การพัฒนาเม็ดพีวีซีสีเข้มข้นสำหรับขวดพีวีซีและสายไฟพีวีซี

นายสุนทร มากสุข

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2542

ISBN 974-334-440-3

DEVELOPMENT OF PVC COLOR MASTERBATCH
FOR BOTH OF PVC BOTTLE AND PVC CABLE COMPOUND

MR. SOONTHORN MARKSOOK

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
Faculty of Science
Chulalongkorn University
Academic Year 1999
ISBN 974-334-440-3

Thesis Title	Development of PVC Color Masterbatch for Both of PVC Bottle Compound and PVC Cable Compound
By	Mr. Soonthorn Marksook
Department	Petrochemistry and Polymer Science
Thesis Advisor	Associate Professor Supawan Tantayanon

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the requirements for the Master's Degree

.... Dean of Faculty of Science
(Associate Professor Wanchai Phothiphichitr, Ph.D.)

Thesis Committee :

.... Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

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

.... Member
(Associate Professor Prapaipit Chamsuksai Ternai, Ph.D.)

.... Member
(Professor Bela Ternai, Ph.D.)

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

.... Member
(Wilaiporn Chetanachan, Ph.D.)

สุนทร มากสุข : การพัฒนาเม็ดพีวีซีสีเข้มข้นสำหรับขวดพีวีซีและสายไฟฟ้าพีวีซี (DEVELOPMENT OF PVC COLOR MASTERBATCH FOR BOTH OF PVC BOTTLE AND PVC CABLE COMPOUND) อ.ที่ปรึกษา : ร.ศ. ดร.ศุภวรรณ ตันตยานนท์ , 50 หน้า, ISBN 974-334-440-3 .

แคลเซียมซิงค์สเตบิไลเซอร์ถูกนำมาใช้เป็นส่วนผสมของเม็ดพีวีซีสีเข้มข้นสำหรับผสมในขวดพีวีซีและสายไฟพีวีซี แทนสารประกอบตะกั่วและสารประกอบซัลเฟอร์ของดีบุก เพื่อลดปัญหาการเกิดปฏิกิริยาระหว่างสารประกอบตะกั่วและสารประกอบซัลเฟอร์ และปัญหาการหลอมตัว ขั้นตอนแรก เป็นการทดลองปรับชนิดและปริมาณของพีวีซีเรซิน, สเตบิไลเซอร์, โคสเตบิไลเซอร์, พลาสติกไซเซอร์ และสารหล่อลื่น ซึ่งมีผลกระทบต่อสมบัติการทนต่อความร้อน, สมบัติทางกายภาพและสมบัติทางไฟฟ้า ขั้นที่สองเป็นการศึกษาผลกระทบต่อกระบวนการผลิตเม็ดพีวีซีสีเข้มข้นเมื่อใช้ผงสีในปริมาณ 10, 20 และ 30 ส่วนโดยน้ำหนักของพีวีซีเรซิน ขั้นตอนสุดท้ายเป็นการทดสอบสมบัติทางกายภาพ และทางไฟฟ้า เมื่อผสมด้วยเม็ดพีวีซีสีเข้มข้นในอัตราส่วน 100:1, 100:3 และ 100:5

จากการทดลองพบว่า สูตรพื้นฐานของเม็ดพีวีซีสีเข้มข้นประกอบด้วย พีวีซีเรซินซึ่งมีค่าเคเท่ากับ 56 , สารประกอบดีโอพี, น้ำมันถั่วเหลือง, สเตบิไลเซอร์ชนิด แคลเซียมซิงค์ และ สารประกอบเอสเตอร์ของกรดไขมัน ในสัดส่วน 100,25,5,4 และ0.3 โดยน้ำหนักตามลำดับ ขั้นตอนที่สองพบว่า ปริมาณสีไม่เกิน 20 ส่วนต่อ 100 ส่วนโดยน้ำหนักของพีวีซี ไม่กระทบต่อกระบวนการผลิตเม็ดพีวีซีสีเข้มข้น หากใส่สีที่ปริมาณ 30 ส่วน ต้องเพิ่มอุณหภูมิขึ้น 3 องศาเซลเซียส ในขั้นตอนที่สุดท้าย พบว่าสมบัติทางกายภาพ และสมบัติทางไฟฟ้า ของสายไฟพีวีซีซึ่งผสมด้วยเม็ดพีวีซีสีเข้มข้นที่อัตราส่วน 100 : 5 ไม่เปลี่ยนแปลงอย่างมีนัยสำคัญ อย่างไรก็ตามค่าการทนต่อแรงกระแทกของขวดพีวีซีซึ่งผสมด้วยเม็ดพีวีซีสีเข้มข้นลดลง 15% แต่ยังคงอยู่ในช่วงที่ยอมรับได้ในการผลิตขวดพีวีซีขนาดไม่เกิน 500 มิลลิลิตร

ภาควิชา..	ลายมือชื่อนิสิต ....
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์	ลายมือชื่ออาจารย์ที่ปรึกษา ....
ปีการศึกษา 2542	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม ....

„„ 3972743123 MAJOR PETROCHEMISTRY

KEY WORD: PVC COLOR MASTERBATCH/ PVC CABLE COMPOUND/ PVC BOTTLE COMPOUND

SOONTHORN MARKSOOK : DEVELOPMENT OF PVC COLOR MASTERBATCH FOR BOTH OF PVC BOTTLE AND PVC CABLE COMPOUND. THESIS ADVISOR : ASSO. PROF. SUPAWAN TANTAYANON, Ph .D. , 50 pp. ISBN 974-334-440-3

Ca/Zn stabilizer was used in PVC color masterbatch for both of PVC bottle and PVC cable compound instead of the lead and tin stabilizer in order to solve the sulfur staining and the melting problem. The first part of this work concerns a type and an amount of PVC resin, stabilizer, co-stabilizer, plasticizer, and lubricant that effect the heat stability, the physical properties and the electrical property. In the second part, the effect of varied amounts of a pigment at 10, 20 and 30 phr on processing was investigated. Finally the physical properties and the electrical property of the blending with the master batch at the ratio of 100:1, 100:3 and 100:5 were investigated.

It was found that the optimal formula is composed of the PVC resin which K value 56, the di-octyl phthalate, the oxidized soybean oil, the Ca/Zn stabilizer and the ester of fatty acid at 100,25,5,4, and 0.3 phr respectively. In the second part, it was found that there is no effect on the processing when the amount of the pigment is less than 20 phr but at 30 phr, the temperature profile is increased by 3°C. Finally the physical properties and the electrical property of the cable blended with the masterbatch at ratio 100 : 5 show no significant effect while the impact strength of the blending in the bottle has a tendency to decrease by 15 %. However the impact strength is in the range of acceptance for a PVC bottle which the size is not larger than 500 ml.

ภาควิชา.. ลายมือชื่อนิสิต M. Soonthorn.

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา ....

ปีการศึกษา 2542 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม ....

ACKONWLEDGEMENTS

I would like to express my sincere gratitude to my advisors, Associate Professor Dr. Supawan Tantayanon, Assistant Professor Dr. Prapaipit Chamsuksai Ternai and Dr. Wilaiporn Chetanachan for their precious advice and encouragement throughout the course of this research.

Grateful acknowledgment is made to Professor Dr. Bela Ternai for his valuable suggestions.

Finally, I would like to thank the Thai Plastic and Chemicals Public Company Limited for helpfulness of materials and testing machines and all of staff for good suggestions.

CONTENTS

TABLES

Tables Page

FIGURES

ABBREVIATION

PVC	poly(vinylchloride)
Pb	lead
Sn	tin
Ca	calcium
Zn	zinc
Mg	magnesium
Al	aluminium
DOP	di(2-ethylhexyl) phthalate
DINP	di(isononyl) phthalate
ESBO	epoxidized soybean oil
MBS	methyl methacrylate butadiene styrene copolymer
PA	processing aid
rpm	round per minute
phr	part per hundred PVC resin

CHAPTER I

INTRODUCTION

The use of PVC color masterbatches is the most popular way of coloring PVC. The advantages are optimum pigment dispersion, elimination of coloristic work, accuracy of shade, almost dustfree operation and reduction in cleaning cost. PVC color masterbatches are made up of PVC compounds in which a high loading of pigment has been dispersed. PVC color masterbatches can be single pigment or multi-pigment masterbatches formulated to the processor's color requirements. The processor uses the color masterbatches in a specified "let down" ratio, the ratio of base compounds blended with color masterbatches. In Thailand most of the PVC color masterbatches for PVC bottle compounds use sulfur-containing compounds as stabilizers while lead-containing compounds are used as stabilizers for PVC cable compounds and color masterbatches for PVC cable compounds. Sulfur staining (1) will occur when PVC color masterbatches for bottle are blended to PVC cable compounds while PVC bottle compounds when blended with PVC color masterbatches for PVC cable compound has melting problem.

To avoid this problem the use of Ca/Zn stabilizers and tin maleate was investigated. PVC and another additive; plasticizers, and lubricants were used in various formulations to solve the melting problem. The objective of this research is to develop the PVC color masterbatch for both of PVC bottle and PVC cable compound and investigate the effect of the masterbatch on thermal stability, physical properties and electrical property of the blending.

CHAPTER II

THEORETICAL CONSIDERATIONS

2.1) Color masterbatch

Normally the carrier polymer used for formulating color masterbatches is the same as the let-down polymer to ensure good compatibility.(2) Color masterbatches are compounded with the same formulation base of the compound to be colored with high loading of pigment to avoid adverse effect on their physical and mechanical property and thermal stability. The addition of an adhesion promoter or dispersing agent may possibly be necessary.(3) The melt flow index of acceptable color masterbaches is not higher than the compound to be colored due to good color dispersion.(4) However, the ease of processing is the important consideration.

2.2) Degradation of PVC

According to the literature, PVC polymers are thermally unstable at normal processing temperatures. This inherent thermal instability is reflected in the low energy of activation for heat degradation of PVC, which is approximately 20 - 25 kcal/mol while it is 55,46 and 65 kcal/mol for PS,PE and PP respectively.(5) Dehydrochlorination reaction, a reaction during processing at elevated temperature, leads to increasing discoloration and degradation. (Fig. 2.1) Additionally PVC is degraded by autooxidation and mechanochemical chain scission.

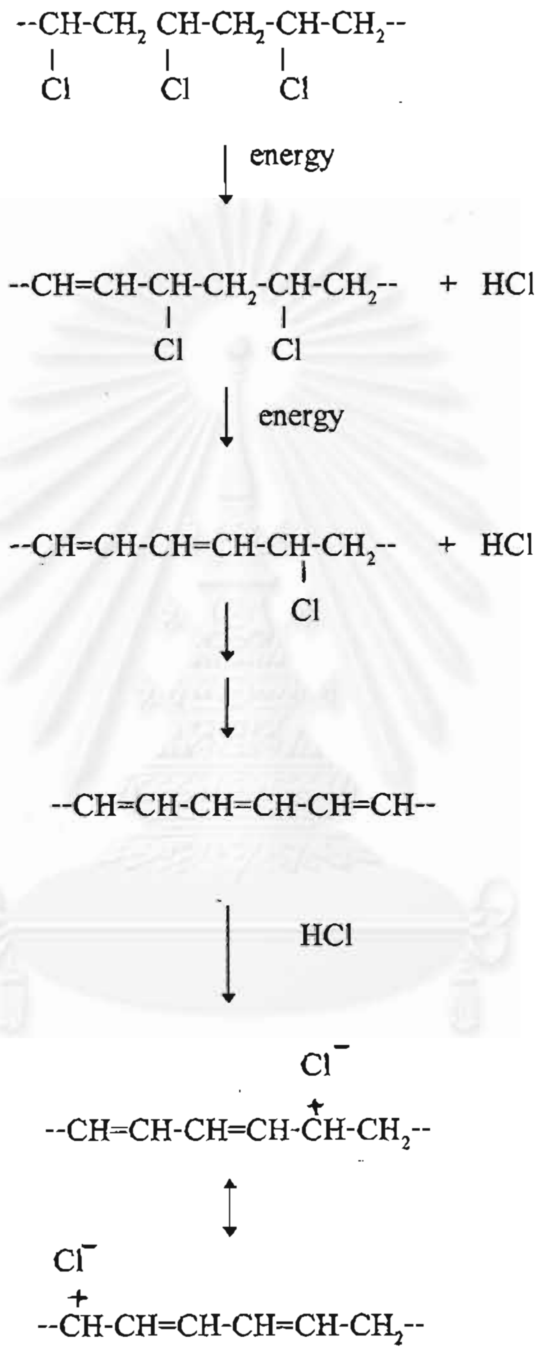


Figure 2.1 Degradation of PVC by dehydrochlorination

Autooxidation, an autocatalytic effect in the process of dehydrochlorination of PVC, is considerably faster in the presence of oxygen than in an inert atmosphere. Oxygen attack on methylene groups leads to the formation of hydroperoxides in a radical chain reaction followed by the decomposition by an ionic reaction mechanism of hydroperoxides. (Fig.2.2)

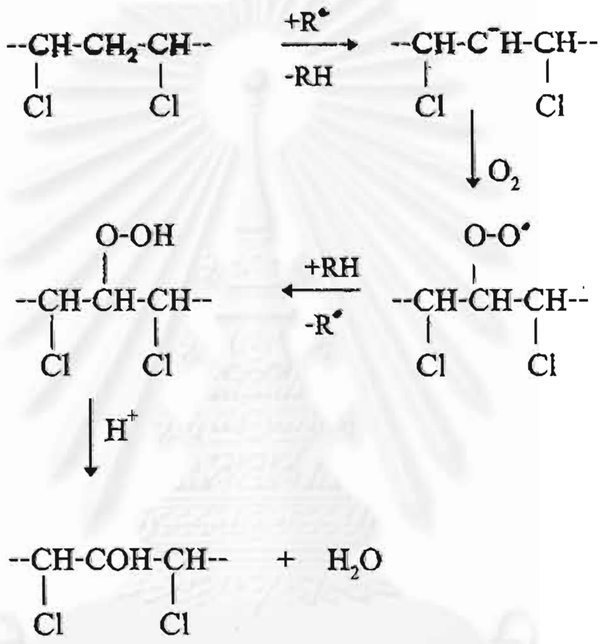


Figure 2 .2 Autooxidation of PVC

2.3) Stabilization of PVC

Generally the degradation of PVC can be reduced by added heat stabilizers to protect the PVC compound or product from the undesirable discoloration caused by the heat necessary to process and to minimize the effects of heat and the environment during the useful life of the product, by preventing or retarding the dehydrochlorination reaction.(6,7) These are summarized below :

- Absorption of hydrogen chloride

$$(C_4H_9)_2Sn\text{-}(\text{-}S\text{-}CH_2\text{-}CO\text{-}O\text{-}C_8H_{17})_2 + HCl$$

$$\downarrow$$

$$(C_4H_9)_2SnCl\text{-}S\text{-}CH_2\text{-}CO\text{-}O\text{-}C_8H_{17} + HS\text{-}CH_2\text{-}CO\text{-}O\text{-}C_8H_{17}$$

$$\downarrow$$

$$(C_4H_9)_2SnCl_2 + HS\text{-}CH_2\text{-}CO\text{-}O\text{-}C_8H_{17}$$

- Elimination of initiation sites

$$\text{--}CH\text{-}_2CH{=}CH\text{-}CHCl\text{-}CH_2\text{--} \quad + \quad RS_2\text{-}SnR'_2$$

$$\downarrow$$

$$\text{--}CH\text{-}_2CH(SR)\text{-}CH{=}CH\text{-}CH_2\text{--} \quad + \quad R\text{-}Sn(Cl)R'_2$$

- Prevention of autooxidation
- Addition of polyene sequences
- Destruction of carbenium salts

2.4) Pb, Sn, and Ca/Zn stabilizers

2.4.1) Pb stabilizers

The advantages of lead stabilizers are due to their ability in complex formation which is necessary for the substitution of labile chlorine atoms. Lead chloride is formed during the stabilizing process. Lead stabilizers have no effect on the conductivity of PVC, however, they are not suitable for the transparent compound because they act as pigments. Furthermore, they are sensitive to sulfur-containing compounds leading to discoloration and they react with some pigments leading to color changes.(1) Typical applications are electric insulations and coverings, profiles, pipes, and pipe fitting.

2.4.2) **Sn stabilizers**

Organotin mercaptides have one or more mercapto groups involved in the stabilizing reaction, as opposed to the alkyl or esteralkyl groups which only influence processibility, volatility, and toxicity. They are used in all types of PVC compounds when high thermal stability or clarity is required. They have a typical odor during the processing but not evident in the finished product. Typical applications are in bottles, containers, packaging film and transparent products.

2.4.3) **Ca/Zn stabilizers**

They are widely used as non-toxic stabilizers in PVC compounds, especially in food packaging and containers, medical products and toys. In general, other co-stabilizers are also added in one-pack Ca/Zn stabilizers for synergism. Additionally, advantages of this system are freedom from odor and sulphide staining in the finished products.

2.5) **Melt behavior**

PVC is a mixture of macromolecules of generally low to high molecular weight with highly viscous melts. It is processed in the molten state under shear with internal and external friction. The increase of temperature to decrease the viscosity of the melts is limited by the thermal degradation of PVC. Lubricants are additives to improve flow properties, reduce adherence of the melt to machine parts, acting as melt promoters; antiblock, antitack and antisatic agents as well as color and impact improvers. Plasticizers serve to decrease melt temperature and melt viscosity and increase gelation capacity.(8,9)

CHAPTER III

EXPERIMENTAL

3.1) Apparatus and Instruments

1. High speed mixer

   PAPENMEIER ; model TGEHKV 10

2. Single screw extruder

   WEBER ; model FB70

3. Hardness tester

   BAREISS ; model HHP-2000

4. Tensile strength tester

   TOYOSEIKI ; model RS-500

5. Oven

   GOTECH ; model GT7017L

6. Melt flow index tester

   TOYOSEIKI ; model T-1001

7. Izod impact strength tester

   TOYOSEIKI ; model 612

8. Ultra megaohmmeter

   TOA ; model SM-10E

9. Densitometer

TOYOSEIKI ; model 265

10. Colorimeter

DATACOLOR ; model ST1

11. Sawing device

TOYOSEIKI ; model S529

12. Notching device

ATLAS ELECTRIC DEVICES ; model CS93E

13. Two roll machine

LABTECH ; model LR150

3.2) Materials

	Materials	Supplier
1.	PVC resin SG560	Thai Plastic and Chemical Co., Ltd.
2.	PVC resin SG580	Thai Plastic and Chemical Co., Ltd.
3.	PVC resin SG660	Thai Plastic and Chemical Co., Ltd.
4.	Lead stabilizer	Siam Stabilizer Co., Ltd.
5.	Tin mercaptide	Morton Co., Ltd.
6.	Tin maleate	Ciba-Geigy Co., Ltd.
7.	Ca/Zn/Epoxy complex	Akcros Chemical Co., Ltd.
8.	Ca/Zn/Mg stabilizer	Adaka Thailand Co., Ltd.
9.	Epoxidized soybean oil (ESBO)	Adaka Thailand Co., Ltd.
10.	Oxidized polyethylene wax (OP)	Hoechst Co., Ltd.
11.	Esters of long chain fatty acids	Henkel Co., Ltd.
12.	Acrylic processing aid	Rohm and Hass Co., Ltd.

13. Methyl methacrylate butadiene styrene copolymer (MBS)	Kureha Chemicals Pte., Ltd.
14. Di(isononyl) phthalate (DINP)	Thai Chemical Co., Ltd.
15. Di(2-ethylhexyl) phthalate (DOP)	Thai Chemical Co., Ltd.
16. Filler	Surin Omya Co., Ltd.
17. Tris(nonylphenyl)phosphite	Rhone-Poulenc Co., Ltd.
18. Stearoylbenzoylmethane	Ciba-Geigy Co., Ltd.

3.3) Compounding method

PVC resin was mixed with the solid additives in the high speed mixer at 2000 rpm. When the temperature of the mixture increased to 80°C, the speed was reduced to 800 rpm., then the liquid additives were added. After three minutes, the speed was increased to 2000 rpm. again and the components were mixed while the temperature was increased to 110°C. Then the speed was reduced to 800 rpm. and the mixture was cooled down to 60°C by cooling water . This mixture is called "dryblend".

This dryblend was extruded by extruder (30 mm. diameter) with the screw speed of 60 rpm, then it was cut to pellets. The temperature profile is shown in Table 3.1.

The reference cable and bottle compound which their formulation shown in Tables 3.2 and 3.3 were prepared with the same procedure.

Table 3.1 The condition of extrusion

Compound	Temperature of Extruder (^{o}C)			
	Zone1	Zone 2	Zone 3	Die
Cable and its color masterbatches	142	146	150	152
Bottle and its color masterbatches	150	154	156	160
Color masterbatches for both cable and bottle	136	140	144	146

Table 3.2 Formulation of the cable compound (unit:phr)

PVC SG660	100
Lead stabilizer	4
DINP	45
Filler	30

Table 3.3 Formulation of the bottle compound (unit:phr)

PVC SG580	100
Tin stabilizer	1.0
ESBO	1
Acrylic processing aid (PA)	1.5
Methyl methacrylate butadiene styrene copolymer (MBS)	8
Lubricant (Esters of long chain fatty acids)	0.3

3.4) Physical Characterization

3.4.1) Heat stability test

The milled sheet, thickness 1 mm., was aged in the oven at constant temperature of 190°C. Every 15-20 minutes samples were taken and obtained a color change of the sample, according to DIN 53382.

3.4.2) Melt flow index

The melt flow index was measured by using the melt flow index tester with 10 kg loading and at 180°C according to ASTM D 1238.

3.4.3) Hardness

The hardness of the cable compound was measured by using the pressed sheet, 6 mm. thickness, of the compound with shore A scale at 15 second, according to ASTM D-2240-68.

3.4.4) Tensile strength and elongation

The tensile strength and elongation were measured by using type II dumbbell specimens, 1 mm. thickness, with the speed of 300 mm./min. and the loading of 5 kg force, according to JIS K 6723.

3.4.5) Izod impact strength

The izod impact strength was measured by using the 2 mm. notch marked specimen , 12.7 mm. width X 63.5 mm. length X 3mm. thickness, according to ASTM D-265

3.4.6) Volume resistivity

The volume resistivity was measured by using the pressed sheet, 1 1mm. thickness, at 500 V and 25°C, according to JIS K 6723.

3.4.7) Color index

Color index of the compounds was carried out on the micro colorimeter (DATACOLOR). It was measured on the surface of the pressed sheet.

3.4.8) Surface appearance

The compounds were extruded with a screw speed of 50 rpm. and the temperature profile as 145/150/155/160 °C for bottle compound, and 135/140/145/150 °C for cable compound. The surface appearance of the strand was obtained.

3.5) Development of the base masterbatch

3.5.1) Effect of stabilizers and co-stabilizers on physical properties

In this part, the one pack Ca/Zn/epoxy complex stabilizer, the Mg containing Ca/Zn stabilizer and the tin maleate stabilizer were used with epoxidized soybean oil (ESBO), stearoylbenzoylmethane and tris(nonylphenyl)phosphite as co-stabilizer.

Firstly, the Ca/Zn stabilizer, the Ca/Zn/Mg stabilizer and the tin maleate stabilizer were used at 4 phr., as shown in formulation Nos. A1-A3 in Table 3.4, to obtain the heat stability at 180°C, the volume resistivity and the haze property.

Secondly, the Ca/Zn stabilizer was used in various amounts in a range of 2 to 8 phr., as shown in formulation Nos. B1-B4 in Table 3.5. The static heat stability at 195°C of the compounds was obtained.

Thirdly, the ESBO, tris(nonylphenyl)phosphite and stearoylbenzoyl-methane were added at 5 phr., 0.5 phr. and 0.5 phr. respectively in the compound containing 6 phr. of Ca/Zn stabilizer, as shown in formulation Nos. B5-B7 in Table 3.5, study their effect as co-stabilizers on the heat stability and the acting as an inhibitor of the growth of polyene sequence. The heat stability at 195°C of the compounds was obtained.

Table 3.4 Formulations with varied type Ca/Zn stabilizer (unit:phr)

Formulation No	A1	A2	A3
PVC SG580	100	100	100
Ca/Zn stabilizer	4		
Ca/Zn/Mg stabilizer		4	
Tin maleate stabilizer			4
DOP	30	30	30
Lubricant #1	0.3	0.3	0.3

Table 3.5 Formulations with varied amounts of Ca/Zn stabilizer (unit:phr)

Formulation No	B1	B2	B3	B4	B5	B6	B7
PVC SG580	100	100	100	100	100	100	100
Ca/Zn stabilizer	2	4	6	8	6	6	6
DOP	30	30	30	30	30	30	30
Lubricant #1	0.3	0.3	0.3	0.3	0.3	0.3	0.3
ESBO					5	0	5
tris(nonylphenyl)phosphite						0.5	0.5
stearoyl benzoyl methane						0.5	0.5

Fourthly, the compounds with varied ratios of DOP/ESBO from 25:5 to 0:30 at 4 phr. of Ca/Zn stabilizer were produced, as shown in formulation Nos. C1-C6 in Table 3.6, and obtained the heat stability at 195°C. The heat stability at 180°C of the blending in the bottle compound with them was also obtained and the heat stability at 190°C of the blending in the cable compound with them was also obtained.

Table 3.6 Formulations with varied DOP/ESBO ratio (unit:phr)

Formulation No	C1	C2	C3	C4	C5	C6
PVC SG580	100	100	100	100	100	100
Ca/Zn stabilizer	4	4	4	4	4	4
DOP	25	20	15	10	5	0
ESBO	5	10	15	20	25	30
Lubricant	0.3	0.3	0.3	0.3	0.3	0.3

Finally, the ESBO, acting as plasticizer, also, was substituted to the DOP at 30 phr. and the Ca/Zn stabilizer was varied from 1-5 phr., as shown in formulation Nos. D1-D5 in Table 3.7. The heat stability at 190°C of them was obtained and the heat stability at 180°C of the blending in both of the bottle compound and the cable compound were also obtained. Then the amount of the ESBO was varied from 30-50 phr. while the Ca/Zn was fixed at 1 phr., as shown in formulation Nos. E1-E5 in Table 3.8 and the blending in both of the bottle compound and the cable compound with them were obtained.

Table 3.7 Formulations with varied amounts of Ca/Zn in the ESBO system (unit:phr)

Formulation No	D1	D2	D3	D4	D5
PVC SG580	100	100	100	100	100
Ca/Zn stabilizer	1	2	3	4	5
DOP	0	0	0	0	0
ESBO	30	30	30	30	30
Lubricant	0.3	0.3	0.3	0.3	0.3

Table 3.8 Formulations with varied amounts of ESBO (unit:phr)

Formulation No	E1	E2	E3	E4	E5
PVC SG580	100	100	100	100	100
Ca/Zn stabilizer	1	1	1	1	1
DOP	0	0	0	0	0
ESBO	30	35	40	45	50
Lubricant	0.3	0.3	0.3	0.3	0.3

3.5.2) Effect of plasticizers and the K value of PVC resin on physical properties

Di(2-ethylhexyl) phthalate (DOP) was used in various amounts, in a range of 20 to 40 phr., as shown in formulation Nos. F1-F3 in Table 3.9. The PVC resin which has different K value, (another factor that effects the melt property, its detail is shown in appendix a), was compounded in the formulation Nos. F4-F6 in Table 3.9. The fusion behavior and the melt flow index were obtained. The surface appearance, hardness, tensile strength and elongation of the blending in the cable compound with them at the let down ratio 5:100 were obtained. In addition, the surface appearance and the izod impact strength of the blending in the bottle compound with them at the same ratio as the blending in the cable compound were also obtained.

Table 3.9 Formulations with varied amounts of DOP and K value of PVC resin

(unit:phr)

Formulation No	F1	F2	F3	F4	F5	F6
PVC SG560				100	100	100
PVC SG580	100	100	100			
Ca/Zn stabilizer	4	4	4	4	4	4
DOP	15	25	35	15	25	35
ESBO	5	5	5	5	5	5
Lubricant	0.3	0.3	0.3	0.3	0.3	0.3

3.6) Effect of amount of the pigment on the processing

In this experiment, the amount of the pigment, Blue 59245 from the World Pigment Co., Ltd., was varied from 10 to 30 phr. at the optimized formula of the masterbatch compound, as shown in formulation no. G1-G3 in Table 3.10, to obtain the optimum condition of the processing and the dispersion ability at the high pigment concentration. The melt flow index and the surface appearance of the blending in both of the bottle compound and the cable compound were obtained additionally.

Table 3.10 Formulations with varied amounts of pigment (unit:phr)

Formulation No	G1	G2	G3
PVC SG580	100	100	100
Ca/Zn stabilizer	4	4	4
DOP	25	25	25
ESBO	5	5	5
Lubricant	0.3	0.3	0.3
Pigment (Blue 59245)	10	20	30

3.7) Effect of the masterbatches on blending

The optimized color masterbatch, formulation no. G1, was blended in both of the cable compound and the bottle compound at the ratio 1:100, 3:100, and 5:100. The surface appearance, the physical properties; hardness, tensile strength, elongation, izod impact strength and the electrical property, the volume resistivity, were obtained compared to the blending with the bottle color masterbatch and the cable color masterbatch which the formulation are shown in Tables 3.11 and 3.12.

Table 3.11 Formulation of the cable color masterbatch (unit:phr)

PVC SG660	100
Lead stabilizer	4
DINP	65
Pigment (Blue 59245)	10

Table 3.12 Formulation of the bottle color masterbatch (unit:phr)

PVC SG580	100
Tin stabilizer	1.0
ESBO	1
Acrylic processing aid (PA)	1.5
Methyl methacrylate butadiene styrene copolymer (MBS)	8
Lubricant (Esters of long chain fatty acids)	0.3
Pigment (Blue 59245)	10

CHAPTER IV

RESULTS AND DISCUSSION

4.1) Development of the base masterbatch

4.1.1) The effect of stabilizer and costabilizers

The use of the Mg containing Ca/Zn stabilizer recently developed by Asahi Denka Kogyo K.K.(10) with the same phr as lead stabilizer in the masterbatch, formulation No. A2, shows better heat stability and volume resistivity than the Ca/Zn stabilizer from Akcros Chemical Co., Ltd. with the same phr, formulation No. A1, and the tin maleate stabilizer from Ciba-Geigy Co., Ltd., formulation No. A3, as shown in figures 4.1a and 4.1b. In addition, the heat stability and the volume resistivity of the blending in bottle compound and the cable compound with the masterbatch at the ratio 100:5 are better, as shown in Figure 4.1b. In contrast, it shows higher haze than the other samples. However, there is no difference of the blending in the bottle compound at the ratio of 100:5, as shown in Figure 4.1c. The general mechanism of stabilization by the Ca/Zn (11) is shown in Figure 4.2. The Mg in Ca/Zn/Mg stabilizer is Mg/Al hydroxide carbonate which has been used to improve the heat stability. It consists of positive charged basic layers $[Mg/Al(OH)_2]^+$ and negative charged intermediate layers $[(CO_3).2H_2O]^-$ which neutralizes the positive charge of the basic layers. The CO_3^{2-} in the intermediate layers reacts with HCl while Mg and Al in the basic layers do not react to HCl. Therefore the Mg/Al hydroxide carbonate reacts to the hydrogen chloride generated

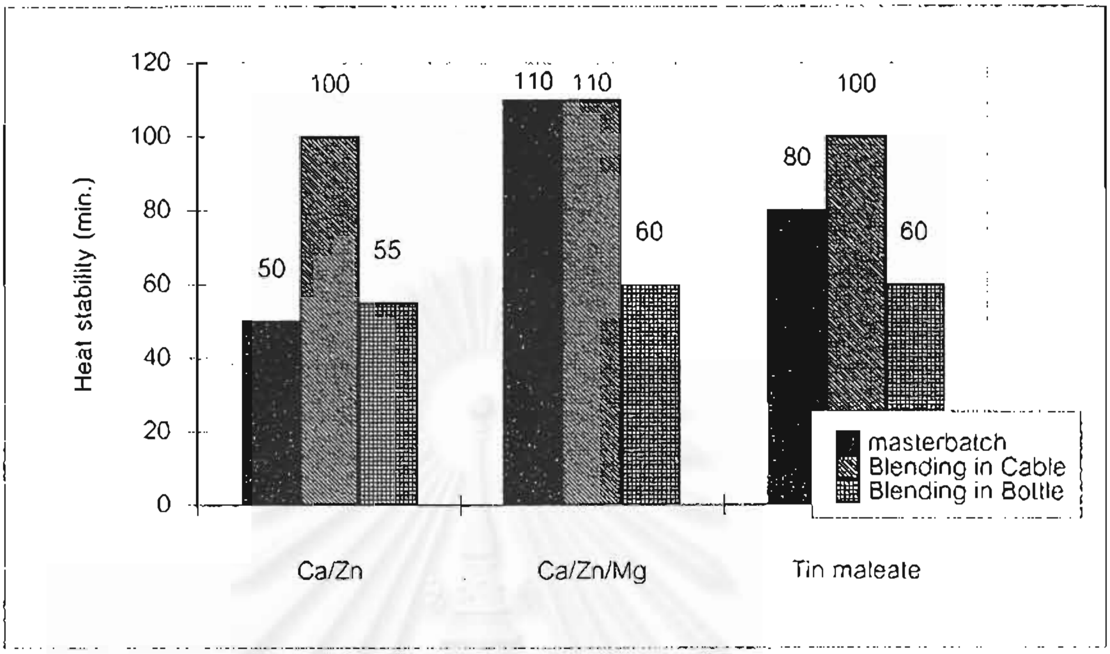


Figure 4.1a The effect of stabilizers on the heat stability of the masterbatch at 180°C and the cable and the bottle compound at 190°C, experiment n=1

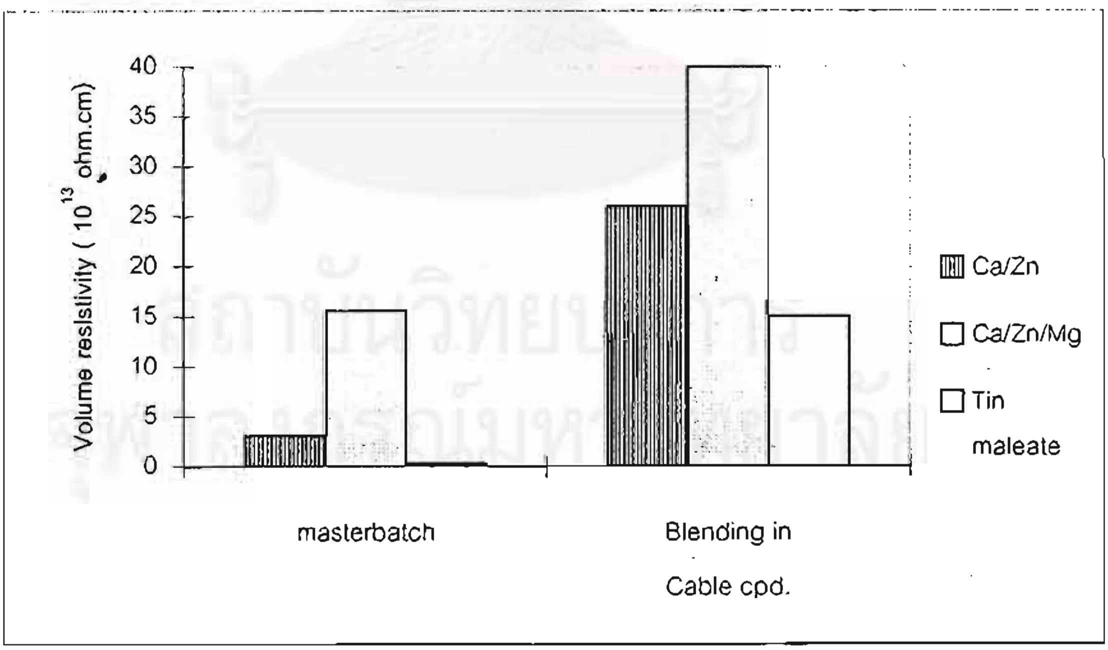


Figure 4.1b The effect of stabilizers on the volume resistivity of the masterbatch and the cable coı experiment n=3

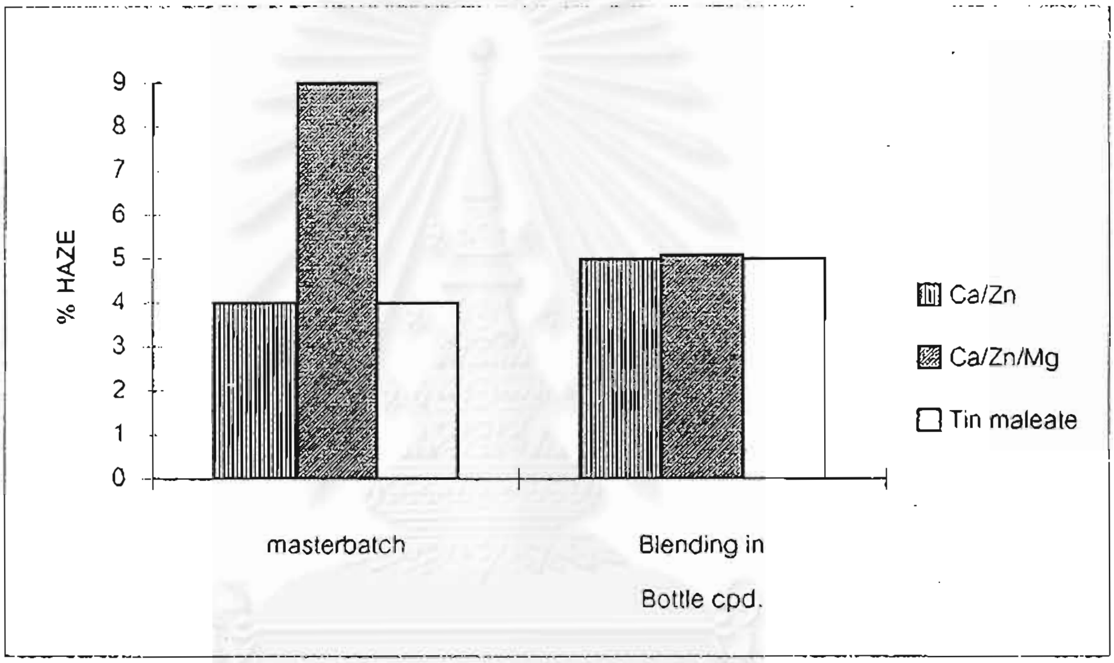


Figure 4.1c The effect of stabilizers on the haze of the masterbatch and the bottle compound (blending at let down ratio 100:5), experiment n=2

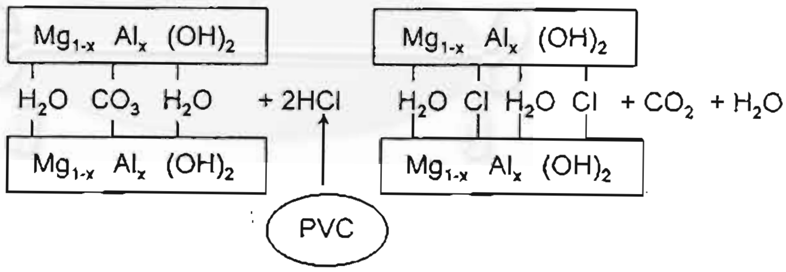
$$Zn(OOCR)_2 + \text{--}CH_2CH(Cl)\text{--} \longrightarrow ZnCl_2 + \text{--}CH_2CH(OOCR)\text{--}$$

$$Ca(OOCR)_2 + 2HCl \longrightarrow 2HCOOCR + CaCl_2$$

$$ZnCl_2 + Ca(OOCR)_2 \longrightarrow Zn(OOCR)_2 + CaCl_2$$

Figure 4.2 The mechanism of stabilization by Ca/Zn stabilizer

- Ca/Zn/Mg : Mg ; Mg/Al hydroxide carbonate
  $[Mg_{1-x}/Al_x(OH)_2]^{x+}\ [(CO_3)_{x/2}.2H_2O]^{x-}$



- $CO_3^{2-} + HCl \longrightarrow HCO_3^{-} + Cl^{-}$

$$HCO_3^{-} \xrightarrow{HCl} H_2O + CO_2 + Cl^{-}$$

Figure 4.3 The scheme of stabilization by Mg/Al hydroxide carbonate

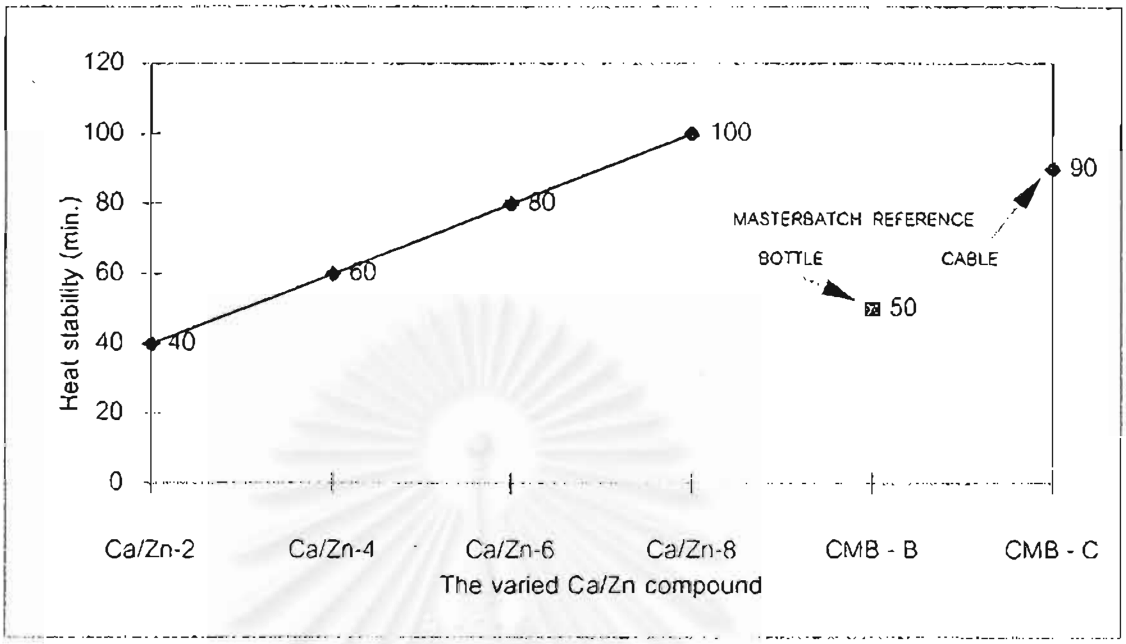


Figure 4.4 The effect of varied amounts of Ca/Zn on the heat stability of the masterbatch at 190°C experiment n=1

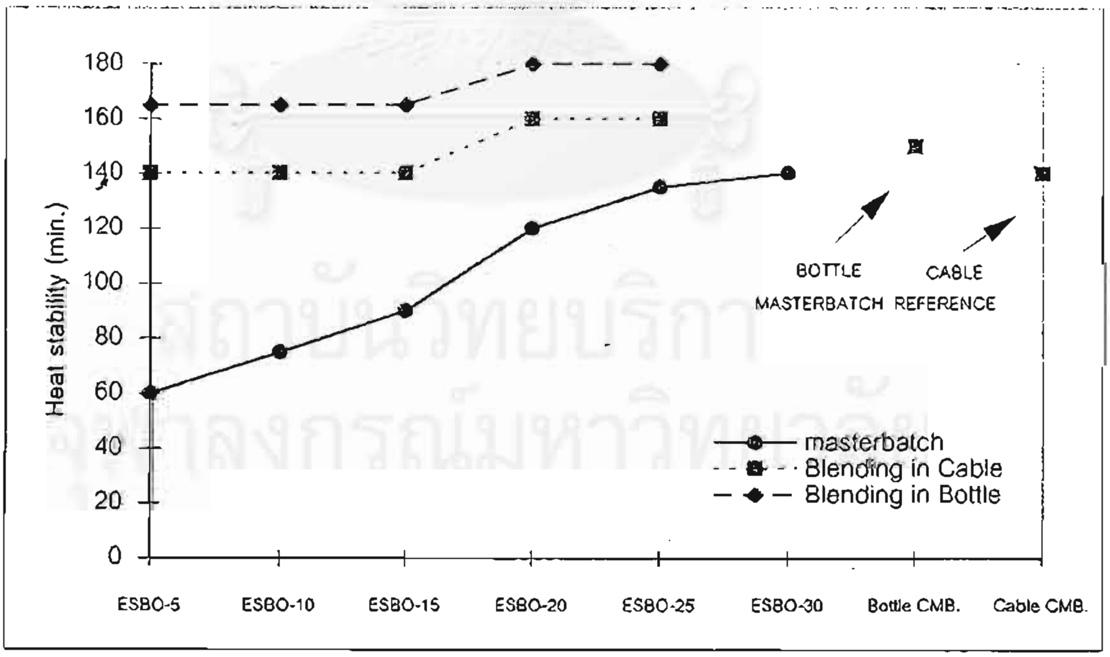


Figure 4.5 The effect of varied amounts of ESBO on the heat stability of the cable and bottle at 190°C, experiment n=1

by the PVC decomposition and blot Cl^-, as shown in Figure 4.3. Commercially Ca/Zn/Mg and tin maleate stabilizers are more expensive than Ca/Zn stabilizer by 10% and 70% respectively, therefore Ca/Zn stabilizer is considered for using in the masterbatch.

In general, the direct replacement of a lead stabilizer or a tin mercaptide stabilizer with a Ca/Zn stabilizer leads to a poorer heat stability.(12) The higher amount of one pack Ca/Zn stabilizer, formulation Nos. B1-B4, shows better heat stability, as shown in Figure 4.4 but at the same amount of stabilizer, it is less effective than the lead stabilizer used in the cable compound and tin stabilizer used in the bottle compound

The Ca/Zn stabilizer is widely used in conjunction with co-stabilizer, epoxidized soybean oil, tris(nonylphenyl)phosphite and stearoylbenzoylmethane, to improve stability against both heat and light. Epoxidized soybean oil (ESBO) varied from 5 to 30 phr, used in formulation Nos. C1-C6, can improve the long term heat stability, as shown in Figure 4.5. Its stabilizing effect is due to its absorption of HCl and displacement of labile chlorine atoms in the PVC chain, as shown in Figure 4.6.

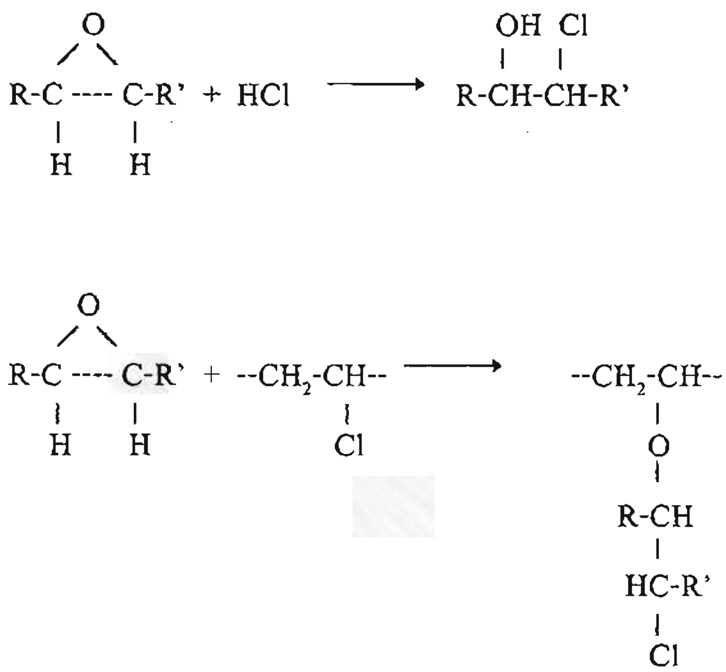


Figure 4.6 Mechanism of stabilization by ESBO

While the higher amounts of ESBO increase the tendency of the initial color to be more yellow, the tris(nonylphenyl)phosphite can improve the initial color of PVC to stabilized by displacement of the labile chlorine atoms of PVC chain and acting as secondary antioxidant that retarded the dehydrochlorination by elimination of initiation sites formed by oxygen attack on the PVC chain, as shown in Figure 4.7.(13) Similarly, stearoyl benzoyl methane was added together with tris(nonylphenyl)phosphaite at the same amount, 0.5 phr, to improve initial color due to preclude the formation of conjugated double bonds.(14)

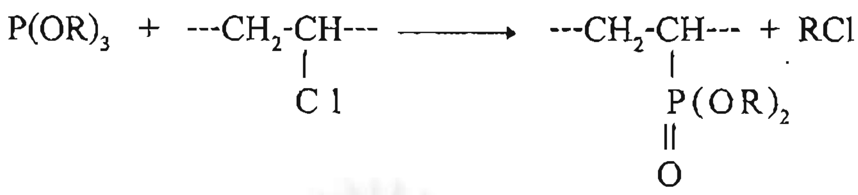


Figure 4.7 Stability mechanism of tris(nonylphenyl)phosphite

However, the effect on the initial color of the blending in both of the cable compound and the bottle compound without the tris(nonylphenyl)phosphite and stearoyl benzoyl methane containing masterbatch at the ratio 100:5 has no signification. Therefore they are not needed to add to the masterbatch compound.

DOP was substituted by ESBO, also acting as plasticizer, to study the effect on heat stability. The experiment was carried out using varied amounts of Ca/Zn stabilizer and ESBO as formulation Nos. D1-D5 and E1-E5. The results show that the heat stabilities of the blends are slightly different, as shown in Figures 4.8 and 4.9. Similarly, the blending with the varied amounts of ESBO is slightly different. Compared to the DOP system, there is not a distinct advantage in heat stability. Generally, the cost of ESBO is much higher than DOP ; e.g. 28 baht/kg DOP, 45 baht/kg ESBO, therefore, the masterbatch that contains 5 phr. of ESBO is optimum.

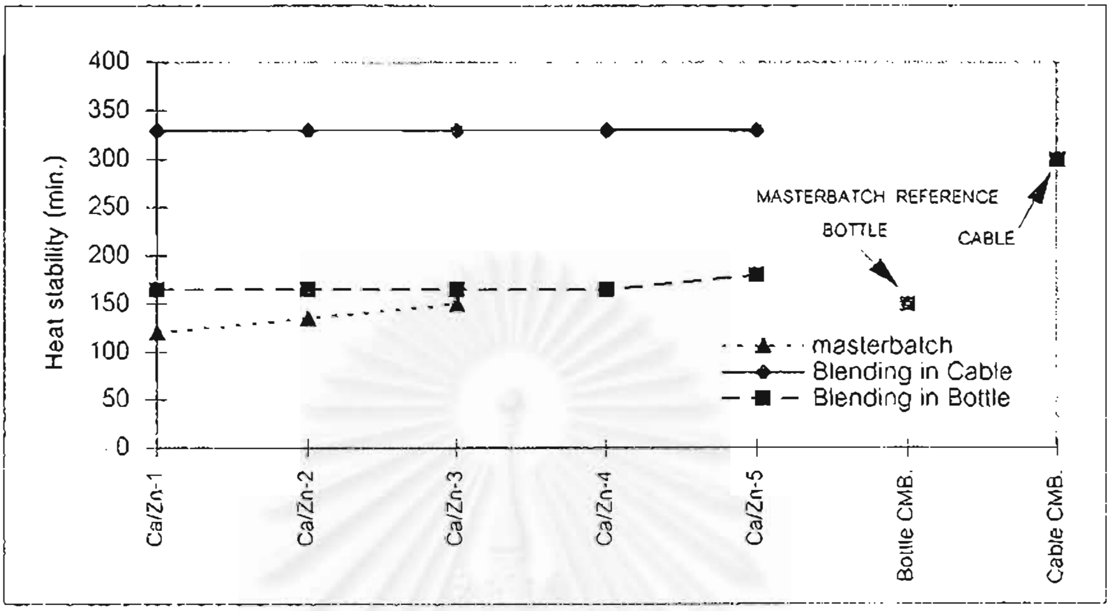


Figure 4.8 The effect of varied amounts of Ca/Zn with ESBO system on the heat stability of the cable and the bottle compound at 180°C, experiment n=1

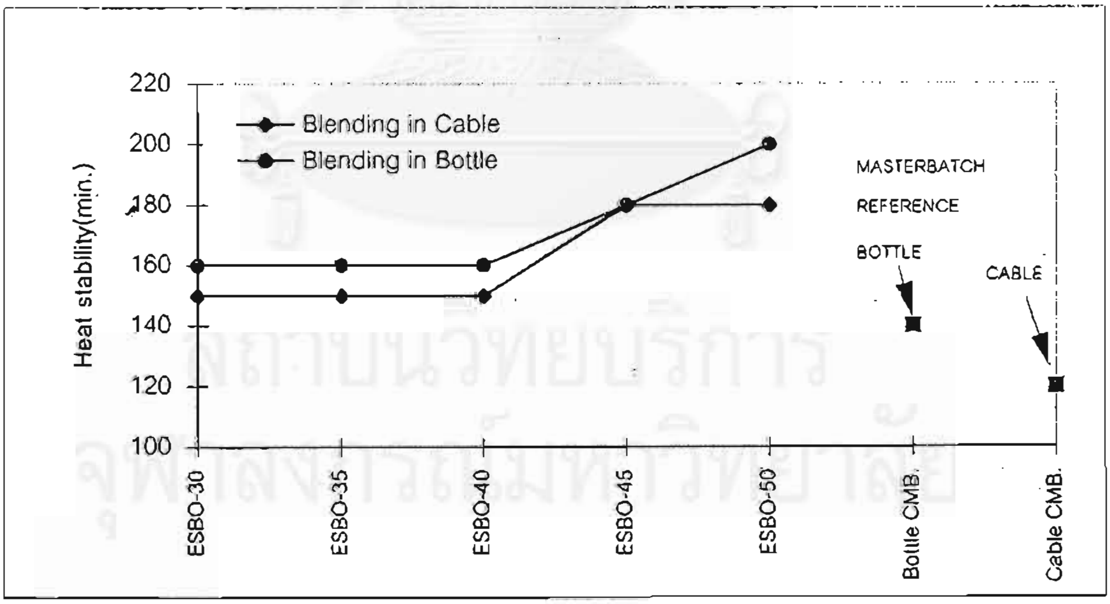


Figure 4.9 The effect of varied amounts of ESBO on the heat stability of the cable compound at 190°C and the bottle compound at 180°C, experiment n=1

4.1.2) The effect of plasticizer and K-value of PVC resin

The melt property, an important characteristic of a color masterbatch, is affected by the amount of plasticizer which controls the ease to fuse and lower melt viscosity.(5) However, the type and the amount of plasticizer affect the properties of the bottle and cable compound, as shown in Figures 4.10-4.11. Figure 4.12 shows the melt flow index of the effect of varied amounts of DOP masterbatches, formulation Nos. F1-F3, compared to the bottle compound and the cable compound. These show that the melt flow index increases dramatically depending on the amount of DOP. Furthermore, the melt flow indexes of the masterbatches are higher than the bottle or the cable compound. The surface and color dispersion of the strip, the extrusion test, of the blending in the bottle and the cable compound with these masterbatches at the ratio 100:5 are not effected. The tensile strength, elongation, the hardness, the volume resistivity of the blending in cable compound have no significant effect, but the tendency of the impact strength of the blending in bottle compound is lower due to DOP containing, as shown in Figures 4.13-4.16.

The lower K value of PVC resin (K=56) used in the masterbatch, formulation Nos. F4-F5, show ease to blend in both compounds while the surface property is not effected. The physical properties do not differ significantly from most of the PVC resin with K value 58, as shown in Figures 4.13-4.16.

The optimized formulation of the basis masterbatch is shown below.

PVC SG560	100
DOP	25
Ca/Zn	4
ESBO	5
Lubricant	0.3

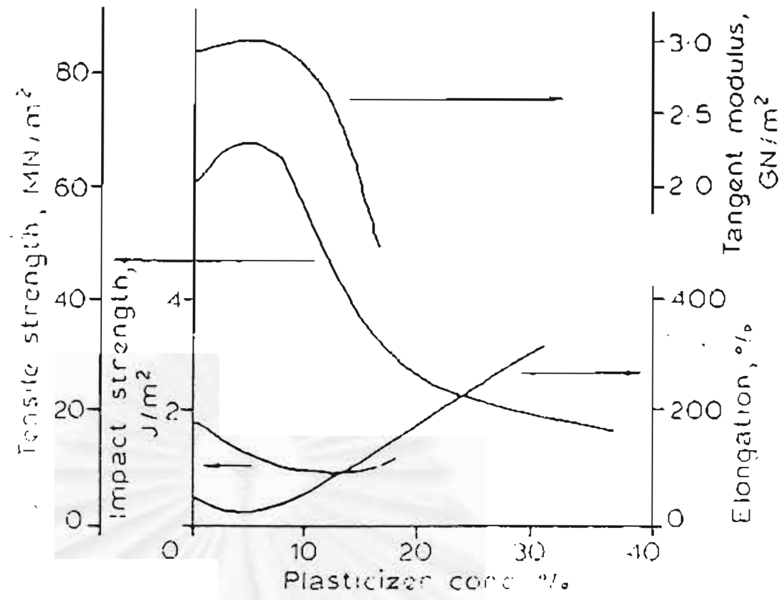


Figure 4.10 Some effect of DOP on the physical properties

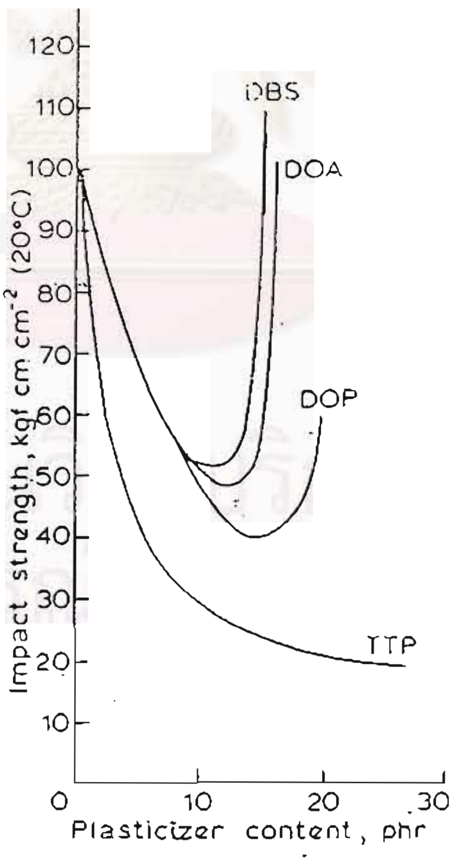


Figure 4.11 Effect of some plasticizers on the impact strength of a PVC composition

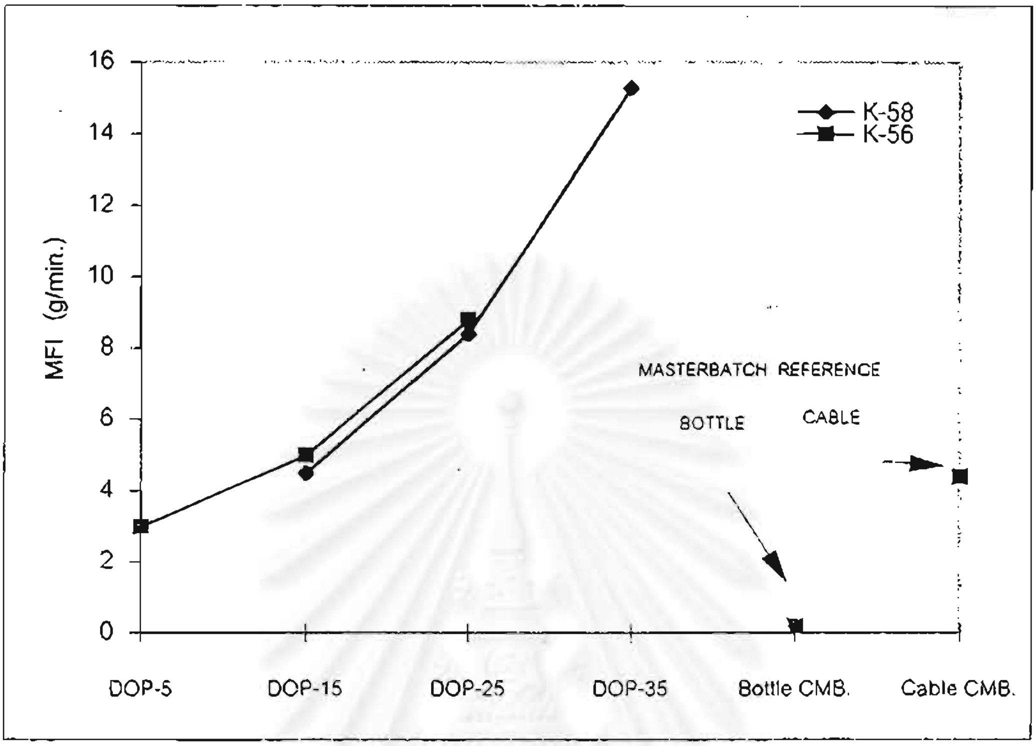


Figure 4.12 The effect of varied amounts of DOP and various K values of PVC resin on the melt flow index (MFI) of the masterbatch, experiment n=2

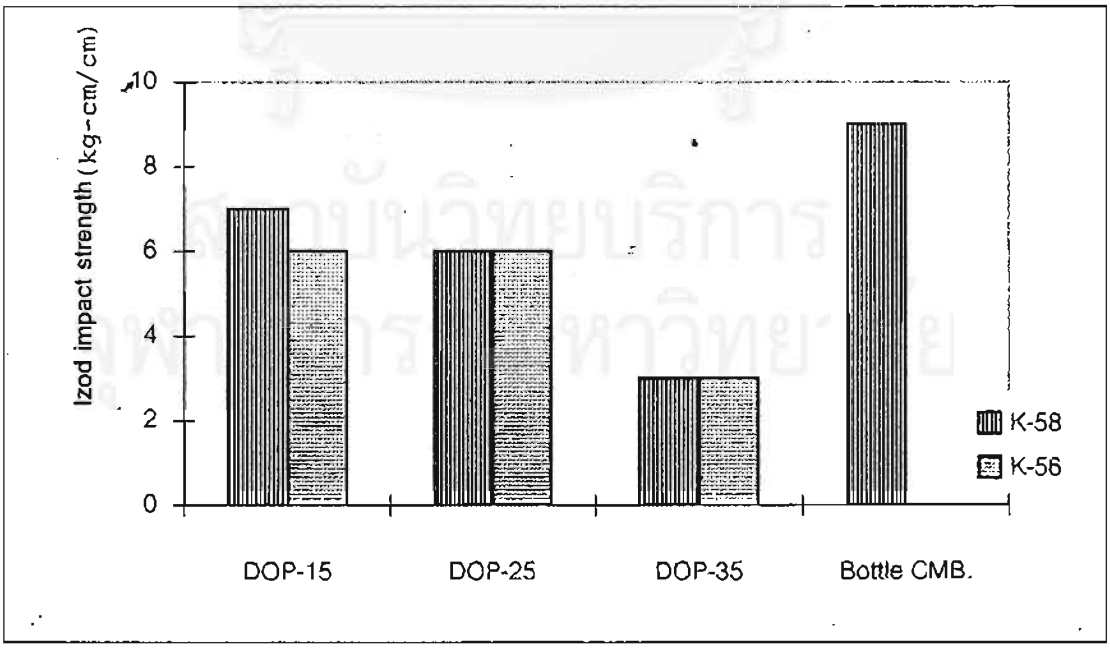


Figure 4.13 The effect of varied amounts of DOP and various K values of PVC resin on the izod impact strength of the bottle compound, experiment n=2

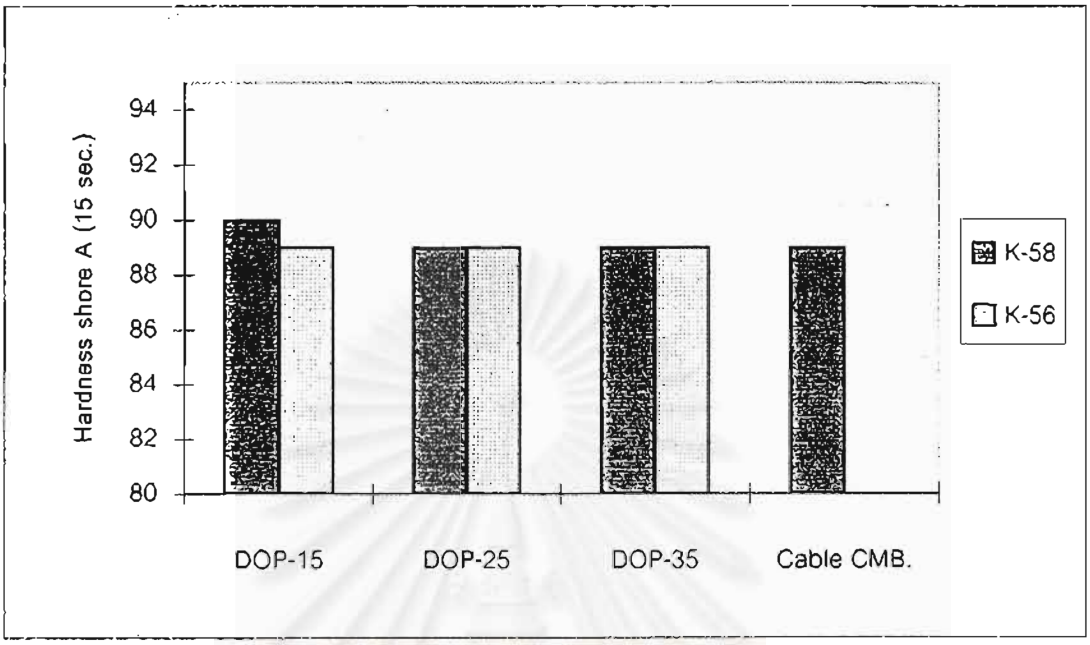


Figure 4.14 The effect of varied amounts of DOP and various K values of PVC resin on the hardness shore A (15 sec.) of the cable compound, experiment n=1

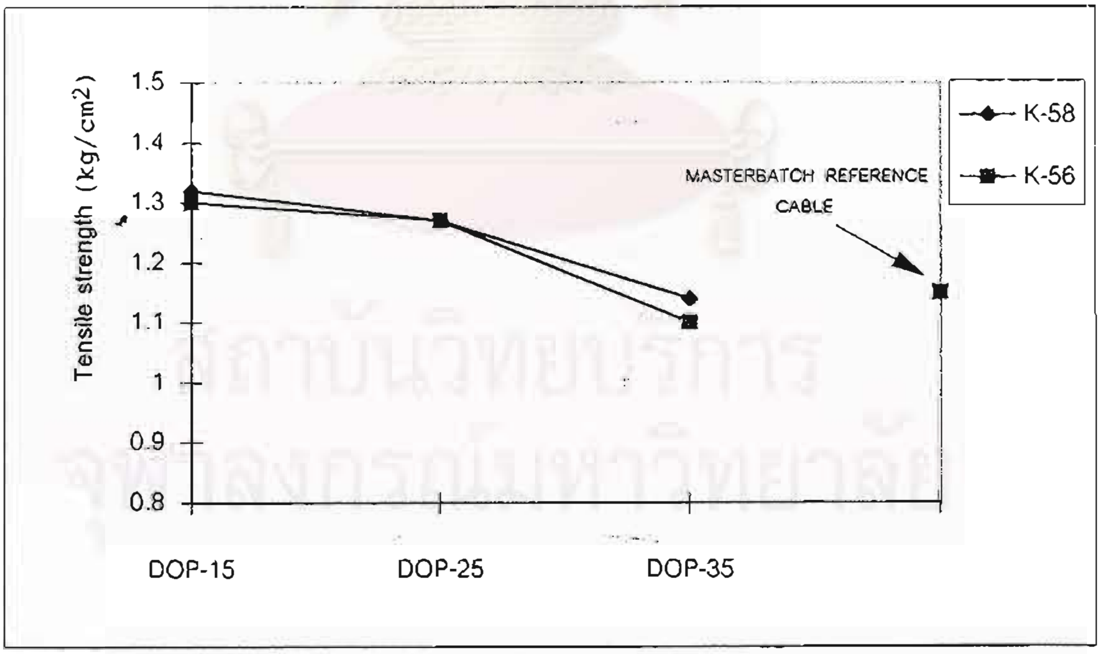


Figure 4.15 The effect of varied amounts of DOP and various K values of PVC resin on the tensile strength of the cable compound, experiment n=3

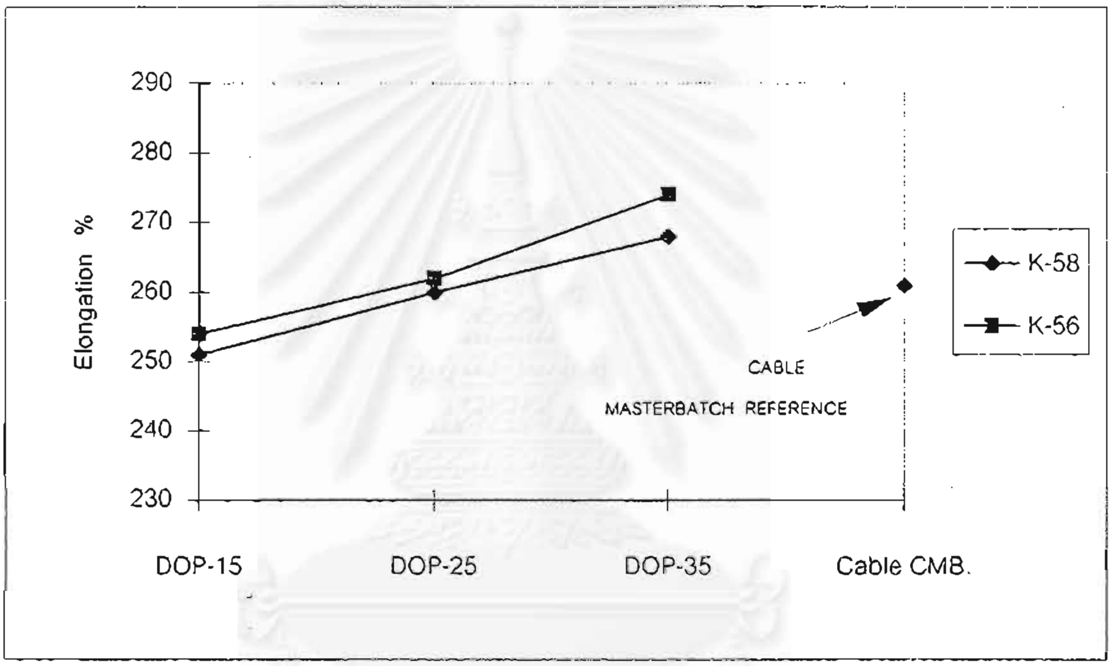


Figure 4.16 The effect of varied amounts of DOP and various K values of PVC resin on the elongation of the cable compound, experiment n=3

4.2) The effect of the amount of pigment on the processing

The establishment of the required amount of the pigment, Blue 59245 from the World Pigment Co., was carried out by varying its amount from 10 to 30 phr under the same processing conditions, with the temperature profile of extrusion of 136-140-144-146°C. At the low amount of the pigment, the processing condition is the same as for the base masterbatch compound, but at the 30 phr the temperature profile of extrusion should be increased 3°C due to the change of fusion property.

4.3) The properties of the blending with the color masterbacth

The color masterbatches were blended in the cable compound and the bottle compound at varied ratios of 100:1, 100:3 and 100:5. Most of their properties were not significantly different from the blending with the reference color masterbatch, as shown in Figures 4.17-4.22, but the impact strength is decreased by 15 % approximately. However it is in the range of acceptance for a PVC bottle which its volume is not over than 500 ml.

When blending the masterbatch in the bottle compound at the ratio of 5:100 in the blow molding process with the color masterbatch at 10 phr. of pigment, the appearance of the 1 liter bottle was good. Although the blending in the cable compound in the cable processing cannot be done, the blending in the extrusion process is similar in that they were extruded with the extruder but without the inner conductivity wire. The surface property or its general appearance of the strand is good..

The cost of the color masterbatch for both the bottle and the cable containing 10 phr of pigment is higher than the one for the cable by approximately 13%, but it is 11 % lower than for the masterbatch for bottle. The cost of any amounts of pigment is shown in the appendix c. However, the convenience of using only one color masterbatch is also an importance in that the storage, handling, and working are greatly simplified thereby further streamlining operations. In addition, the possibility of using the incorrect color masterbatch is eliminated.

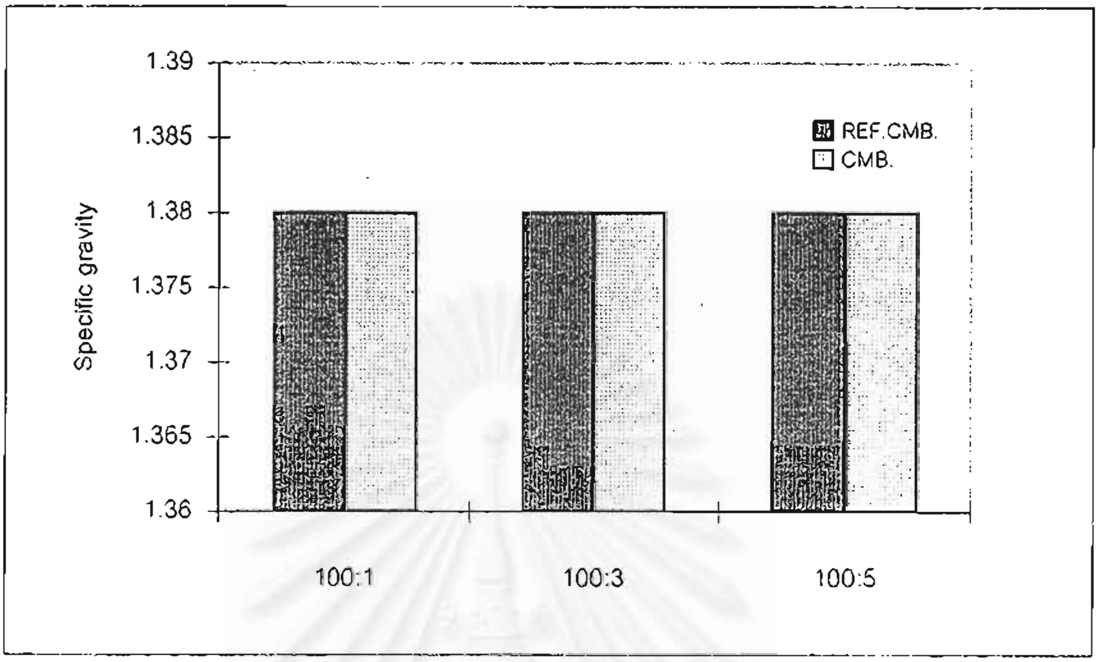


Figure 4.17 The effect of varied blending ratios on the specific gravity of the cable compound, experiment n=2 REF. CMB. : reference color masterbatche CMB. : the masterbatch

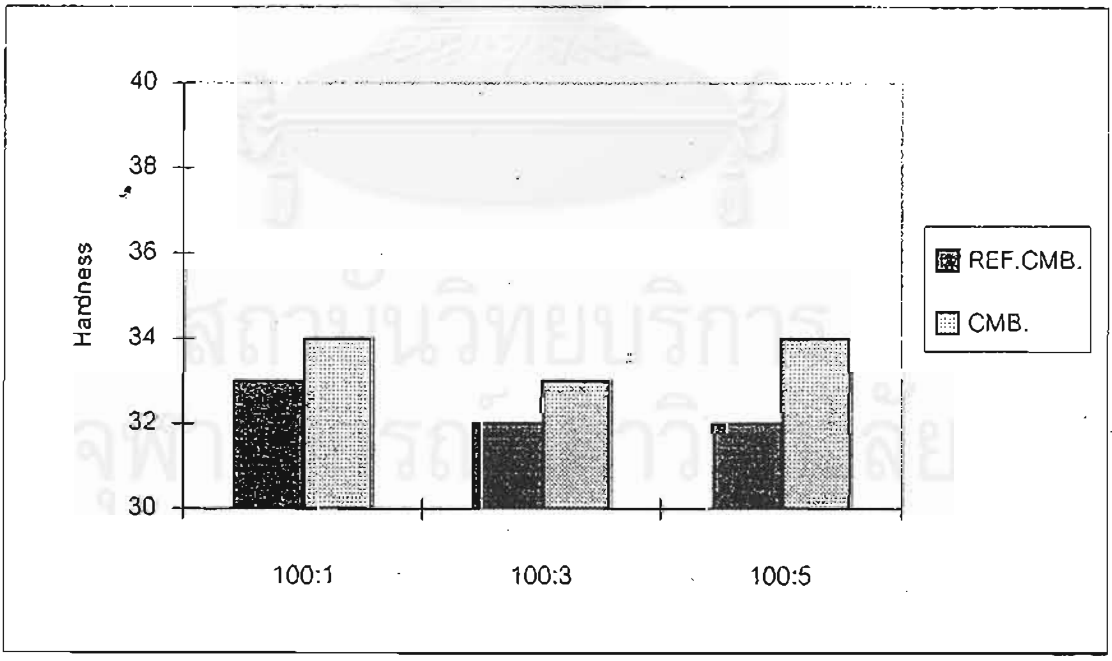


Figure 4.18 The effect of varied blending ratios on the hardness shore D (15 sec.) of the cable compound, experiment n=3 REF. CMB. : reference color masterbatche CMB. : the masterbatch

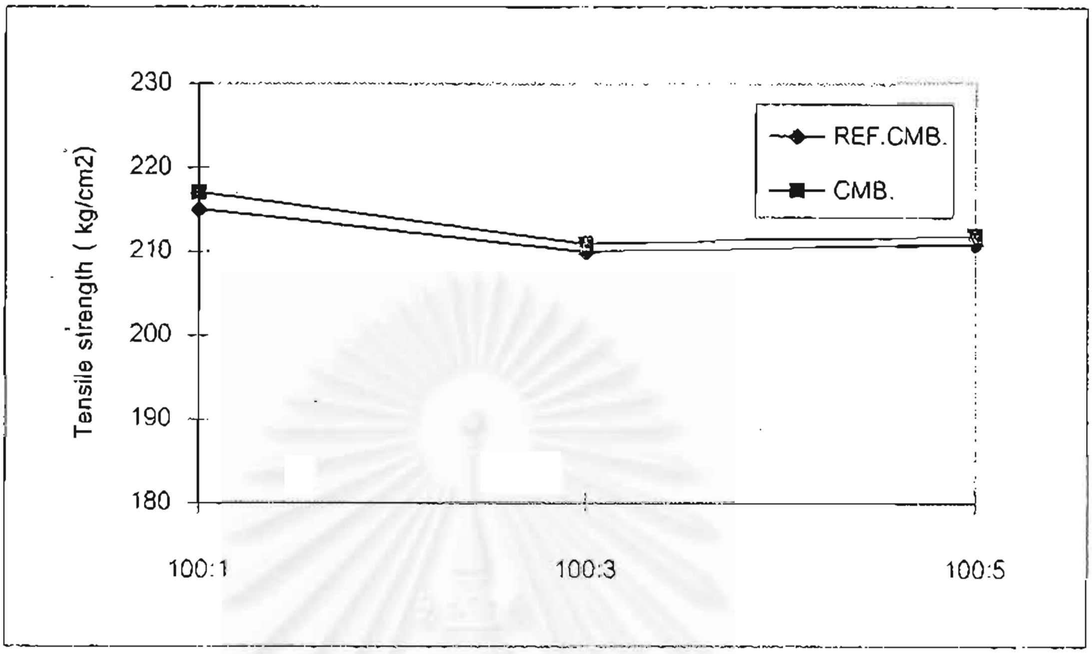


Figure 4.19 The effect of varied blending ratios on the tensile strength of the cable compound, experiment n=3 REF. CMB. : reference color masterbatche CMB. : the masterbatch

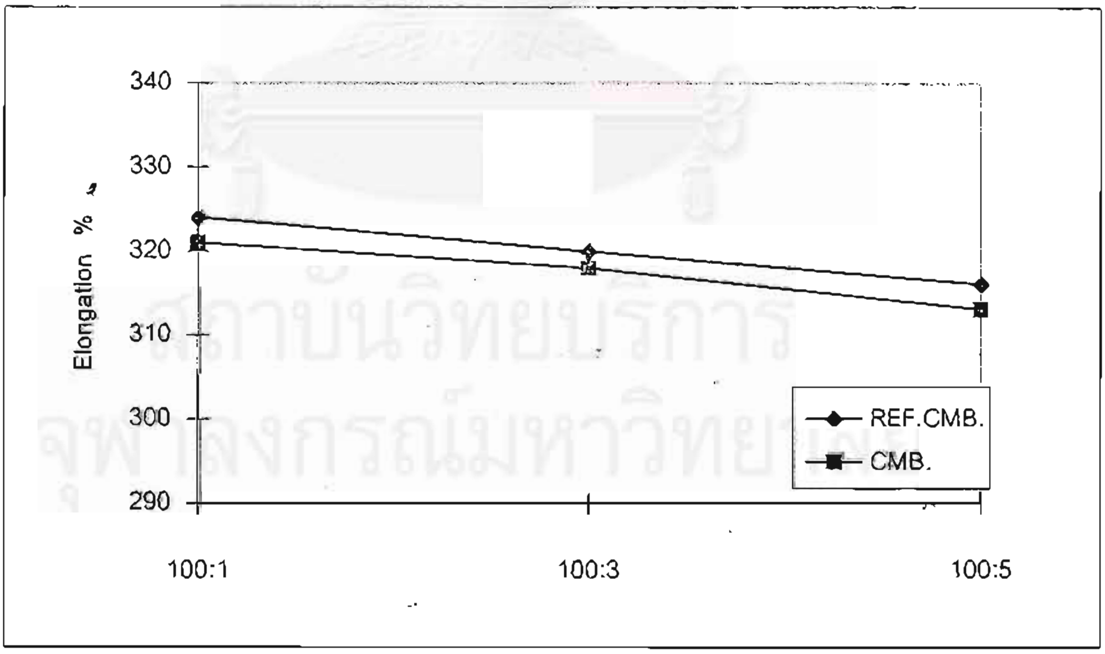


Figure 4.20 The effect of varied blending ratios on the elongation of the cable compound, experiment n=3

REF. CMB. : reference color masterbatche CMB. : the masterbatch

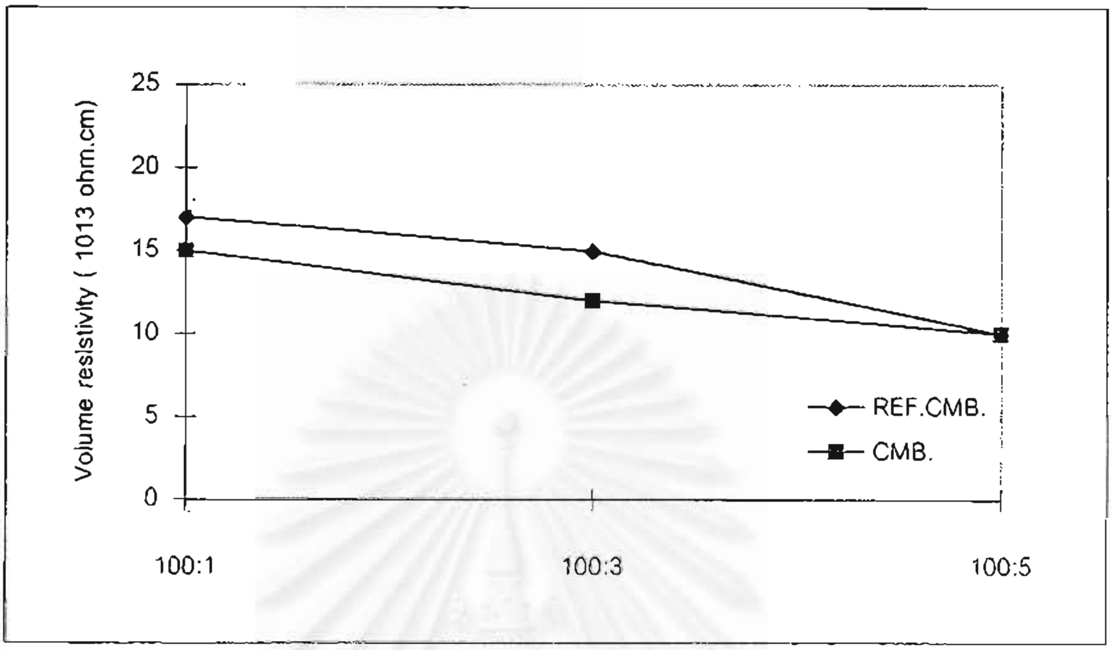


Figure 4.21 The effect of varied blending ratios on the volume resistivity at 25°C of the cable compound, experiment n=2 REF. CMB. : reference color masterbatche CMB. : the masterbatch

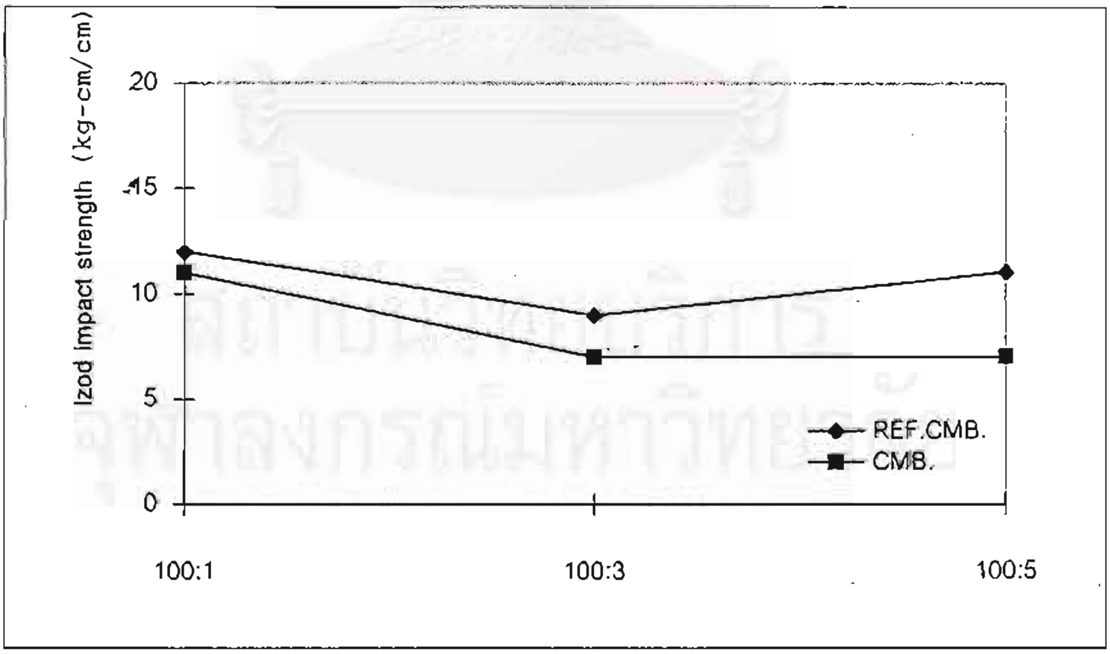


Figure 4.22 The effect of varied blending ratios on the izod impact strength of the bottle compound, experiment n=6 REF. CMB. : reference color masterbatche CMB. : the masterbatch

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

5.1 Conclusions

The color masterbatches for blending both of the cable and the bottle compound have been developed from the one pack stabilizers with the costabilizers to improve initial color and long term heat stability and prevent sulfur staining. It was found that the compound containing the Ca/Zn stabilizer at 4 phr and the ESBO at 5 phr is optimal.

The melting property is another important one to be optimized since it must be used for two systems ; a plasticized system : the cable compound and an unplasticized system : the bottle compound. The compound containing DOP at 25 phr and ESBO at 5 phr whose melting property was compatible with both the cable and the bottle mixes was used to optimize the final melting property. PVC resin, SG560, which K value 56 provides better melting property, it also slightly effects the other physical properties of the blending compound. In addition, the extrusion profile and the blow molding bottle of the blending compound has been optimized. These compounds are also suitable for processing with high shear machines which can provide homogeneous melts.

In conclusion, the color masterbatch compound for both of the PVC cable and the PVC bottle compound has been developed for blending at the ratio of 5:100 without having significant effect on the surface appearance, heat stability, hardness, tensile strength, elongation, and volume resistivity, while the impact strength shows a tendency to decrease. In general the ratio of the blending in the PVC bottle is less than 100:1, therefore, the impact strength is not effected.

5.2) Suggestions

The following suggestions are given for future research.

1. Develop the lower cost masterbatch as the cost of the masterbatch is higher than that of the reference color masterbatch for the cable.
2. Study the lubricant system to reduce the amount of DOP for improvement of impact strength.

REFERENCES

1. Titow, W. V. PVC plastic properties. Barking : Elsevier Science, 1990.
2. Popli, R., Mauer, D. H., and Witenhafer, D. E. Carrier resin for a muti-polymer solid color concentrate. J. of Vinyl Technology. 13, No.4, (December 1991) : 208-211.
3. Gachter, R., and Muller, H., Plastic additive handbook. Munchen Wien : Carl Hauser Verlag, 1983.
4. Sarvis, H. E. The coloring of PVC. J. of Vinyl Technology. 15, No.3, (September 1993) : 148-152.
5. Nass, L. I. Encyclopedia of PVC. Vol. 1-2. New York : Marcel Dekker, Inc., 1976.
5. Patsis, V. A. Advances in the stabilization and controlled degradation of polymers. Pennsylvania : Technomic, 1989.
7. Schnabel, W. Polymer degradation principles and practical applications. Munchen Wien : Carl Hauser Verlag, 1981.
8. Edenbaum, J. Plastics additives and modifiers handbook. Great Yarmouth: Galliard, 1996.
9. Brydson, J. A. Flow properties of polymer melts. New York : Van Nostrand Reinhold, 1980.
10. Tetsuo, T. and Taro, M. Recently developed non-lead stabilizers for wire and cable. ANTEC.'97 (1997) : 3496-3502.
11. Othmer, K. Encyclopedia of chemical technology. New York : Wiley, 1982
12. Hawkins, W. L. Polymer Degradation and Stabilization. Berlin, Heidelberg : Springer Verlag, 1984.

13. Solera, P. New trend in polymer stabilization. J. of Vinyl& additive Technology. 4, No.3, (September 1998) : 197-210.

14. Joseph, W. Organic costabilizers for the stabilization of PVC. J. of Vinyl Technology. 3, No.3, (September 1997) : 205-209.

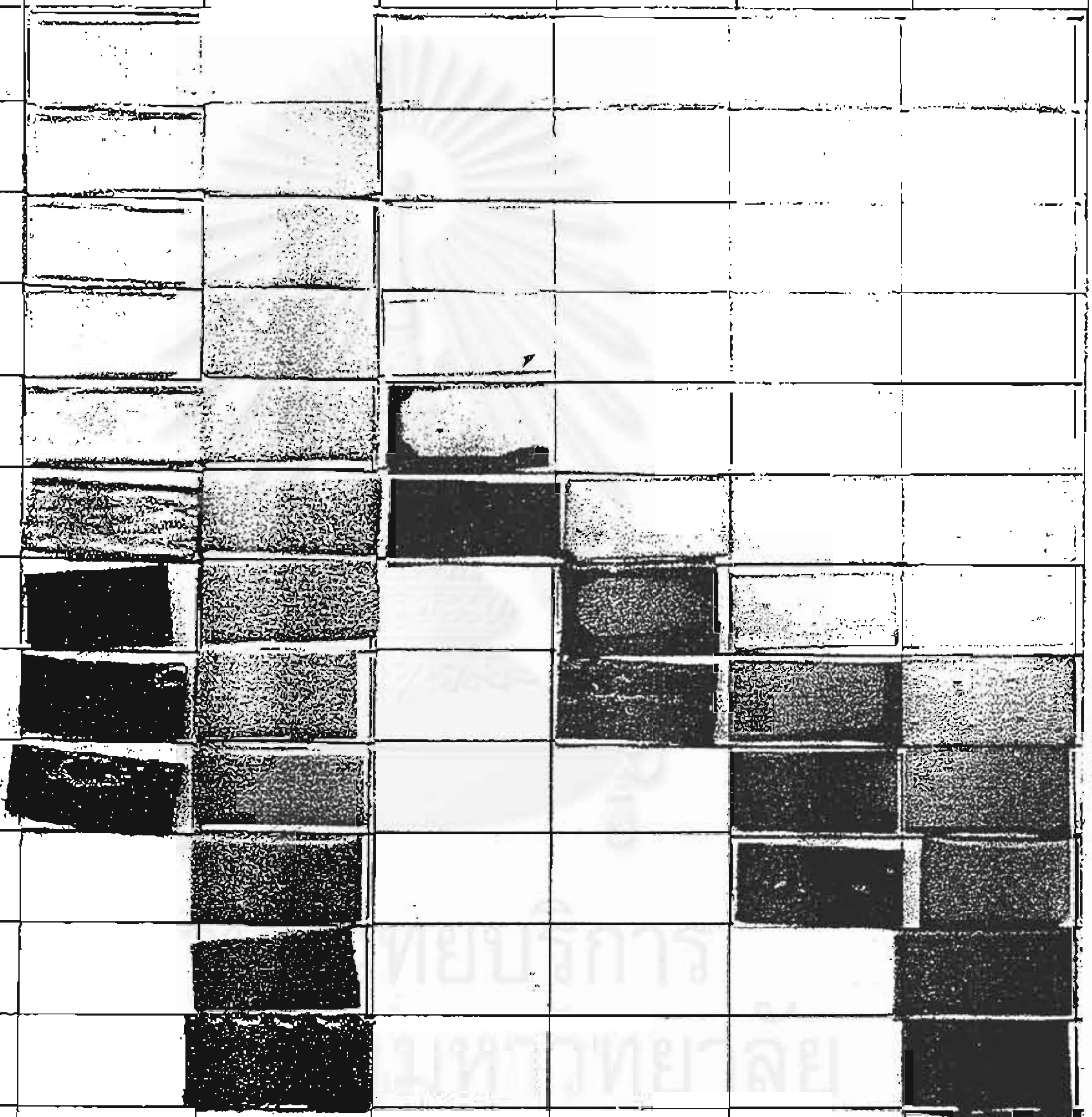
APPENDIXES

APPENDIX A

The effect of various amounts of Ca/Zn stabilizer on heat stability

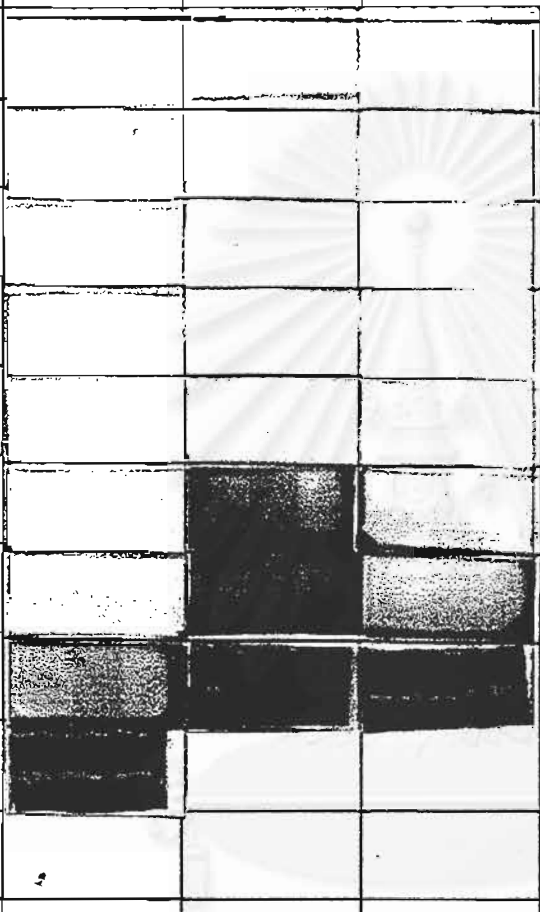
TEMPERATURE 195°C

TIME (min.)	FORMULATION NO.					
	Bottle compound	Cable compound	B1	B2	B3	B4
0						
5						
10						
20						
30						
40						
50						
60						
70						
80						
90						
100						
Ca/Zn (phr)			2	4	6	8



The effect of various co-stabilizer on heat stability

TEMPERATURE 195^{o}c



TIME (min.)	FORMULATION NO.					
	B5	B6	B7			
0						
5						
10						
20						
30						
40						
50						
60						
70						
80						
90						
100						
Ca/Zn (phr)	6	6	6			
ESBO (phr)	3	0	3			
Co-sta. A/B* (phr)	0	0.5/0.5	0.5/0.5			

Remark A : tris(nonylphenyl)phosphaite, B : stearoyl benzoyl methane

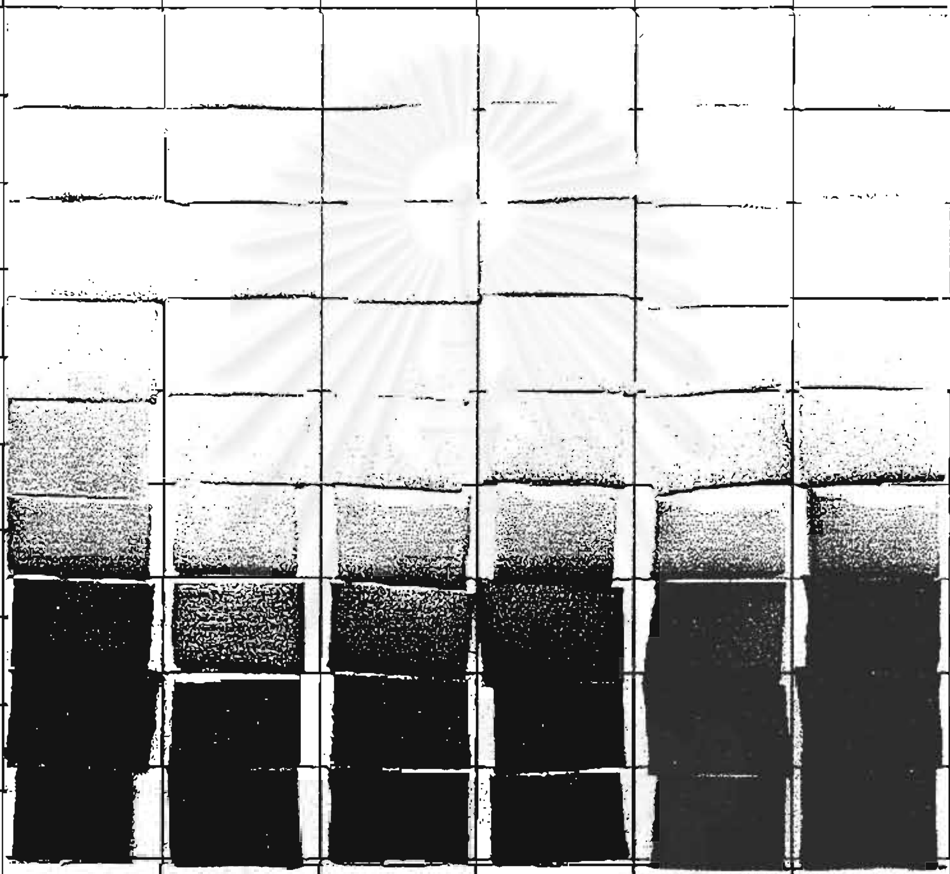
The effect of various DOP/ESBO ratio of the masterbatch on heat stability

TEMPERATURE 195°C

TIME (min.)	FORMULATION NO.						
	Cable compound	C1	C2	C3	C4	C5	C6
0							
15							
30							
45							
60							
75							
90							
105							
120							
135							
150							
100							
ESBO (phr)		5	10	15	20	25	
DOP (phr.)		25	20	15	10	5	

The effect of various DOP/ESBO ratio of the cable compound on heat stability

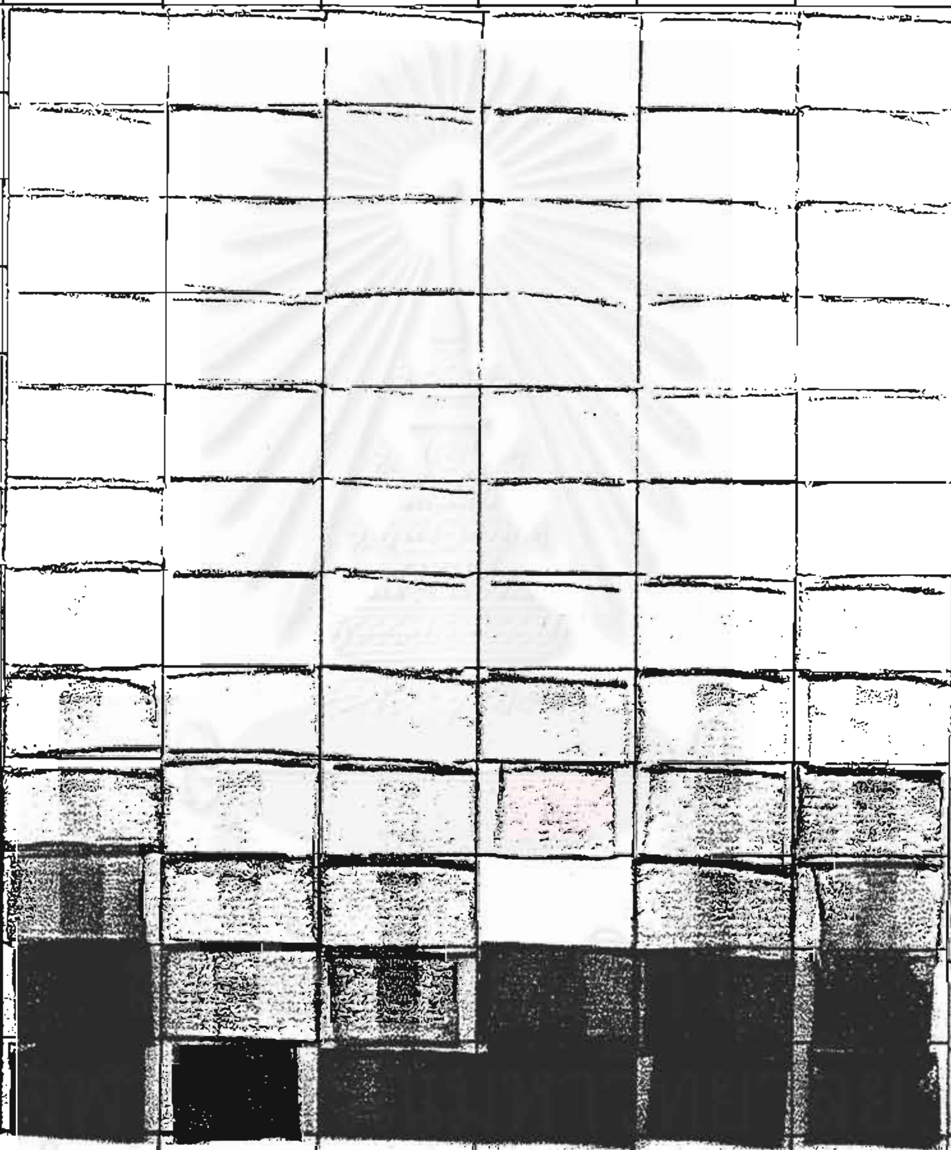
TEMPERATURE 190°c



TIME (min.)	FORMULATION NO.						
	Cable compound	C1	C2	C3	C4	C5	C6
0							
20							
40							
60							
80							
100							
120							
140							
180							
180							
ESBO (phr)		5	10	15	20	25	30
DOP (phr.)		25	20	15	10	5	0

The effect of various DOP/ESBO ratio of the bottle compound on heat stability

TEMPERATURE 190°C

TIME (min.)	FORMULATION NO.						
	Bottle compound	C1	C2	C3	C4	C5	
0							
15							
30							
45							
60							
75							
90							
105							
120							
135							
150							
165							
180							
ESBO (phr)		5	10	15	20	25	30
DOP (phr.)		25	20	15	10	5	0

APPENDIX B

Fikentscher K value or K value is a number using as an index of molecular weight that common use in PVC polymer. It is related to the viscosity ratio (η/η_o) by the expression

$$\ln(\eta/\eta_o) = \frac{cK}{1000}\left(\frac{75K}{1.5cK + 1000} + 1\right)$$

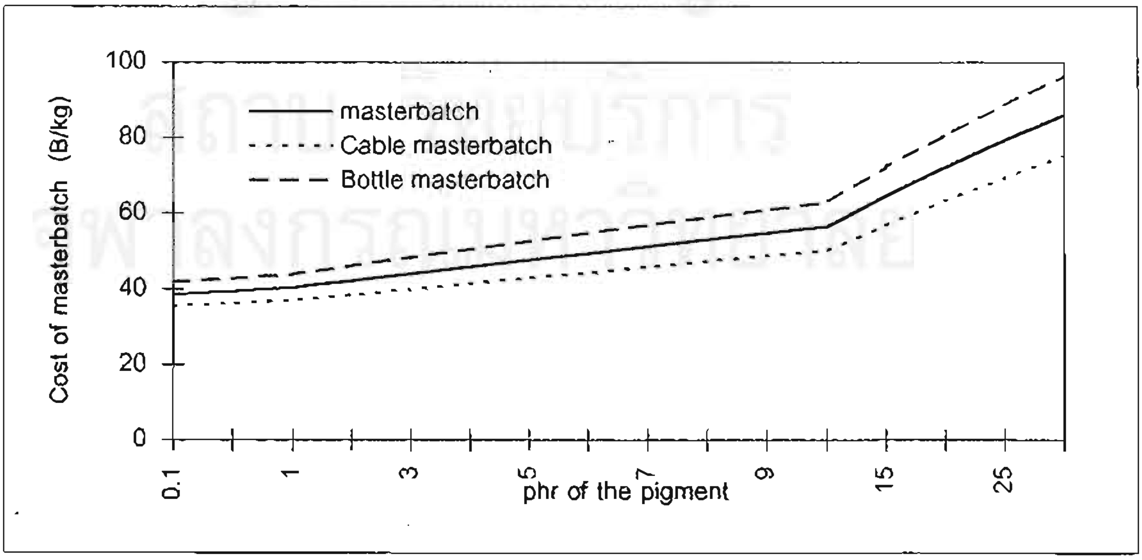
η	viscosity of the polymer solution
η_o	viscosity of the solvent
c	concentration, in g per ml. of solution

Most commercial PVC polymers have K values within the range 50-80.

APPENDIX C

Cost of the masterbatch, reference cable and bottle color masterbatch

Amount of pigment, phr	Masterbatch	Ref. cable masterbatch+M17		Ref. bottle masterbatch	
	baht/kg (1)	baht/kg (2)	% (1-2)	baht/kg (3)	% (1-3)
0.1	38.5	35.6	-7.7	41.9	8.6
0.5	39.4	36.2	-8	42.8	8.8
1	40.3	37	-8.3	43.9	9
2	42.2	38.5	-8.8	46.2	9.4
3	44.1	40	-9.2	48.4	9.8
4	45.9	41.5	-9.6	50.5	10.1
5	47.7	43	-9.9	52.7	10.3
6	49.5	44.4	-10.3	54.8	10.6
7	51.3	45.9	-10.6	56.9	10.8
8	53.1	47.4	-10.8	58.9	10.9
9	54.8	48.8	-11	60.9	11.1
10	56.5	50.2	-11.2	62.9	11.2
15	64.7	56.9	-11.9	72.2	11.6
20	72.3	63.3	-12.3	80.8	11.8
25	79.4	69.4	-12.5	88.8	11.8
30	86.1	75.2	-12.6	96.3	11.8



CURRICULUM VITAE

Mr. Soonthorn Marksook was born on August 27, 1965 in Phuket. He graduated a B.Sc. in Chemistry from the Faculty of Science, Prince of Songkla University. He has been working at the Thai Plastic and Chemicals Public Co., Ltd. as a chemist in quality control department. Presently he is also a graduate student at the Program of Petrochemistry and Polymer Science, Chulalongkorn University for his Master degree in Petrochemistry.