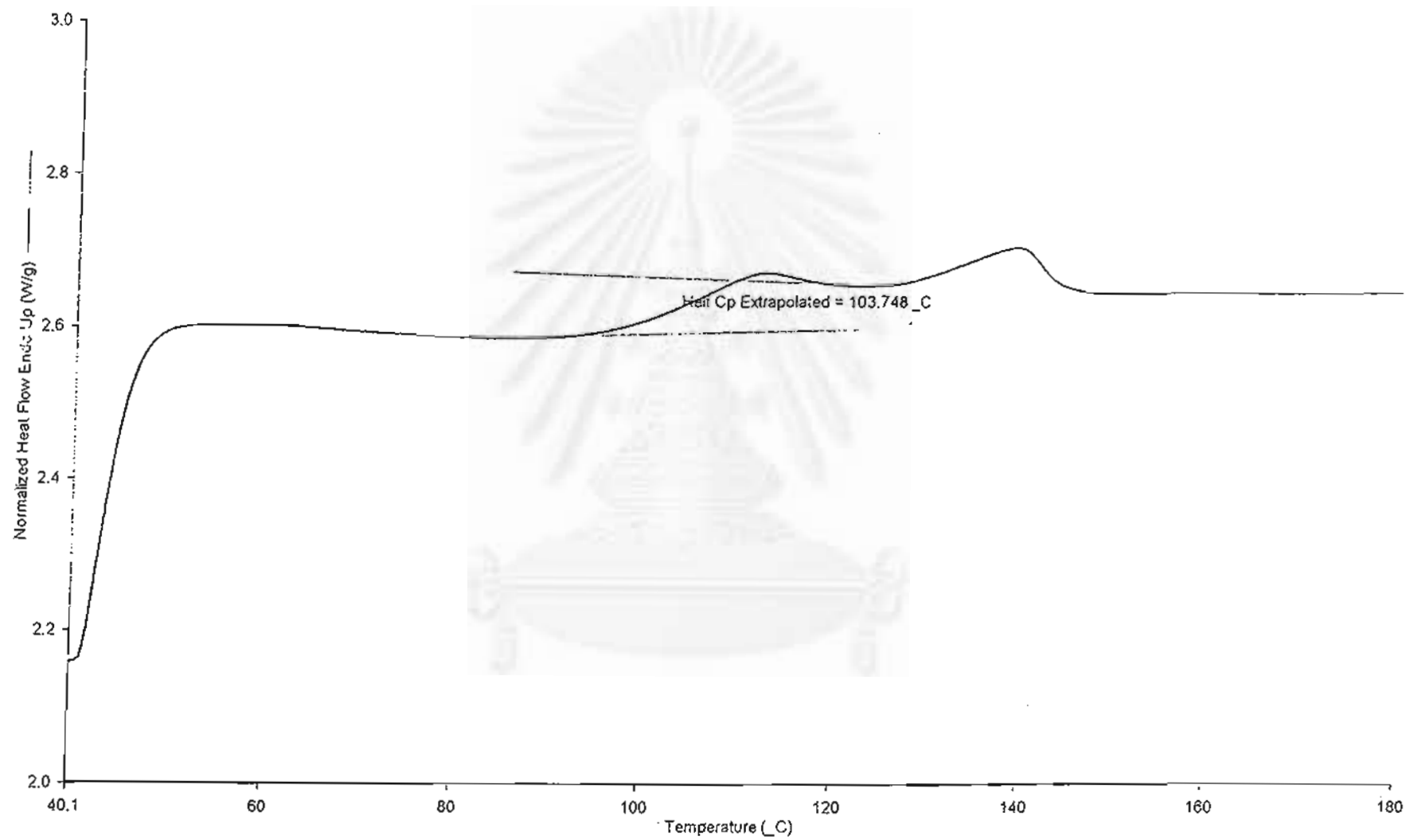
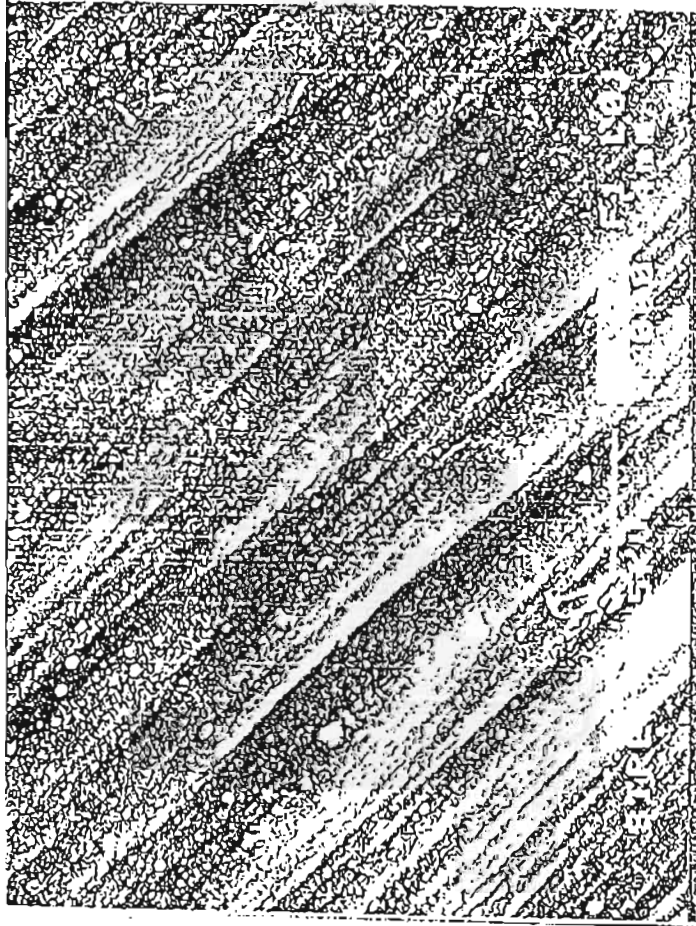
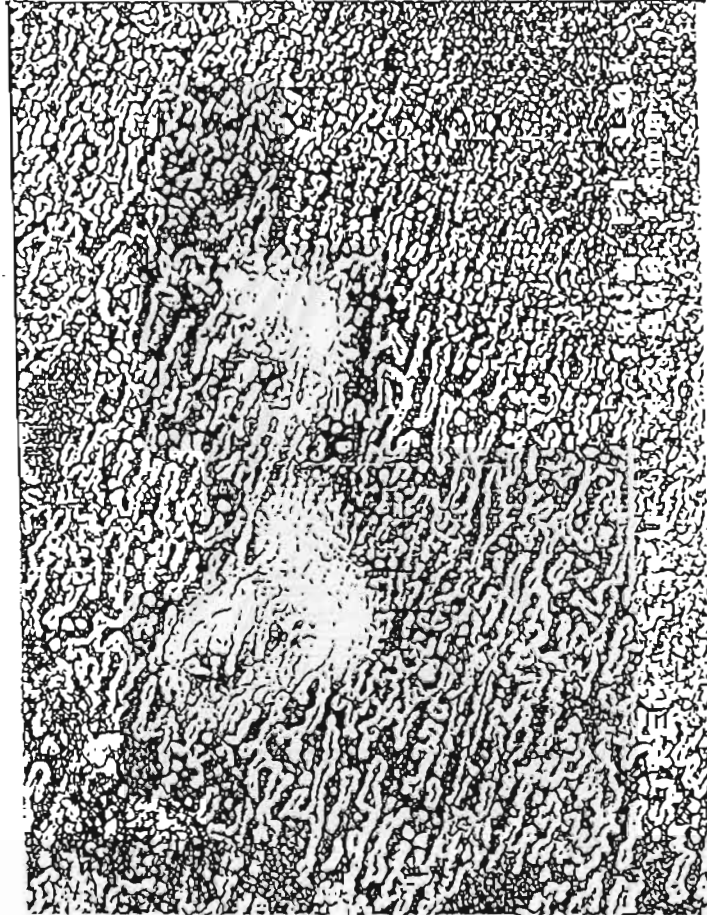


Figure B5. DSC curve of ABS/BulkSAN/PMMA blend.



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Figure R8 SEM micrograph of wires DNAAA



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Figure R10 STM image of a surface.

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Table B1 Mechanical analysis data sheet of ABS/PMMA composites.

Sample No	Analysis no	MFI	NI	HR	FS
1	1	18.7	1.2	118	789
	2	18.4	0.9	117	792
	3	18.1	1.1	119	794
	Average	18.4	1.1	118	792
2	1	23.5	2.4	119	782
	2	23.2	2.5	117	775
	3	23.4	2.3	118	789
	Average	23.4	2.4	118	782
3	1	13.2	3.4	118	774
	2	13.2	3.2	119	775
	3	13.5	3.5	119	778
	Average	13.3	3.4	119	776
4	1	15.3	4.3	119	775
	2	15.5	4.4	121	771
	3	15.3	4.6	120	771
	Average	15.4	4.4	120	772
5	1	9.8	5.4	119	759
	2	9.4	5.2	120	762
	3	9.9	5.3	119	764
	Average	9.7	5.3	119	762
6	1	21.3	23.4	106	557
	2	20.8	23.6	105	557
	3	20.5	23.8	107	556
	Average	20.9	23.6	106	556
7	1	19.2	15.3	113	639
	2	19.5	15.6	111	643
	3	19.3	15.7	112	645
	Average	19.3	15.5	112	642

Table B1 Mechanical analysis data sheet of ABS/PMMA composites (continued).

Sample No	Analysis no	MFI	NI	HR	FS
8	1	20.8	6.8	117	723
	2	20.6	7.2	119	722
	3	20.9	7.4	118	721
	Average	20.8	7.1	118	722
9	1	13.2	3.4	121	784
	2	13.5	3.6	120	779
	3	13.2	3.5	118	786
	Average	13.3	3.5	120	783
10	1	18.7	10.1	111	594
	2	18.6	10.4	110	591
	3	18.5	10.2	110	593
	Average	18.6	10.2	110	593
11	1	20.8	7.8	115	689
	2	20.9	8.0	117	687
	3	20.7	7.9	115	690
	Average	20.8	7.9	116	689
12	1	21.9	14.8	115	625
	2	21.1	14.3	113	628
	3	22.0	14.7	113	624
	Average	21.7	14.6	114	626
13	1	23.4	11.4	114	639
	2	23.1	11.7	116	632
	3	23.8	11.5	115	636
	Average	23.4	11.5	115	636
14	1	25.1	8.9	117	652
	2	25.8	9.0	118	649
	3	25.6	9.4	118	650
	Average	25.5	9.1	118	650
15	1	25.9	7.6	117	664
	2	25.6	7.5	118	663
	3	26.2	7.9	118	667
	Average	25.9	7.7	118	665

Table B1 Mechanical analysis data sheet of ABS/PMMA composites (continued).

Sample No	Analysis no	MFI	NI	HR	FS
16	1	25.7	20.8	113	612
	2	26.2	20.1	114	616
	3	25.8	20.5	113	611
	Average	25.9	20.5	113	613
17	1	11.2	12.7	115	668
	2	11.5	11.9	117	666
	3	10.9	12.7	116	670
	Average	11.2	12.4	116	668
18	1	12.7	13.7	116	657
	2	11.8	13.2	115	652
	3	12.0	13.9	116	659
	Average	12.2	13.6	116	656
19	1	12.4	13.8	116	661
	2	12.6	13.5	117	663
	3	12.1	13.4	118	659
	Average	12.4	13.6	118	659
20	1	11.2	10.4	116	687
	2	11.8	10.7	117	689
	3	11.5	11.5	117	685
	Average	11.5	10.9	117	687
21	1	12.7	9.8	117	706
	2	13.1	9.7	118	707
	3	12.6	9.6	118	709
	Average	12.8	9.7	118	707
22	1	9.7	10.7	118	783
	2	9.6	11.0	119	785
	3	10.0	10.8	118	782
	Average	9.8	10.8	118	783

Table B1 Mechanical analysis data sheet of ABS/PMMA composites (continued).

Sample No	Analysis no	MFI	NI	HR	FS
23	1	11.8	13.4	119	776
	2	12.0	12.9	120	771
	3	12.1	13.2	120	779
	Average	12.0	13.2	120	775
24	1	11.8	12.4	118	745
	2	11.4	12.9	117	748
	3	12.0	12.4	117	751
	Average	11.7	12.6	117	748
25	1	14.1	14.3	117	726
	2	13.9	14.2	116	729
	3	13.8	14.6	118	721
	Average	13.9	14.4	117	725

Remark :

MFI = Melt flow index (g/10 min)

NI = Impact strength (Kg-cm/cm²)

HR = Hardness (R-scale)

FS = Flexural strength (Kg/cm²)

Table B2 Mechanical analysis data sheet of ABS/PMMA composites (repeated).

Sample No	Analysis no	MFI	NI	HR	FS
1-1	1-1	18.7	1.1	118	789
	1-2	18.8	1.2	119	793
	1-3	18.9	1.1	120	791
	Average	18.8	1.1	119	791
2-1	2-1	23.0	2.2	120	785
	2-1	23.4	2.3	118	787
	2-3	23.3	2.4	119	783
	Average	23.2	2.3	119	785
3-1	3-1	13.3	3.3	118	777
	3-2	13.2	3.1	119	776
	3-3	13.4	3.6	118	775
	Average	13.3	3.3	118	776
4-1	4-1	15.4	4.5	119	776
	4-2	15.3	4.6	118	773
	4-3	15.6	4.3	120	769
	Average	15.4	4.5	119	773
5-1	5-1	9.5	5.0	120	762
	5-2	9.3	5.2	119	761
	5-3	9.7	5.1	120	758
	Average	9.5	5.1	120	760
6-1	6-1	21.0	23.1	107	553
	6-2	21.3	23.8	106	558
	6-3	20.5	23.6	108	551
	Average	20.9	23.5	107	554
7-1	7-1	19.7	15.7	111	638
	7-2	18.9	15.3	111	642
	7-3	19.8	15.2	112	644
	Average	19.4	15.4	111	641

Table B2 Mechanical analysis data sheet of ABS/PMMA composites (repeated) (continued).

Sample No	Analysis no	MFI	NI	HR	FS
8-1	8-1	21.1	7.1	118	721
	8-2	20.9	7.2	117	718
	8-3	21.1	7.0	119	721
	Average	21.0	7.1	118	720
9-1	9-1	13.0	3.5	119	785
	9-2	13.2	3.3	120	784
	9-3	13.1	3.5	120	789
	Average	13.1	3.4	120	786
10-1	10-1	18.6	10.2	110	594
	10-2	18.3	10.1	111	594
	10-3	18.9	10.4	110	593
	Average	18.6	10.2	110	594
11-1	11-1	20.9	7.8	116	689
	11-2	21.3	7.9	117	686
	11-3	20.8	7.7	115	690
12-1	Average	21.0	7.8	116	688
	12-1	20.9	14.1	115	628
	12-2	21.1	14.9	116	625
	12-3	21.4	15.0	114	629
	Average	21.1	14.7	115	627
13-1	13-1	23.4	11.9	116	637
	13-2	23.9	12.0	115	631
	13-3	24.0	11.5	115	639
	Average	237.0	11.8	115	636
14-1	14-1	26.0	9.4	117	652
	14-2	25.1	9.2	119	648
	14-3	25.4	8.8	118	651
	Average	25.5	9.1	118	650
15-1	15-1	25.6	7.4	117	667
	15-2	26.2	7.3	117	664
	15-3	25.9	7.7	118	667
	Average	25.9	7.5	117	665

Table B2 Mechanical analysis data sheet of ABS/PMMA composites (repeated) (continued).

Sample No	Analysis no	MFI	NI	HR	FS
16-1	16-1	25.4	20.1	112	610
	16-2	25.7	19.8	113	613
	16-3	26.0	19.9	114	614
	Average	25.7	19.9	113	612
17-1	17-1	11.6	12.9	116	671
	17-2	11.2	12.7	117	669
	17-3	12.0	12.6	117	670
	Average	11.6	12.7	117	670
18-1	18-1	12.6	13.2	117	652
	18-2	11.7	13.5	115	656
	18-3	12.4	13.9	116	659
	Average	12.2	13.5	116	656
19-1	19-1	12.4	13.9	118	658
	19-2	12.7	13.0	117	662
	19-3	12.8	13.8	117	659
	Average	12.6	13.6	117	660
20-1	20-1	11.4	11.2	118	685
	20-2	12.2	10.8	117	680
	20-3	11.5	10.5	118	684
	Average	11.7	10.8	118	683
21-1	21-1	12.8	9.6	119	710
	21-2	13.0	9.7	118	706
	21-3	12.6	9.5	118	711
	Average	12.8	9.6	118	709
22-1	22-1	9.8	10.7	117	781
	22-2	10.0	11.1	119	779
	22-3	9.7	10.9	118	784
	Average	9.8	10.9	118	784

Table B2 Mechanical analysis data sheet of ABS/PMMA composites (repeated) (continued).

Sample No	Analysis no	MFI	NI	HR	FS
23-1	23-1	11.8	13.1	119	774
	23-2	11.6	12.9	118	773
	23-3	12.1	13.3	120	778
	Average	11.8	13.1	119	775
24-1	24-1	11.6	12.3	118	752
	24-2	12.1	12.9	116	746
	24-3	11.3	12.4	117	749
	Average	11.6	12.5	117	749
25-1	25-1	14.2	14.4	118	721
	25-2	14.1	14.6	118	726
	25-3	13.9	14.3	118	723
	Average	14.0	14.4	118	723

Remark :

MFI = Melt flow index (g/10 min)

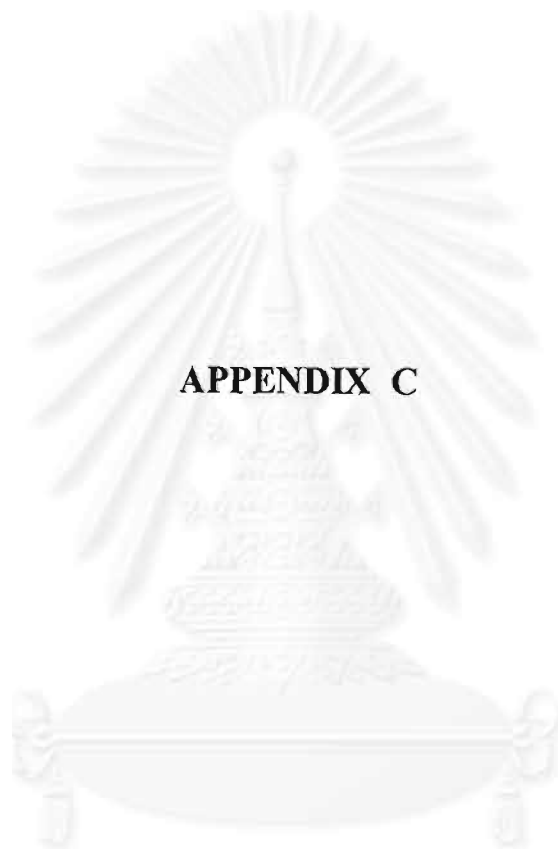
NI = Impact strength (Kg-Cm/Cm²)

HR = Hardness (R-scale)

FS = Flexural strength (Kg/Cm²)

Table B3 Average mechanical analysis of ABS/PMMA composites.

Sample No	ABS/Bulk SAN1/Bulk SAN2/PMMA	MFI	NI	HR	FS
PC/ABS	/EBS/Ca-St/Si-oil/Mg-st/Modifier				
PC/ABS		11.3	13.8	120	792
1	35/65/ - / - /2.0/0.2/0.1/ - / -	18.6	1.1	119	791
2	35/ - /65/ - /2.0/0.2/0.1/ - / -	23.3	2.4	119	784
3	35/32.5/ - /32.5/2.0/0.2/0.1/ - / -	13.3	3.4	119	776
4	35/ - /32.5/32.5/2.0/0.2/0.1/ - / -	15.4	4.5	120	773
5	35/ - / - /65/2.0/0.2/0.1/ - / -	9.6	5.2	120	761
6	100/ - / - / - /1.8/ - / - /1.0/ -	20.9	23.6	107	555
7	75/ - / - /25/1.8/ - / - /1.0	19.4	15.5	112	642
8	50/ - / - /50/1.8/ - / - /1.0/ -	20.9	7.1	118	721
9	25/ - / - /75/1.8/ - / - /1.0/ -	13.2	3.5	120	785
10	75/ - / - /25/1.8/ - / - /1.0/5	18.6	10.2	110	593
11	50/ - / - /50/1.8/ - / - /1.0/10	20.9	7.9	116	689
12	70/ - /10/20/1.8/ - / - /1.0/ -	21.4	14.6	114	625
13	65/ - /10/25/1.8/ - / - /1.0/ -	23.6	11.7	115	636
14	60/ - /10/30/1.8/ - / - /1.0/ -	25.5	9.1	117	650
15	55/ - /10/35/1.8/ - / - /1.0/ -	25.9	7.6	118	664
16	30/ - /70/ - /1.5/ - /0.05/ - / -	25.8	20.2	113	612
17	30/ - / - /70/1.5/ - /0.05/ - / -	11.4	12.6	116	669
18	30/ - /5/65/1.5/ - /0.05/ - / -	12.2	13.6	116	656
19	30/ - /10/60/1.5/ - /0.05/ - / -	12.5	13.5	117	660
20	25/ - / - /75/1.5/ - /0.05/ - / -	11.6	10.6	117	685
21	25/ - /10/65/1.5/ - /0.05/ - / -	12.8	9.7	118	708
22	25/ - / - /75/2.0/0.2/0.1/ - / -	9.8	10.9	118	782
*23	25/ - /20/55/2.0/0.2/0.1/ - / -	11.9	13.1	119	775
24	28/ - / - /72/2.0/0.2/0.1/ - / -	11.7	12.6	117	749
25	28/ - /20/52/2.0/0.2/0.1/ - / -	14.0	14.4	118	724



APPENDIX C

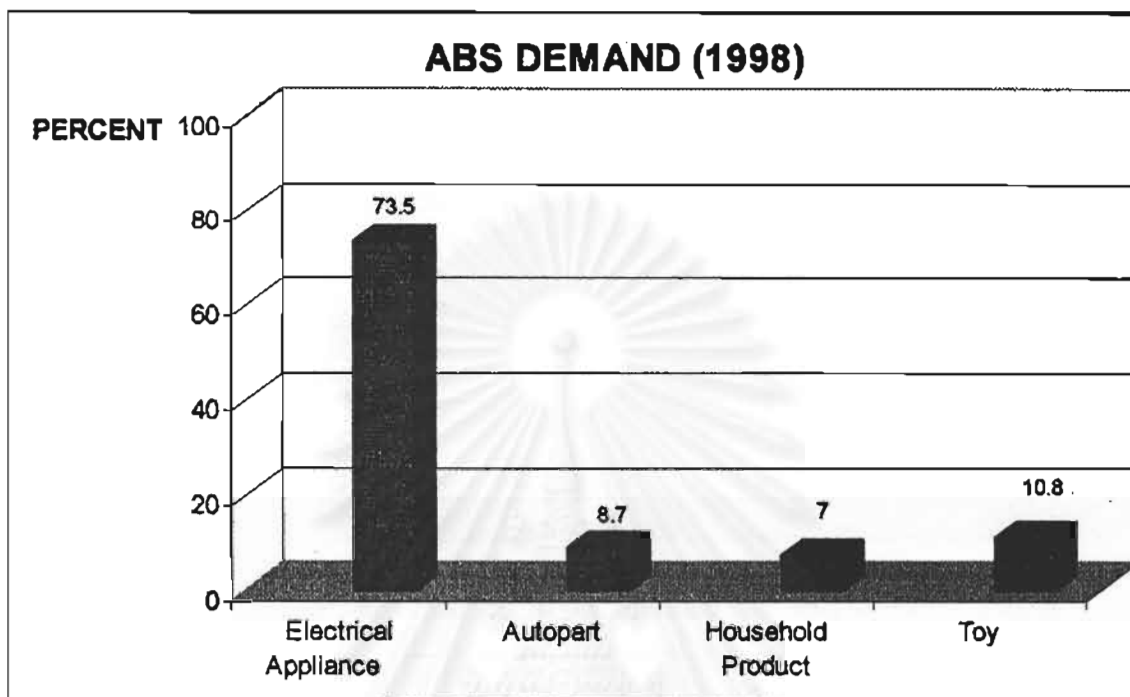


Figure C1 ABS demand 1998.

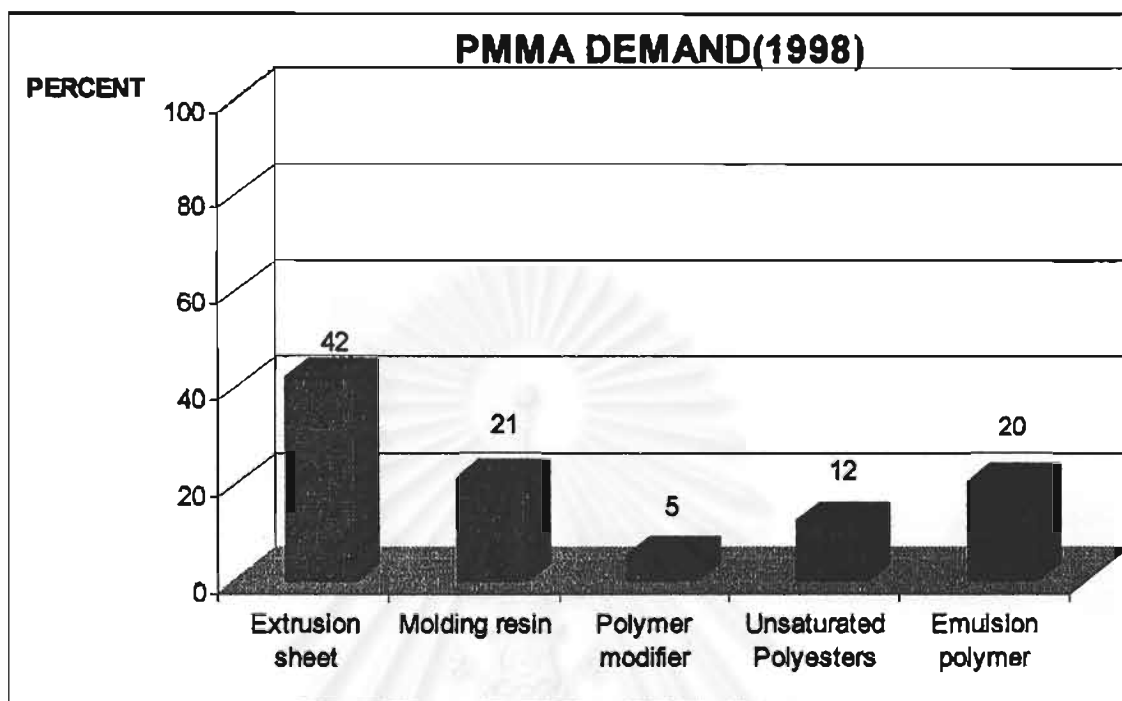


Figure C2 PMMA demand 1998.

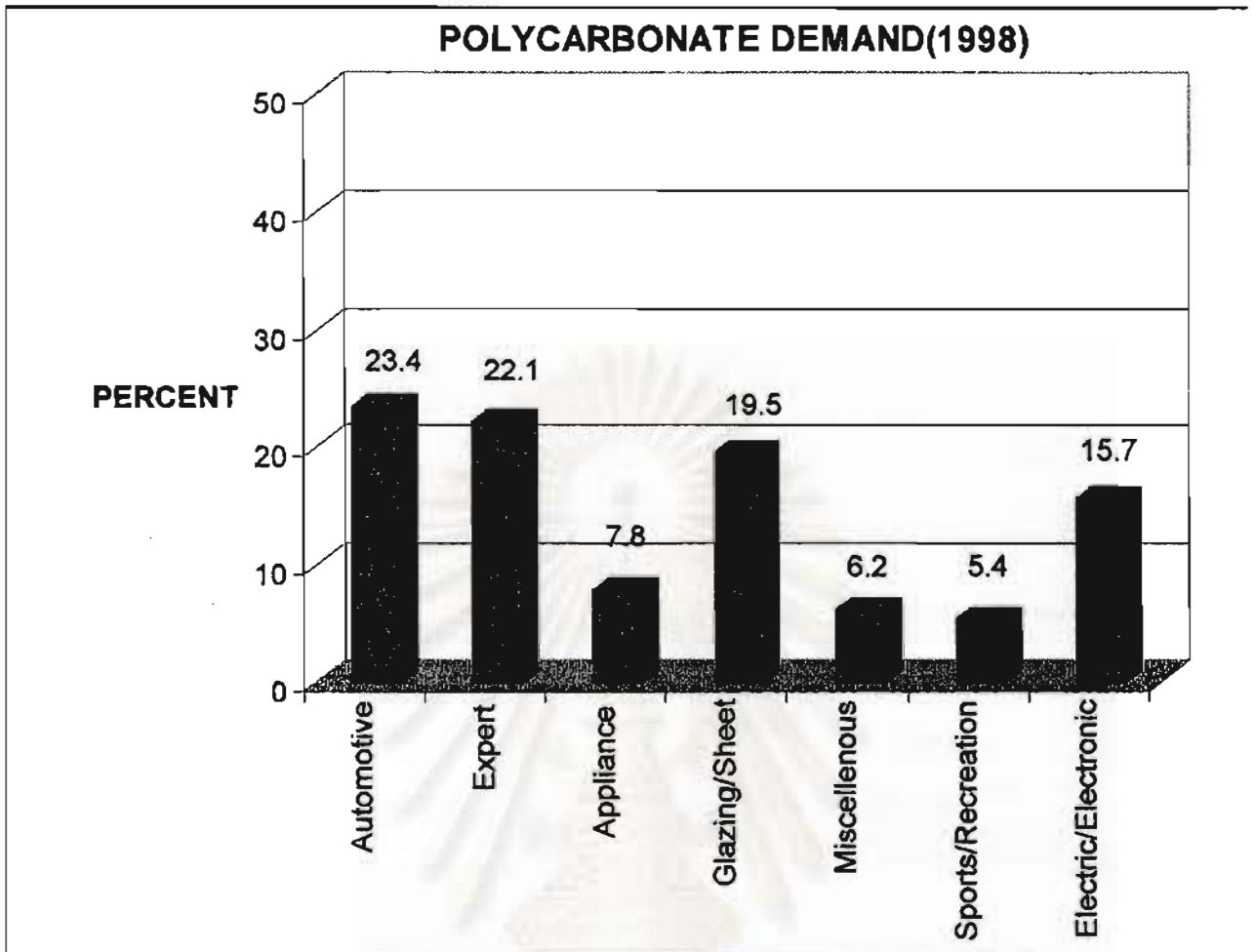


Figure C3 Polycarbonate demand.

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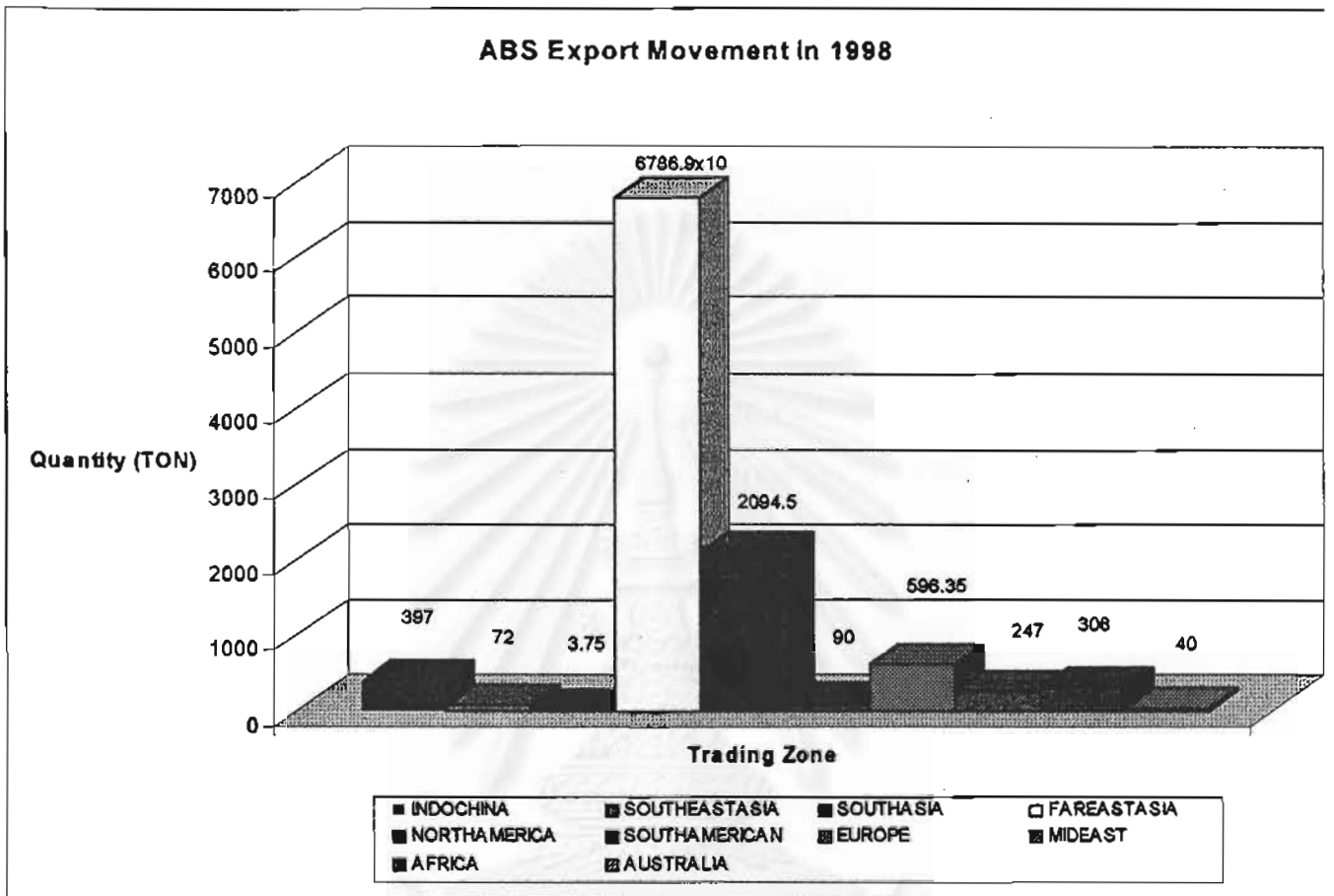


Figure C4 ABS Export movement in 1998.

VITAE

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