ผลของสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีนคอมพาวนด์ต่อสมบัติเชิงกลของพอลิไวนิลคลอไรด์

นางสาวบูรณินทร์ แสงเอียด

จุฬาลงกรณ์มหาวิทยาลัย
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

EFFECTS OF STYRENE-METHYL METHACRYLATE/STYRENE-BUTADIENE COMPOUND ON MECHANICAL PROPERTIES OF POLY(VINYL CHLORIDE)

Miss Buranin Saengiet

จุฬาลงกรณ์มหาวิทยาลัย
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A Thesis Submitted in Partial Fulfillment of the Requirements
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Field of Study	Petrochemistry and Polymer Science
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โดยทั่วไปพอลิไวนิลคลอไรด์ (พีวีซี) ที่ไม่มีการเติมสารเสริมสภาพพลาสติกหรือสารเพิ่มความทนทานต่อแรงกระแทกจะแข็งเปราะ จุดมุ่งหมายของงานวิจัยนี้เน้นการปรับปรุงสมบัติเชิงกลของพีวีซีด้วยสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีนเบลนด์ (ยางสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีน) ซึ่งทำหน้าที่เป็นสารเพิ่มความทนทานต่อแรงกระแทก ทำการเตรียมพีวีซีเบลนด์ที่มีสัดส่วนของยางสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีนในปริมาณ 2.5, 5, 7.5 และ 10 phr กระบวนการผสมอาศัยเครื่องผสมสองลูกกลิ้งที่อุณหภูมิ 170 °C เป็นเวลา 5 นาที จากนั้นทำการขึ้นรูปด้วยเครื่องขึ้นรูปแบบอัดเบ้า ตรวจสอบหมู่ฟังก์ชันด้วยเทคนิค FTIR พบว่า เกิดการเปลี่ยนแปลงตำแหน่งของหมู่คาร์บอนิลของยางสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีนจาก 1730 cm^{-1} ไปยัง 1736 cm^{-1} ซึ่งบ่งบอกถึงสภาพผสมเข้ากันได้ของพีวีซีกับยางสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีน เมื่อศึกษาสมบัติเชิงกลทางด้านความทนแรงกระแทก มอดุลัส ความทนแรงดึง ความทนแรงดัดโค้ง ความทนต่อแรงกด และอุณหภูมิโก่งตัวด้วยความร้อนพบว่า ผลของความทนแรงกระแทกของพีวีซีเพิ่มขึ้นเมื่อเพิ่มปริมาณยางสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีนเป็นผลจากการกระจายตัวที่ดีของยางในพีวีซี จากผลการทดลอง ที่ปริมาณยางสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีน 5 และ 10 phr มีค่าความทนแรงกระแทก 3.30 and 6.38 kJ/m^2 ตามลำดับ เป็นผลเนื่องจาก ยางสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีนทำหน้าที่เป็นสารเพิ่มความทนทานต่อแรงกระแทก ซึ่งยืนยันผลการทดลองจากภาพ SEM จากการทดสอบสมบัติเชิงกลทางด้านมอดุลัส ความทนแรงดึง ความทนแรงดัดโค้ง ความทนต่อแรงกดพบว่า มีค่าลดลงเมื่อปริมาณยางสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีนเพิ่มขึ้น ในขณะที่อุณหภูมิโก่งตัวด้วยความร้อนมีแนวโน้มเปลี่ยนแปลงเล็กน้อย อีกทั้งค่าความยืดสูงสุด ณ จุดขาดเพิ่มขึ้นอย่างต่อเนื่องเมื่อเพิ่มปริมาณยางสไตรีน-เมทิลเมทาคริเลต/สไตรีน-บิวทาไดอีน นอกจากนี้ยังมีการศึกษาการแพร่ของสารเสริมสภาพพลาสติกพบว่า สารเสริมสภาพพลาสติกในพีวีซีที่มียางเป็นองค์ประกอบนั้นเป็นผลทำให้สารเสริมสภาพพลาสติกมีการแพร่ออกมายังพื้นผิวที่รวดเร็วกว่าการมีเฉพาะสารเสริมสภาพพลาสติกในพีวีซี

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต ....
ปีการศึกษา 2557 ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

5472014423 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORDS: POLY(VINYL CHLORIDE), SMMA/SBR RUBBER, IMPACT MODIFIER, 88 STRENGTH

BURANIN SAENGIET: EFFECTS OF STYRENE-METHYL METHACRYLATE/STYRENE-BUTADIENE COMPOUND ON MECHANICAL PROPERTIES OF POLY(VINYL CHLORIDE). ADVISOR: ASST. PROF. FUANGFA UNOB, Ph.D., CO-ADVISOR: ASSOC. PROF. KAWEE SRIKULKIT, Ph.D., 88 pp.

Generally, poly(vinyl chloride) (PVC) without the addition of plasticizer or impact modifier is rigid and brittle. The aim of this research was to improve the mechanical properties of PVC using styrene-methyl methacrylate/styrene-butadiene blend (SMMA/SBR rubber) as an impact modifier. PVC containing SMMA/SBR rubber having SMMA/SBR contents of 2.5, 5, 7.5 and 10 phrs were prepared using two-roll mill set the conditions as follows: temperature of 170 °C and time of 5 min. Then, compression molding was carried out to prepare testing samples. FTIR analysis of SMMA/SBR rubber containing PVC samples showed the slight shift of absorption peak of methyl methacrylate carbonyl group (C=O) from 1730 to 1736 cm^{-1}, indicating the compatibility between additives and PVC. The effects of SMMA/SBR rubber on mechanical properties including impact strength, tensile properties, flexural strength, hardness and heat distortion temperature (HDT) were evaluated by standard tests. The impact strength of SMMA/SBR rubber containing PVC increased significantly with an increase in the SMMA/SBR content (ex. 5 phr and 10 phr SMMA/SBR rubbers produced impact strengths of 3.30 and 6.38 kJ/m^2 respectively), resulting from the action of SMMA/SBR rubber phase as an impact modifier as revealed by SEM images. Regarding to the modulus, tensile strength, flexural strength and hardness, these values decreased with an increase in the SMMA/SBR rubber content. In contrast, the HDT slightly increased and elongation at break gradually increased. These results were related to the weak interfacial adhesion between PVC matrix and rubber phase. Furthermore, the migration ability of DINP in PVC containing SMMA/SBR rubber was relatively faster than those in neat PVC due to the fact that DINP migration ability in the interphase was faster than those DINP in PVC matrix.

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

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CHAPTER I

INTRODUCTION

1.1 Introduction

Thermoplastic materials including poly(vinyl chloride) are commonly found in household products which become more and more important in everyday life. Poly(vinyl chloride), commonly known as PVC, is one of versatile polymers that has been widely used from the past until now [1]. The usage of PVC was pervasively applied, for example, in the part of packaging (food packaging and wrap film), decorative construction part (pipe, window frame and hose) and in the part of medical applications (blood bags and medical tubes). Because of its good properties such as chemical resistance, good insulator and wide range usage of PVC that depend on the levels of plasticizer, PVC was one of the stars of plastic era [2]. Even though PVC is thermoplastic but processing of PVC without additives addition is not possible due to the heat deteriorated problem. Therefore, the additives addition is imperative. In order to obtain further various properties of PVC, the amount of additives in PVC formulation is the most important. Especially the amount of plasticizer should be fallen in the range between 5 and 20% w/w for rigid products and more content of plasticizers for the desired flexibility. Phthalate esters are the most widely applied in compounding of PVC and its utilization depends on proportion of plasticizer content. However, the usability of plasticized PVC is harmful to humans, animals and environments because plasticizers tend to release to the surface of products. Migration of plasticizers to the surface of products caused the decrease in final properties and terrible toxicity to the nature. Recently, the U.S. Consumer Product Safety Commission (CPSC) prohibited the usage of phthalate plasticizers because these plasticizers are harmful to human health and

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environments. Furthermore, it has been addressed that the plasticizers can accumulate in body fluid like blood or plasma and tissues like liver, pituitary gland or testicles. Because of vicious toxicity of used plasticizer, thus health-concerned products, especially medical devices, children toys and food packaging are not allowed to contain toxic plasticizer. Importantly, enhancement of the toughness of PVC requires not only the addition of the plasticizers but also the usage of impact modifiers. Many impact modifiers that are commercially used in PVC industry such as chlorinated polyethylene (CPE) [3], acrylonitrile-butadiene-styrene (ABS) [4, 5] and methyl methacrylate-butadiene-styrene (MBS) [6, 7]. Principally, the rubber particles dispersed in polymer is a key for improving toughness property of PVC [4]. Importantly, the good compatibility between PVC and the impact modifier has to be considered in order to obtained the required properties of the products [8]. In the previous work, plasticizers have been used to improve the flexibility of rigid PVC but its toxicity is the main disadvantage. Impact modifier is also the major of additives for enhancement of the rigidity of PVC. Mostly, ABS is used to enhance toughness of rigid PVC which its partial miscibility with PVC is the major drawback and also the products are opaque. In this work, styrene-methyl methacrylate/styrene-butadiene rubber (SMMA/SBR rubber) as the impact modifier was employed to improve the toughness properties of rigid PVC and reduce the usage of plasticizer in PVC. It was believed that PVC and SMMA/SBR rubber were compatible due to physical interaction between carbonyl groups (C=O) of methyl methacrylate and hydrogen atom of PVC CH-Cl group [9]. Consequently, the aim of this work was to determine the influences of plasticizer and SMMA/SBR rubber content on physical interaction, morphology analysis and mechanical properties.

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1.2 Objectives

1.2.1 To improve the impact strength of PVC using styrene-methyl methacrylate/styrene-butadiene blend (SMMA/SBR rubber) as an impact modifier.

1.2.2 To reduce the usage of plasticizer for rigid PVC.

1.3 Scope of the investigation

1.3.1 Study the previous and related literature researches.

1.3.2 Prepare the plasticized PVC, PVC/SMMA/SBR blends and plasticized PVC/SMMA/SBR blends using two-roll mill machine with proportions as follows:

1.3.2.1 Plasticizer (2.5, 5 and 10 phr)

1.3.2.2 SMMA/SBR rubber (2.5, 5, 7.5 and 10 phr)

1.3.3 Produce the specimens of PVC blends using compression molding machine.

1.3.4 Characterize the PVC blends using various techniques as follows:

1.3.4.1 The functional groups observation by Fourier transform infrared spectroscopy (FTIR)

13.4.2. The morphology analysis by scanning electron microscopy (SEM)

1.3.5 Investigate the mechanical properties of samples as follows:

1.3.5.1 Tensile properties

1.3.5.2 Impact strength

1.3.5.3 Flexural strength

1.3.5.4 Heat distortion temperature (HDT)

1.3.5.5 Hardness durometer shore (type D)

1.3.6 Study the migration ability of plasticizer by different scanning calorimetry (DSC).

1.3.7 Conclude and discuss the results.

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CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Poly(vinyl chloride) (PVC)

2.1.1 Production of PVC [10, 11]

Poly(vinyl chloride), commonly known as PVC, was the first synthetic organic polymer which was found unexpectedly in 1872 by Baumann. It has been widely used since World War II. PVC has been one of the major manufacturing thermoplastics of the world and the second most used among plastic industry. Figure 2.1 shows the proportion of different polymer used in plastic consumptions.

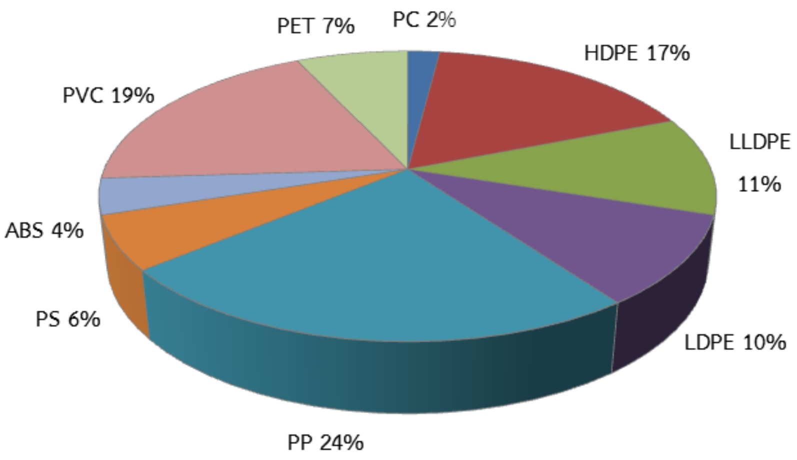

Figure 2.1 Plastic consumptions in 2007

The manufacture of PVC is shown in Figure 2.2. Oil, refined natural gas and cracked ethylene were used as raw materials in PVC manufacturing. Ethylene and chlorine as products from salt (NaCl) electrolysis reacted together to form intermediate called ethylene dichloride (EDC), then EDC was thermally cracked to vinyl chloride monomer (VCM). The beginning of polymerization reaction is thermal decomposition to generate free radical initiators. An initiator fragment reacts with olefin double bond of VCM, producing free radicals on the chain end which subsequently propagate into the next VCM to obtain the series of sequential additions of monomer unit.

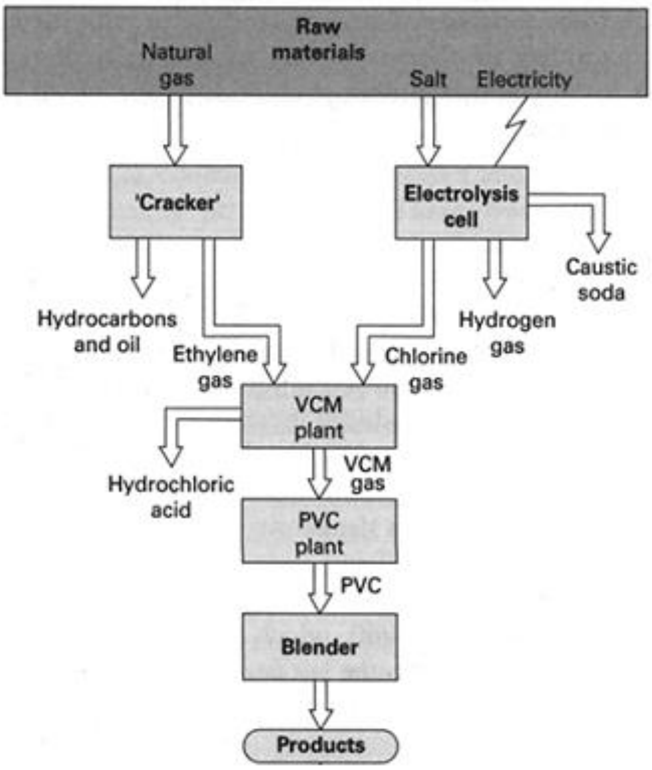

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Figure 2.2 Manufacturing of PVC [12]

2.1.2 Polymerization process of PVC [10]

Vinyl chloride monomer (VCM) is colorless liquid having boiling point at -13 °C. VCM is polymerized via free-radical polymerization process as shown in Figure 2.3. Due to the low boiling point of VCM, the polymerization process of VCM must be carried out at the condition at low temperature (50 °C). Mostly, PVC is produced via suspension polymerization which is better controllable reaction than the other processes.

Decomposition initiation: $I \longrightarrow 2R\bullet$

Initiation monomer: $R\bullet + H_2C{=}CHCl \longrightarrow R\text{-}CH2\text{-}CHCl\bullet$

Propagation: $R\text{-}CH_2\text{-}CHCl\bullet + nH_2C{=}CHCl \longrightarrow R\text{-}(CH_2\text{-}CHCl)\text{-}CH_2\text{-}CHCl\bullet$

Chain transfer to monomer: $\sim CH_2\text{-}CHCl\bullet + H_2C{=}CHCl \longrightarrow \sim CH_2\text{-}CH_2Cl + H_2C{=}CCl\bullet$

$\searrow \sim CH{=}CHCl + H_3C\text{-}CHCl\bullet$

Termination: $2 \sim CH_2\text{-}CHCl\bullet + H_2C{=}CHCl \longrightarrow \sim CH_2\text{-}CHCl\text{-}ClHC\text{-}CH_2\sim$

$\searrow \sim CH_2\text{-}CH_2Cl + \sim CH{=}CHCl$

$\sim CH_2\text{-}CHCl\bullet + R\bullet \longrightarrow \sim CH_2\text{-}CHCl\text{-}R$

Figure 2.3 Polymerization reaction pathway of VCM

2.1.3 Structure formulation of PVC [12]

PVC is a well-known commercial resin used in the polymer industry. The molecular weight of PVC is in a broad range depending on applications: from 39000 g/mol to 168000 g/mol and the degree of polymerization ranges from 625 to 2700. The chemical structure of PVC is presented in Figure 2.4.

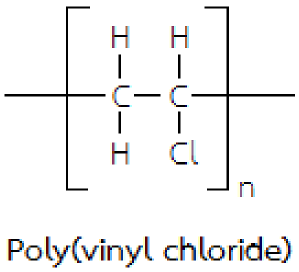

Figure 2.4 Chemical structure of PVC, where: n = degree of polymerization

Normally, PVC has linear structure that can be divided as formed into two types: first, head-to-tail (mostly) and others, head-to-head. The chemical structure of PVC contains units of –CH_2- alternated with –CHCl- units as illustrated in Figure 2.5.

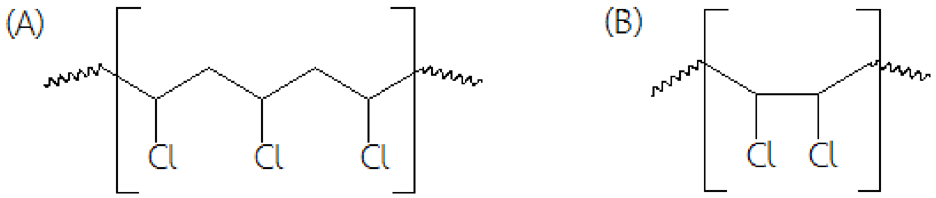

Figure 2.5 Molecular structure of PVC (A) head-to-tail and (B) head-to-head

The stereochemistry of approximately 56% syndiotactic type is found at polymerization temperature of 50 °C, causing the low crystallinity PVC type. Thus PVC is classified as the amorphous polymer. However, PVC is rigid polymer arising from the interaction force among pendant Cl group.

2.1.4 Additives for PVC

2.1.4.1 Plasticizers [13]

Plasticizers are low molecular weight materials incorporated into polymer to tailor desirable properties, especially flexibility. Plasticizers when added into polymers cause the decrease in melt viscosity, glass transition temperature and modulus of processed polymers. Plasticizers can be classified as internal, external, primary and secondary plasticizers. Internal plasticizers can reduce crystallinity and intermolecular force between chains of polymers. Mechanism action of external plasticizers is physical reaction, but not chemical interaction with polymer. Primary and secondary plasticizers concern the compatibility with polymers. Primary plasticizers infiltrate in the part of crystalline polymer and secondary plasticizers are used as diluents for primary plasticizers.

2.1.4.2 Stabilizers [14]

During the processing of PVC, high temperature (around 180 °C) causes PVC degradation, losing atoms of chlorine and hydrogen which further accelerate the release of hydrogen chloride (HCl) gas. Addition of stabilizers is required in order to prevent initial elimination of HCl. Accordingly, the main additive constituents are metal soaps, metal salts and organometallic compounds thus these stabilizers can improve heat aging as well.

2.1.4.3 Lubricants [15]

During processing of PVC, excellent rheological behavior requires lubricants because lubricants can reduce friction between surface of materials and machines. Lubricants are commonly divided into internal and external lubricants. The internal lubricant improves flow characteristics of PVC and reduces melt viscosity in PVC matrix. In addition, external lubricant reduces gelation and enhances gloss of PVC.

2.1.4.4 Fillers [16]

Fillers are inorganic substances of which prominent role is to reduce costs. The required properties of fillers are to improve the stiffness of polymer. Calcium carbonate ($CaCO_3$) is a reinforcing filler that is widely used in PVC industry. There are two types of calcium carbonate which are ground calcium carbonate and precipitated calcium carbonate.

2.1.4.5 Pigments [17]

Pigments are additive which can be broadly categorized as inorganic and organic pigments. Inorganic pigments are oxides and salts of metals. There are plenty of essential inorganic pigments widely used in plastics, for example, titanium dioxide (whitening pigment), ultramarine (blue and violet pigment), chromes (yellow, orange and brown pigment), cadmiums (red, orange and yellow pigment) and iron oxide (brown and black pigment). In addition, organic pigments include phthalocyanines (blue and green pigment) and chromophthals (red and orange pigment). Inorganic pigments are cheaper and more stable than organic pigments but color strength and brightness of inorganic pigments are lower than organic pigments.

2.1.5 Properties of PVC

2.1.5.1 Thermal stability [10]

The thermal stability of neat PVC is low, especially during processing and preservation. At high temperature during processing, high mechanical stress and high exposure in UV light induce the degradation of PVC. The degradation of PVC occurs when hydrogen chloride (HCl) is prosperously eliminated as so called dehydrochlorination reaction that is illustrated in Figure 2.6. Consequently, it causes the discoloration of products, regression of mechanical properties and lowering of chemical resistance.

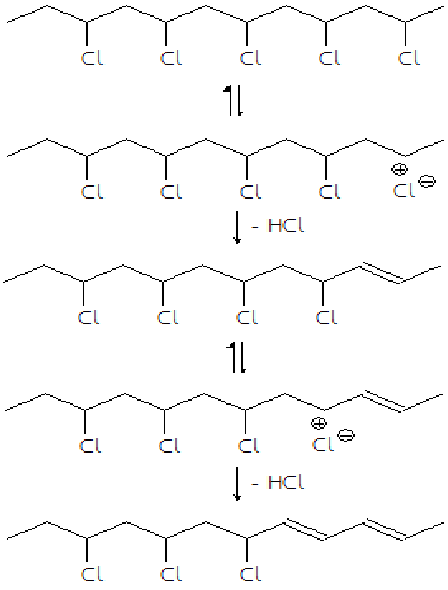

Figure 2.6 Dehydrochlorination reaction of PVC

Thereby, stabilizers are filled in PVC for finishing products in order to maintain excellent properties. The stabilizers used in polymer include metal oxides, carbonates and fatty acid salts which act as HCl acceptors. The mechanism of these additives in the stabilization of PVC is too slow down dehydrochlorination reaction by absorbing the evolved hydrogen chloride.

2.1.5.2 Chemical stability

1. Flame retardant property

PVC has high ignition temperature at 455 °C as shown in Figure 2.7 due to the presence of chlorine atoms in PVC structure. Therefore the products of PVC do not require the addition of flame retardant. Besides, PVC has poor heat radiation and fire expansion while burning (Table 2.1) compared with polyethylene (PE) and polypropylene (PP). Consequently, PVC is an appropriate material for the use in flame retarding needed products such as household furnishings.

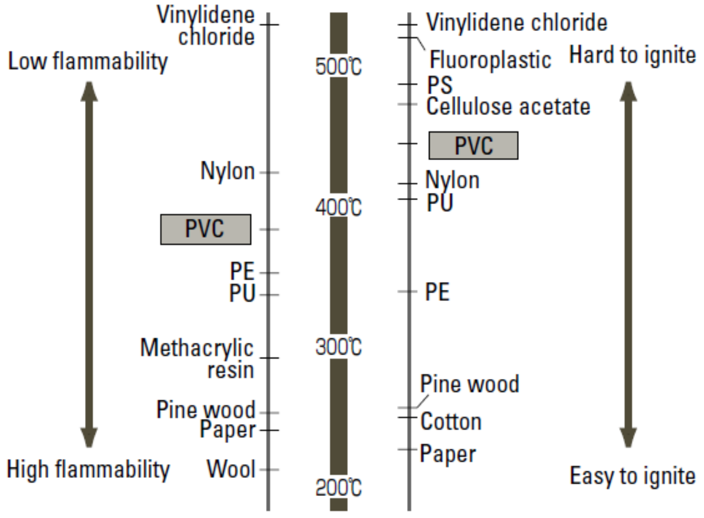

Figure 2.7 Flash ignition and ignition temperature of materials

Table 2.1 Maximum heat release by various polymers

Polymer	Maximum heat release (kW/m^2)
Poly(vinyl chloride) (PVC)	91
Acrylonitrile-butadiene-styrene (ABS)	746
Fire resistant ABS	250
Polystyrene (PS)	859
Fire resistant PS	315
Polyethylene (PE)	1325
Polypropylene (PP)	1335
Polyester	1216

2. Durability property

Durability property is concerning the oxidation resistance of materials. Under ambient conditions, PVC has high durability due to the presence of chlorine atom in molecular structure thus PVC products tend to have a long lifetime.

3. Oil/chemical resistance

PVC has resistance to whole inorganic, acid and alkali chemicals. Although PVC is swelled in aromatic hydrocarbons, ketones and cyclic ethers, PVC is hardly dissolved in other organic solvents. With this remarkable property, PVC is used to produce bottles, tubes, gas ducts, hoses and sheets used in construction.

2.1.5.3 Processability and moldability

Melt viscosity of thermoplastic polymer indicates its processability. PVC has high melt viscosity therefore it is not suitable for injection molding process. However, the characteristic of PVC is that it is stable at molten temperature thus forming with extrusion is a proper process for PVC molding as well as calendaring of films and sheets. Products of PVC produced from extrusion and calendaring process include housing materials and films/sheets, respectively. The extrusion and calendering process is illustrated in Figure 2.8. Other processes include fabrication, welding, screen printing and coating. In addition, PVC is an amorphous polymer and the product of PVC has high dimensional stability.

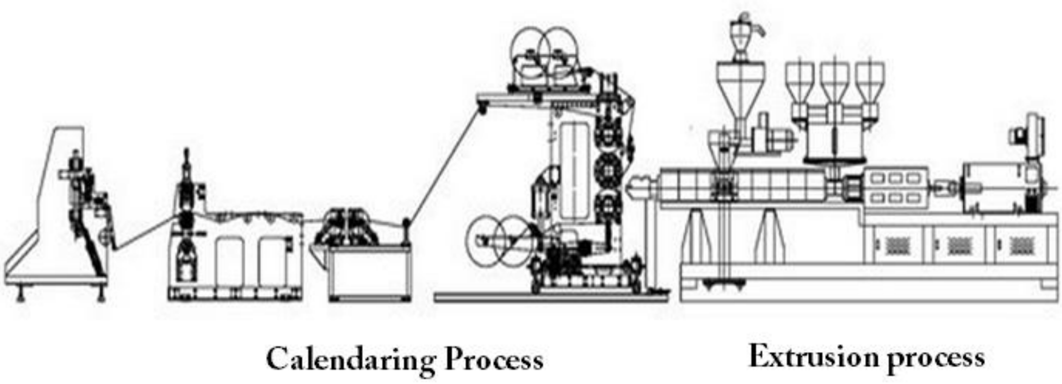

Figure 2.8 Extrusion and calendering process [18]

2.1.5.4 Versatility (depending on compounding)

PVC has amorphous phase and contains polar groups (chlorine atom) in molecular structure; hence incorporation of PVC with other material requires excellent physical interaction in order to obtain good physical properties such as flexibility, elasticity, impact resistance and anti-bacteria. It has been applied in coloring, printing and adhesive substance industry due to the polarity of PVC.

2.1.6 Grades of PVC production

PVC resins are classified following polymerization method as suspension grade, emulsion grade and bulk polymerized grade.

2.1.6.1 PVC suspension grade

PVC suspension grade is widely used in PVC manufacturing. This grade is produced by polymerization of vinyl chloride monomer (VCM) droplets in water. After that, the slurry is centrifuged and dried by special heater because resins are not

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thermally stable and can be decomposed. The particles sizes are range from 50 to 250 microns and have porous structures which are suitable for adsorption of plasticizers. Low porous types are extensively used for rigid PVC applications such as pipes, windows or sidings. And high porous types are used in cables, footwear, soft sheet and film applications, etc.

2.1.6.2 PVC emulsion grade

PVC emulsion polymerization grade or paste grade is preferentially used for plastisols. Paste grade resin has very small particle size as it was produced by spray dry of PVC emulsion in water. High energy input is required in this process and thus this product is more expensive than the suspension grade. The production of paste grade resins needs chemicals and catalysts, resulting in lower purity polymer grade compared to suspension or bulk polymerized grade. Paste grade resins are mostly used for cushion vinyl floorings of wide widths and coating on substrate paper.

2.1.6.3 PVC bulk polymerized grade

PVC bulk polymerized grade is the purest form of PVC resin because of needless of emulsifying or suspending agents in the production. This grade is mainly used to make transparent products, especially blister packaging and other extruded or calendered transparent sheets or films.

2.1.7 Classification grades of PVC following K-value

PVC resins can be classified by K-value which indicates the molecular weight and degree of polymerization. Details and applications for each of K-value are summarized in Table 2.2

Table 2.2 Specification and applications for PVC of different K-value

K-values	Specification	Applications
K70-75	- This grade is high K value resins which give the best mechanical properties, whereas it is more difficult to process. - This grade needs higher extent of plasticizer to produce flexible grade.	- Cable insulations - Tough coatings for conveyor belts - Industrial flooring
K65-68	- This grade is medium K value resins which are the most popular. - This grade has a good balance of mechanical properties and processibility.	- Transparent sheets - Electrical wires and cables - Rigid and soft profiles
K58-60	- This grade has low K value ranges. - They have the lowest mechanical properties, but their processing is the easiest. - Their prices are higher than medium K-value resins	- Calendered packaging films - Credit card and other rigid sheet or profiles - Rigid foam sheet
K50-55	- This resin grade is made for some demanding applications.	- Battery separator

2.1.8 Applications of PVC

PVC is used in various application fields ranging from rigid to flexible products. Rigid PVC products contain small contents of plasticizer with approximately 5-20 % by weight of polymer, applied in the production of water pipe, credit card and plastic sheet. On the other hand, flexible PVC products consist of large contents of plasticizer with approximately 40-90 % by weight of polymer, used in leather industry blood bags, food wraps, stickers, toys and furniture fabrication [4]. Table 2.3 summarizes PVC applications.

Table 2.3 PVC applications [10]

PVC types	Categories	Applications
Rigid PVC	Films/sheets	Food trays
		Cards, electronic equipment
	Corrugated sheets	Construction materials (corrugated sheet, terrace roofing)
	Pipes	Agricultural water pipes
		Cable wires
	Fittings	Adaptor for steel pipes
		Right angle elbows
		Y-shaped fittings
	Spouts	Rainspouts
	Construction materials	Window profiles, wire screen, trim, panels
Flexible PVC	Laminated products	PVC laminated steel plates, printed films
	Medical products	Blood bags, medical tubes
	Consumption products	Furniture
		Toys
	Artificial leather	Baggage, vehicle seats
		Footwear

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2.2 Plasticizers [1, 19, 20]

2.2.1 Characteristic of plasticizers

Plasticizers are materials which are incorporated with polymers in order to achieve the required flexibility, stretchability and processibility of the polymer. Plasticizers are actually low molecular weight liquid or resin. When plasticizers are added into polymer, they will incorporate in the amorphous phase of polymer while the structure of any crystalline phase remains unaffected and form secondary bonding to polymer chains. This kind of plasticizer is called external plasticizer. Commercial external plasticizers are summarized in Table 2.4. Plasticizers can be divided into internal and external plasticizers where the external plasticizers reduce intermolecular force between polymer-polymer chains and provide an easier movement of polymer chain. On the contrary, internal plasticizers can reduce crystallinity and intermolecular force between chains of polymers. Plasticizers may also be divided into primary and secondary plasticizers. Primary plasticizers are used as the main component, whereas secondary plasticizers are typically used together with primary plasticizer to improve properties of polymer and save cost.

Plasticizers are anticipated to decrease the modulus, tensile strength, hardness, glass transition temperature, melt viscosity, electrostatic chargeability and free volume of polymer, while the elongation at break, toughness, flexibility, dielectric constant and power factor are elevated. Moreover, plasticizers can increase the plastic flow ability and viscosity of melted polymer. Because of their low molecular weight and non-bonding interaction with polymer chains, plasticizers can be released from polymer, resulting in changes in properties of finishing products and contamination of plasticizers in contacting foods. It will cause adverse effect on human health and animals.

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Table 2.4 Types of commercial external plasticizers

Plasticizer types	Common plasticizers
Aromatic esters	Dibutyl phthalate
	Dimethoxyethyl phthalate
	Di-2-ethylhexyl phthalate
	Di-n-octyl phthalate
	Diisooctyl phthalate
	Diisodecul phthalate
	Diundecyl phthalate
	Diisotridecyl phthalate
	Diisononyl phthalate
	Butyl benzyl phthalate
	Butyl octyl phthalate
	Tri-2-ethylhexyl trimellitate
Aliphatic esters	Di-2 ethylhexyladipate
	Diisobutylsebacate
	Di-2-ethylhexyl sebacate
	Diisooctylsebacate
	Di-2-ethylhexyl azelate
Epoxy plasticizers	Epoxidized soybean oil
	Epoxidized linseed oil
	Epoxidized tall oil fatty acids
Polymeric plasticizers	Poly(alkyleneadipates, sebacates and azelates
	Acrylonitrile/butadiene copolymer
Flame retardant plasticizers	Aryl and aryl/alkyl phosphates
	Chlorinated paraffins

2.2.2 Evolution of plasticizers [20]

In 1862, Alexander Parkes introduced the first man-made plastic. In 1912, triphenyl phosphate was discovered and has been used as substitute for camphor oil. Later, glycerin acetate was found but its high volatility is the major drawback. Phthalate esters were discovered for the first time in 1920 and have been continuously used. Phthalate esters are the largest classification of plasticizers including; fatty acid ester, benzoate, tartrates and chlorinated hydrocarbons. Adipic, azelaic and sebacic acid are new available plasticizers which can improve the cold fracture temperature of PVC. Generally, phthalate ester plasticizers are the most widely used plasticizers.

2.2.3 Phthalate ester plasticizers [1, 21]

Phthalates are plasticizers which are consisted of ester group. Phthalate esters have low molar mass and they are widely used in PVC to give the polymers flexibility and stress resistance. The application of plasticized PVC having such properties includes the production of food and beverage packaging, medical devices, flexible tubes, and construction products fields. The six commonly used phthalate eaters are di(2-ethylhexyl) phthalate (DEHP), denzyl butyl phthalate(BBP), dibutyl phthalate (DBP), diisononyl phthalate (DINP), di-n-octyl phthalate (DnOP) and diisodecyl phthalate (DIDP). DEHP and DINP are chemicals that are used in vinyl products, especially toys.

2.2.3.1 Di(2-ethylhexyl) phthalate (DEHP)

Di(2-ethylhexyl) phthalate (DEHP) or dioctyl phthalate (DOP) is one of the most widely used phthalate ester incorporated with vinyl PVC as primary plasticizer. DEHP is a clear and colorless liquid, synthesized via esterification reaction between phthalic anhydride and monohydric alcohol. DEHP in products is harmful to newborn, children and chronical sickness people. And toxicology testing in animals indicated that it affected the fertilization and reproduction. Figure 2.9 shows the structure of DEHP.

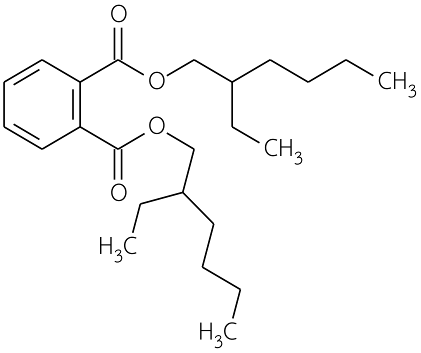

Figure 2.9 Structure of DEHP

2.2.3.2 Diisononyl phthalate (DINP) [22]

Diisononyl phthalate (DINP) is a general purpose plasticizer for using in vinyl polymers to give required flexibility and durability of products. DINP is applied to produce electrical cables, synthetic leathers, automobiles and building and construction materials. The toxicological study has found that the effect of DINP on animals testing is much weaker than DEHP. Figure 2.10 illustrates DINP structure.

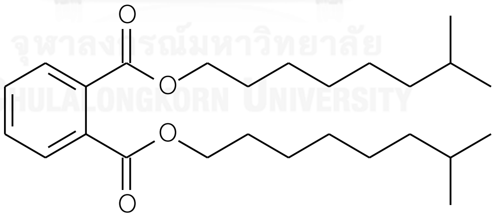

Figure 2.10 Structure of DINP

However, the European Commission has been prohibiting the usage of phthalate plasticizer in toys and fetus-care articles which are in contact with baby aged under three years. In July 2005, the European organization banned the addition of DEHP, DBP, BBP, DINP, DIDP and DnOP into polymers. Furthermore, It was found that plasticizers are still in use in products such as medical devices, blood bags, food wrapping and toys.

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2.2.4 Theories of plasticizer action [13, 23]

2.2.4.1 Lubricity theory

The lubricity theory was introduced by Kirkpatrick, Clark and Houwink. Kirkpatrick proposed that the plasticizers act as a lubricant between molecules of polymer. The action of plasticizers abates friction between polymer molecules so the mobility of polymer chains increases. The model of lubricity theory is illustrated in Figure 2.11.

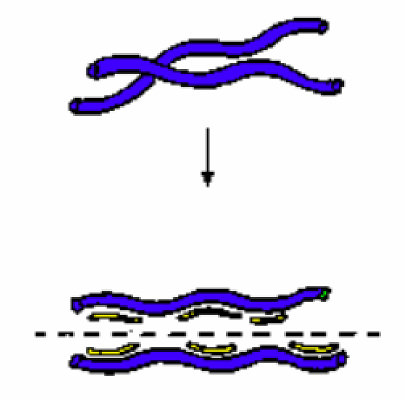

Figure 2.11 Plasticizer polymer response based on lubricity theory

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Clark attributed about the filling the large voids between macromolecules and the planes that can easily glide are formed. The plasticizers were added into the space between glide planes, acting as lubricant as represented in Figure 2.12. Furthermore, Houwink reiterated the idea of gliding planes, which had been previously introduced by Clark.

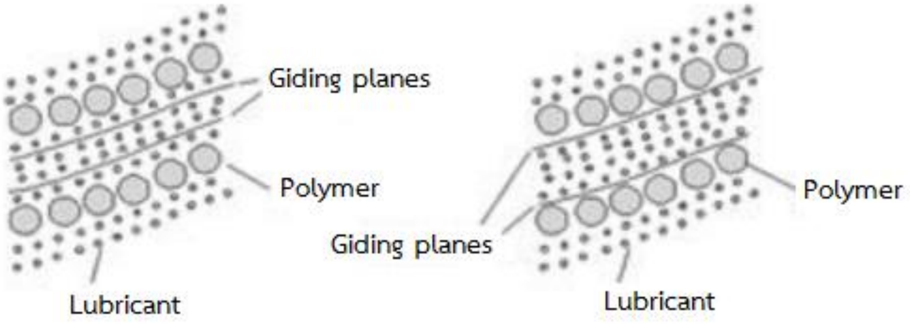

Figure 2.12 Two possibilities of gliding plane

2.2.4.2 Gel theory

Aiken studied the effect of softening, compatibility and structure of molecules of various plasticizers in PVC. He discussed about molecules of plasticizer that compose of polar and non-polar groups which relate to gel theory. Gel theory enumerated that the polar parts of plasticizer penetrate at the polar part of polymer chains and non-polar parts of plasticizer act as shield causing weak attachments and lowering the movement of polymer chains. The model is shown in Figure 2.13.

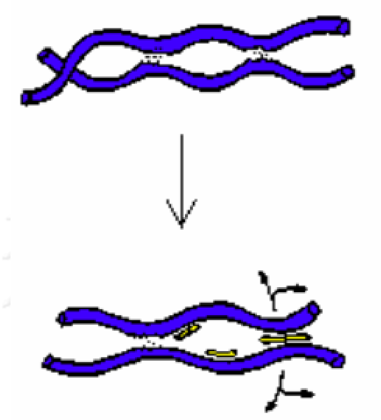

Figure 2.13 Gel theory of plasticizer

2.2.4.3 Free volume theory

The free volume theory has been initiated after the lubricity and gel theories. This theory was proffered by Sears and Derby in 1982 which explained the free volume related to temperature. Furthermore the theory explained to mechanism of plasticization in polymer. When plasticizers are added into polymer, free volume increased, and the glass transition temperature diminished as shown in Figure 2.14. Glass transition temperature (T_g) is the temperature at which the polymer changes from a glass-like material to rubbery state. At temperature of T_g, the chains are intensively incorporated and could slightly move. At temperature above T_g, the molecule chains have enough energy to transpose.

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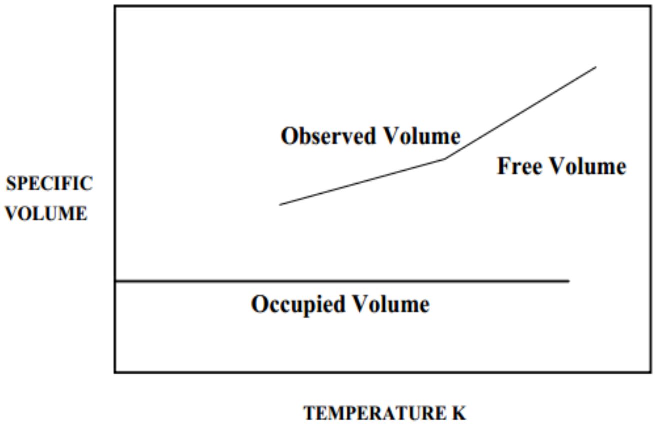

Figure 2.14 Specific volume-temperature curve

According to these phenomena, the addition of small molecules of plasticizer into polymer results in a decrease in T_g to lower value than that of polymer matrix due to greater free volume to the system. The major of this theory clarifies the drop of glass transition temperature when plasticizer is incorporated with polymer matrix. Figure 2.15 presents the concept of plasticization in polymer. In the theory, plasticizer incorporated in the amorphous region because of more free volume, since the conformational tends to be more flexible.

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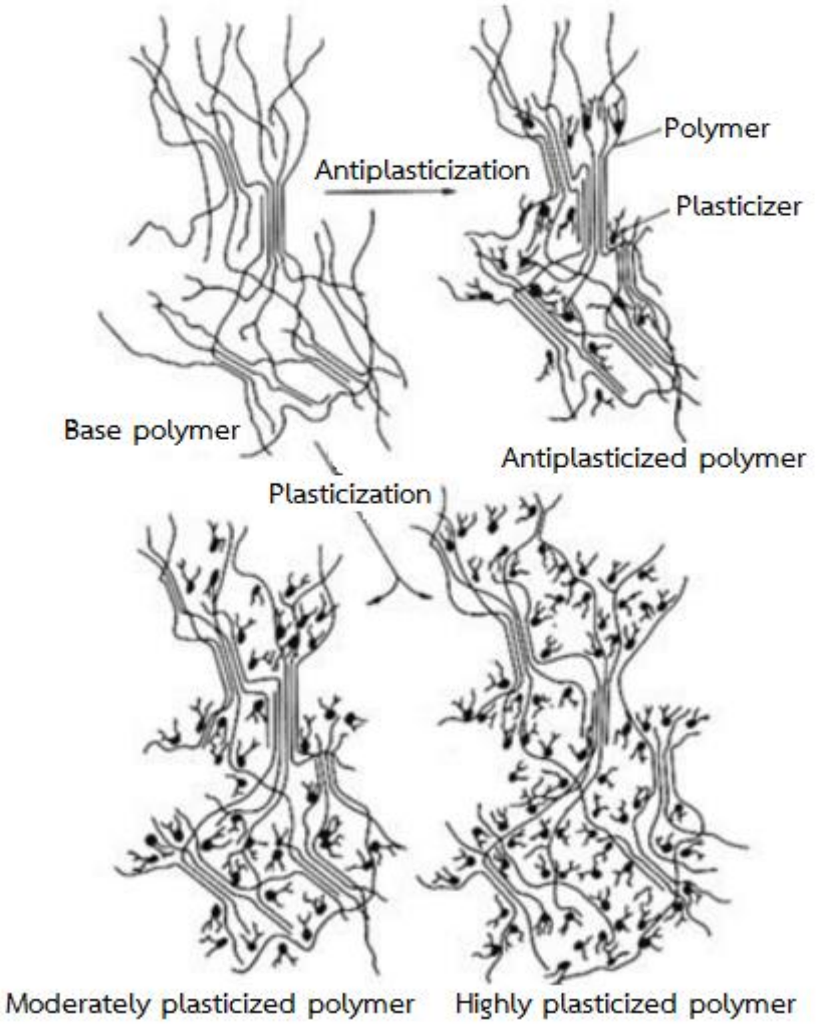

Figure 2.15 The concept of plasticization in polymer

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2.2.4.4 Mechanistic theory

The mechanistic theory of plasticizer is auxiliary of three theories previously described. This theory referred to solvation-desolvation equilibrium and discussed the same concept with gel theory. In gel theory, plasticizers remain attached alongside of polymer chain; in contrast, the mechanistic theory explained that the plasticizers can transfer to another polymer chain. Figure 2.16 demonstrates the mechanistic theory of plasticizer.

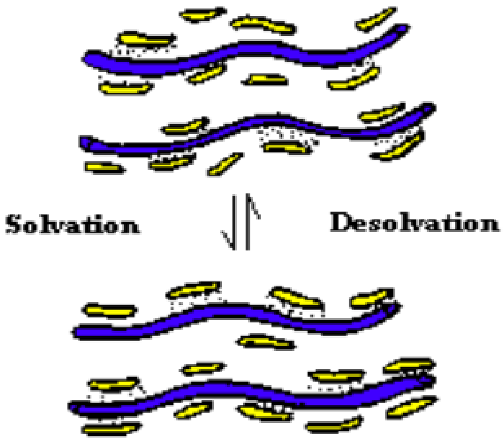

Figure 2.16 Mechanistic theory of plasticizer

Besides, the mechanistic theory was proposed based on the free volume theory which involved glass transition temperature (T_g). The systems of plasticized PVC comprised of the polymer matrix and plasticizer, which correlate with T_{g1} and T_{g2}, respectively. The models were developed by Kanig, Wood, Gordon and Taylor. The equation was presented as follow;

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{2.1}$$

where T_g, T_{g1} and T_{g2} are the glass transition temperatures of the mixture, the polymer and the plasticizer, respectively. w_1 and w_2 are the weight fractions of the polymer and the plasticizer.

2.2.5 Applications of plasticizers

The applications of plasticizers are vastly ranging from the production of products in automobile industry to medical devices and consumer products. Table 2.5 shows examples of applications of plasticizers.

Table 2.5 Applications of commercial plasticizers [20]

Plasticizers	**Applications of plasticized polymer**
Di(-2ethylhexyl) phthalate (DEHP), Diisodecyl phthalate (DIDP), Diisononyl phthalate (DINP), Diisotridecyl phthalate (DITDP), dibutyl phthalate (DBP)	Medical devices, kitchen floors, vinyl wall coverings, carpet backing, wires and cables, toys, hoses, shower curtains, food packaging and vehicle parts
Triphenyl phosphate, Tris (2-ethylhexyl) phosphate, Tricresyl phosphate,	Flame retardant, plasticizer in calendaring of extrusions, plastisol derived products with nylon, sulfonamides and other highly polar compounds, PVC, polyacrylates, cellulose derivatives and synthetic rubbers
Dibutyladipate, Bis(2-ethylhexyl) adipate (DEHA), Diisodecyladipate	Flexible products for automobile parts and aircraft interiors
Bis(2-ethylhexyl) azelate	cellulosic resins and elastomers, food-contact applications
Dibutylsebacate, Dioctylsebacate Butyl epoxystearate, Cyclohexylepoxystearate	Food-contact, medical and pharmaceutical plastics
Benzoplast®, Benzoflex®	Vinyl flooring, PVA adhesives, and sealants, latex caulks, coatings, processing aids, inks, hot melt adhesives

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Plasticizers	Applications of plasticized polymer
Poly(1,3 butyleneglycoladipate), Poly(ethylene glycol) (PEG), Admex®, Paraplex®	vinyl dispersions, films, sheet, floor coverings, cable insulation and sheathing resins only where oil and fat resistance is required
Trioctyltrimellitate (TOTM), Octyldibenzyltrimellitate,	PVC tubes, blood storage bags, catheters and haemodialysis tubing
n-Butyl benzenesulfon amide, Toluenesulfamide	polyamide and cellulose based molding resins
n-Butyl formate, ethyl lactate	rigid and plasticized PVC
Epoxidized soy bean oil (ESO), Epoxidized linseed oil, Tallates	heat stabilizers
Polychlorinated biphenyls (PCBs), Polychlorinated, 1-dodecene, 1-tetradecene, 1-hexadecene	Mainly used as secondary plasticizers, flame retardant
(acetyltri-*n*-hexyl citrate) Citroflex® A-6, (*n*-butyryltri-*n*-hexyl citrate) Citroflex® B-6	Flexible tube used in medical plastics and food contact plastics
(recorcinolbisdiphenyl phosphate) Fyrolflex® RDP-B, Poly (butadiene dimethacrylate)	Automotive, marine and aeronautical applications
Allyl phthalate, Acrylic esters, Monochlorostyrene	Toys, shoe heels and certain industrial articles that must have high stiffness

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2.3 Impact modifier [24]

2.3.1 Mechanism of toughness by impact modifier

Impact modifiers are important additives for enhancing flexibility and impact strength of rigid polymers. Unmodified polymers such as poly(vinyl chloride) (PVC), polystyrene (PS), styrene-acrylonitrile (SAN) have rigid part and they are breakable at room temperature. Although, other polymers such as polyamides and polyolefins are soft, they become fragile at low temperature. Suitability of impact modifier depends on polymer matrix and the impact modifier must be compatible with polymer matrix. Normally, impact modifiers consist of rubber particles or should be elastomeric polymers. Thus their mechanical properties including modulus, tensile strength, flexural strength and hardness are lower compared with polymer matrix. To add rubber particles as impact modifier, the compatibility with the polymer matrix should be considered in order to obtain demanded properties. Uniform dispersion of rubbery phase acting as energy impact absorber instead of main polymer caused the crazing or crack propagation was abated and the good impact properties was achieved.

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2.3.2 Usage of impact modifier in the industry

In 2001, Fred Gastrock reported that the impact modifier consumption was 540 million kg (1.2 billion pounds) of volumes and $1.25 billion of values. Styrenic copolymers, especially acrylonitrile-butadiene-styrene (ABS) and methyl methacrylate-butadiene-styrene (MBS) are the most used as an impact modifiers and their consumption was approximately 45% of the world market. Furthermore, the usage of other type of impact modifier such as acrylics, thermoplastic elastomers and chlorinated polyethylene (CPE) was approximately 30%, 10% and 10% of the modifier consumption in the world market, respectively. Approximately 80% of impact modifier was used to produce the engineering polymers such as polycarbonate (PC), polyamides and polyesters and about 10% for polyolefines. Table 2.6 summarizes the common impact modifiers.

Table 2.6 Common impact modifiers

Polymer matrix	Impact modifiers
Poly(vinyl chloride) (PVC)	Acrylonitrile-butadiene-styrene (ABS) Acrylonitrile styrene acrylate (ASA) Methyl methacrylate-butadiene-styrene (MBS) Chlorinated polyethylene (CPE) Acrylic
Polystyrene (PS)	Poly(styrene-butadiene-styrene) (SBS) Styrene ethylene butylene styrene block copolymer (SEBS)
Polycarbonate (PC)	Styrene ethylene butylene styrene block copolymer (SEBS)
Polyolefins	Ethylene propylene diene monomer (EPDM) Thermoplastic elastomers and plastomer Styrene ethylene butylene styrene block copolymer (SEBS) Non-reactive, modified polyolefins Crosslinkedpolyacrylate in a continuous phase
Polyamides	MA-modified SEBS MA-modified EPDM Ionomers Reactive, modified polyolefins
Polyesters	MA-modified SEBS Crosslinkedpolyacrylate in a continuous phase Reactive, modified polyolefins GMA-modified ethylene-acrylate copolymers
Engineering polymers	Acrylic SAN-modified EPDM
Poly(phenyl ether)	Poly(styrene-butadiene-styrene) (SBS)

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2.3.3 Impact modifiers in PVC

The high impact strength or toughness of PVC is needed properties for many applications. Recently, rubber compounding is a method that is widely used to improve mechanical properties of PVC. However, rubber is not compatible with PVC, so it is necessary to blend or graft it with polar materials. The most broadly used impact modifiers containing rubber in PVC are ABS and MBS.

2.3.3.1 Acrylonitrile-butadiene-styrene (ABS) [25, 26]

ABS polymers were synthesized by using three monomers: acrylonitrile, butadiene and styrene. Figure 2.17 exposes the chemical structure of ABS polymer. Systematic synthesis of ABS is inclusive of styrene and acrylonitrile copolymers (SAN) which were grafted with polybutadiene. The rubber acts as disperse phase that distributes in the continuous phase of SAN. The properties of ABS are toughness due to the containing elastomer phase, solidity, good heat and chemical resistance because of the effect of styrene and acrylonitrile in structure. The good toughness properties of ABS depend on the particle size, the volume and behavior of dispersion phase of elastomer. Products of ABS are turbid because of different refractive index of two phases. If the refractive index of two phases is equal, it appears translucent. This result was achieved by substituting a methyl methacrylate in place of acrylonitrile.

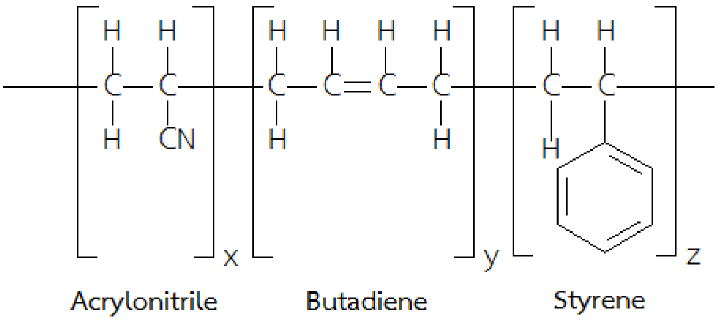

Figure 2.17 Chemical structure of ABS polymer

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2.3.3.2 Methyl methacrylate-butadiene-styrene (MBS)

MBS resins compose of methyl methacrylate, butadiene and styrene. MBS resins are transparent because of the particle size of rubber and equal refractive index of polymer. Particle size of rubber affects to the transparency of MBS resins. The small rubber particles can make the excellent transparency, whereas the impact resistance is diminished. Consequently, the uniform dispersion of rubber particles must be achieved in order to obtain desired impact strength [27]. Mostly, MBS was synthesized by grafting methyl methacrylate and styrene onto butadiene via emulsion polymerization [7, 28-30] or grafting methyl methacrylate onto styrene-butadiene copolymer [29]. The MBS was synthesized as core-shell particle as shown in Figure 2.18. The part of core is usually rubber or copolymer of rubber for absorption the impact energy and the shell is glassy polymer as methyl methacrylate (PMMA) or styrene-methyl methacrylate (SMMA) that is compatible with PVC.

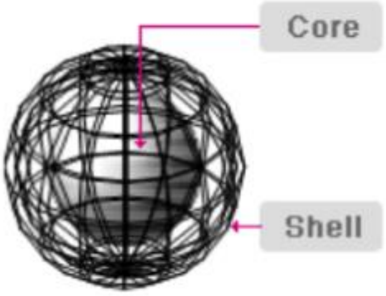

Figure 2.18 Core-shell structures [31]

2.3.4 Styrene-methyl methacrylate/Styrene-butadiene blend (SMMA/SBR rubber)

The impact modifier is an important composition to enhance impact strength of PVC because the impact strength of PVC is very poor. In this work, styrene-methyl methacrylate/styrene-butadiene compound (SMMA/SBR rubber) was used as impact modifier for PVC. The compound was derived by blending between copolymers of styrene-methyl methacrylate (SMMA) and styrene-butadiene (SBR). The uniform dispersion phase of butadiene rubber can improve impact property of PVC.

2.3.4.1 Styrene-methyl methacrylate (SMMA) copolymer [32, 33]

Methyl methacrylate (MMA) is the monomer of methacrylic acid ester which is common used in the synthesis of poly(methyl methacrylate) (PMMA). The predominant feature is that it is a clear and achromatic polymer which is suitable to produce transparent products. PMMA has high modulus, hardness and abrasion resistance whereas low elongation at break. PMMA is one of polymers that resist to UV light as well as ozone. Importantly, PMMA is safe for human tissue, for example, it can be applied in contact lenses. On the other hand, styrene (St) part which is glassy polymer is generally rigid material. The prominent characteristic of styrene is its transparence. Especially, the products made from SMMA copolymer look like crystal. The chemical structure of SMMA is illustrated in Figure 2.19.

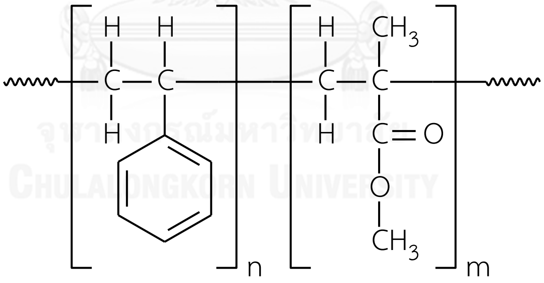

Figure 2.19 Structure of styrene-methyl methacrylate (SMMA) copolymer

2.3.4.2 Styrene-butadiene (SBR) copolymer [33]

Aromatic styrene monomer (St) is consists of benzene ring in molecule chain. The styrene monomers were polymerized via radical polymerization to form polystyrene (PS). PS is an amorphous and glassy polymer which is hard, transparent and high gloss. Generally, neat PS is brittle thus it must be copolymerized or compounded with rubber to achieve desired properties. PS is chemically bonded with polybutadiene (PB) to obtain more flexible product. During polymerization process, if PB forms chemical bonding with PS to yield styrene-butadiene (SBR) copolymer, the products will has high impact strength. On the other hand, if PB and PS are blended in the mixer, the resulting products exhibit poorer impact property. Figure 2.20 displays chemical structure of styrene-butadiene (SBR) copolymer.

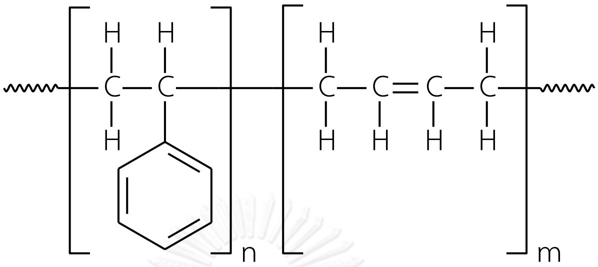

Figure 2.20 Structure of styrene-butadiene (SBR) copolymer

2.4 Literature reviews

The compatibility between PVC and SMMA/SBR rubber was the most important factor for obtaining required properties of polymer. Soman et al. [9] studied the compatibility between PMMA-PVC blends by using FTIR and DSC method. The polymer blends with ratios between PVC and PMMA as 100/0, 90/10, 73/30, 50/50, 30/70 and 0/100 %w/w were prepared. From DSC analysis, the results exhibited a single glass transition temperature (T_g), implying the miscibility of PVC and PMMA in the blends. The FTIR analysis of the blends specified that the vibrational characteristic of carbonyl group shifted to lower wavenumber indicating the miscible blend. The miscibility was explained that hydrogen bonding between carbonyl group (C=O) of PMMA and CHCl of PVC occurred. Moreover, Fekete et al. [34] reported the shift of carbonyl peak to lower wavenumber (from 1735 cm^{-1} to 1732 cm^{-1}), while Ramesh et al. [35] showed the shift of vibration peak of carbonyl to higher wavenumber (from 1721 cm^{-1} to 1732 cm^{-1}). In case of the miscibility of PVC and plasticizer, Elgozali et al. [36] referred that the chlorine atom of PVC was the polar group which interacted with ester group of carbonyl group position of plasticizer.

The addition of plasticizer in PVC matrix which affected the mechanical properties of polymers was studied in many researches. Pita et al. [37] investigated the mechanical properties of the blends between PVC and plasticizers such as di-isodecyl phthalate (DIDP) and di-2-ethylhexyl phthalate (DOP). The samples with varied the plasticizer contents (10, 50 and 90 phr) were prepared by using the twin-screw extruder. With 10 phr of DOP, the polymer blend became hard and brittle materials and using higher content of DOP (with 50 and 90 phr) in mixtures resulted in polymer blends with soft and tough behaviors. The effect of DIDP in PVC was similar with DOP. The modulus and tensile strength continually reduced when higher content of plasticizers was added in PVC. Pita and co-workers explained that the effects of plasticization in PVC matrix depended on the content of plasticizers. At low content of plasticizer, the ester of carbonyl group of plasticizer interacted with the polar group of PVC. The larger number of strong interaction occurred with higher content of plasticizers. In 2010, Unar et al. [38] studied compounding PVC for improvement of mechanical properties. Two types of formulations were considered as un-plasticized and plasticized PVC. The mechanical testings were performed by using tensile properties and shore hardness tests. The tensile strength of plasticized PVC was lower than un-plasticized PVC, whereas the elongation at break was higher than one. Furthermore, the shore hardness slightly decreased with increasing the amount of plasticizer. With these results, Unar and co-workers discussed the presence of plasticizer in PVC that the plasticizer acted as spacer between polymer molecules and could form physical bonding with polymer chains. The intermolecular force occurred between polar groups such as chlorine atom of PVC and ester group of plasticizer. Therefore the polymer linkage was weak which led to the reduction of the tensile strength and hardness.

The mechanical properties of PVC were improved by using the variety of impact modifiers, especially acrylonitrile-butadiene-styrene (ABS). Hosseinpour et al. [4] investigated compatibility, mechanical properties including; tensile and impact strength. The mixture with PVC/ABS ratios of 100/0, 70/30 and 0/100 were prepared. Morphology of mixture was observed after the specimens were etched in *n*-heptane to repel the rubber phase. The rubber particles dispersed greatly in PVC matrix and the fracture surface of mixture appeared roughness indicating more flexible in the mixture. Regarding the mechanical properties in the section of impact strength, PVC has poor mechanical properties compared with ABS. The impact strength increased with increasing the ABS content due to the adsorption of energy by rubber phase instead polymer matrix under impact loading. In addition, the value of tensile strength diminished with the increase of ABS content because rubber particles acted as stress concentrator so the samples were broken abortively. In 2013, Zhang et al. [39] used the copolymer of α-methylstyrene-acrylonitrile-butadiene-styrene (AMS-ABS) blended with PVC to enhance mechanical properties including impact strength, tensile properties, flexural strength and heat distortion temperature (HDT). They also studied the morphology the fracture surface after impact and tensile testing. The blends of PVC/AMS-ABS were prepared in ratios of 100/0, 85/15, 70/30, 50/50, 30/70, 15/85 and 0/100. The results showed that notched Izod impact strength increased with the rise of the AMS-ABS content due to the effect of rubbery phase. The better impact property implied higher toughness of the blends. The modulus and tensile strength decreased with the increase of AMS-ABS content. The result of flexural strength had tendency with tensile properties. With regard to HDT, for the amorphous polymer, HDT increased with increasing the glass transition temperature (T_g) polar group. In addition to morphological observation, the impact and tensile fracture surface were investigated. PVC exhibited smooth impact-fractured surface implying the fracture as brittle type. After filling AMS-ABS, the bumpy surface looked sponge-like with rubber particles as disperse phase indicating the blend is tougher than PVC. With regard to the morphology of tensile-fractured surface, the complete deformation exhibited look root-like, indicating the flexibility of the blend. In 2011, Zhang et al. [40] studied the effect of styrenic polymers of poly(α-methylstyrene-acryloitrile) (α-MSAN) and poly(acrylonitrile-butadiene-styrene) (ABS) on heat distortion temperature (HDT) in PVC. As the result, HDT increased with increasing the styrenic polymer in PVC because of higher stiffness and T_g of styrenic polymer than PVC. The improvement of HDT when using α-MSAN was better than ABS because methyl group in α-MSAN inhibited chain rotation.

The migration behavior of plasticizer in plasticized PVC was discussed in several works. The samples for testing could be prepared by following the research of Marcilla et al. [41]. Small sheets of polystyrene (PS) and plasticized PVC were formed into compressed sheet in diameter of 3 mm × 3 mm × 1 mm (width × length × thickness) at 190 °C of temperature. Before the migration testing, PS sheet was placed between plasticized PVC sheets and kept at 50 °C in the oven for a week. After that PS sheet was analyzed by thermogravimetric analyzer (TGA). In this work, the samples were tested via differential scanning calorimeter (DSC) technique instead of TGA. Bueno-Ferrer et al. [42] used epoxidized soybean oil (ESBO) as a plasticizer to improve thermal stability in PVC because ESBO also acted as stabilizer in PVC which helped to protect PVC from decomposition during manufacturing. They studied the effect of different the amounts of ESBO in PVC on thermal properties. The amounts of ESBO in PVC of 30%, 40% and 50% were investigated. The phenomenon on DSC thermogram showed that T_g values decreased with increasing of plasticizer content. As the results of 30%, 40% and 50% of ESBO in PVC, the observed T_g was -1.8 °C, -19.0 °C and -38.1 °C, respectively.

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Poly(vinyl chloride), PVC resin, produced by suspension polymerization process with degree of polymerization of 680, grade SG580 (a K value of 58) was obtained by Thai Plastic and Chemicals Public Company Limited, Bangkok, Thailand.

3.1.2 Styrene-methyl methacrylate/styrene-butadiene blend (SMMA/SBR rubber) as an impact modifier, SMBC460 grade was purchased from Global Connections Public Company Limited, Samuthprakarn, Thailand.

3.1.3 Diisononyl phthalate (DINP), commercial grade, as a plasticizer for PVC matrix was kindly supplied by Thai Nam Plastic (Public) company Limited, Omnoi, Samuthsakorn, Thailand.

3.1.4 Zinc stearate (AV-1) was bought from Global Connections Public Company Limited, Samuthprakarn, Thailand.

3.1.5 Epoxidized soyabean oil, having density of 0.990 cm^3/g at 20 °C was provided by Chemmin Corporation Limited, Samuthprakarn, Thailand.

3.1.6 Polystyrene (PS) was received from Labtech Engineering, Samuthprakarn, Thailand.

3.1.7 Tetrahyrofuran (THF) as a solvent, used for solution casting was supplied from Quality Reagent Chemical (QRëC) Corporation Limited, Chonburi, Thailand.

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3.2 Equipment

The equipment employed for blend preparation and testing samples was presented in Table 3.1

Table 3.1 Equipment for blend preparation and testing samples.

Equipment	Model	Manufacturer/Country
Two-roll mill machine	LRM-S-110/3E	Labtech Engineering/ Thailand
Compression molding machine	LP-S-50	Labtech Engineering/ Thailand
Fourier transform spectrometer	Nicolet 6700	Thermo Fisher SCIENTIFIC/USA
Scanning electron microscope	JSM-6610LV	JEOL/Japan
Impact testing machine	GT-70-MDH	GOTECH/Taiwan
Universal testing machine (Tensile testing)	LLOYD LR 100K	LLOYD/United Kingdom
Universal testing machine (Flexural testing)	LLOYD500	LLOYD/United Kingdom
Hardness durometer shore type D)	CODE DR	The Shore Instrument & Mfg/USA
Heat distortion temperature tester	148-HD-PC	Yasuda Seiki Seisakusho, Ltd./Japan
Differential scanning calorimeter	DSC 204 F1 Phoenix	LMS INSTRUMENTS/ Germany

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3.3 Experimental

3.3.1 Preparation of PVC blends

Prior to PVC blending, the PVC resin, plasticizer and SMMA/SBR rubber were physically mixed in a 1000 ml beaker. After that, the mixture was melt mixed using two-roll mill (LRM-S-110/3E, Labtech Engineering, Thailand) as shown in Figure 3.1. The mixture was blended at the temperature of 170 °C for 5 min to obtain homogeneous blend. Then, the blend was ground by grinder machine. The blend formulations were summarized in Table 3.2.

Table 3.2 Formulations of PVC blend (in phr unit)

Sample code	PVC	SMMA/SBR rubber	Plasticizer (DINP)	Zinc stearate	Epoxidized soyabean oil
PVC	100	-	-	2	10
R0P2.5	100	-	2.5	2	10
R0P5	100	-	5	2	10
R0P10	100	-	10	2	10
R2.5P0	100	2.5	-	2	10
R2.5P2.5	100	2.5	2.5	2	10
R2.5P5	100	2.5	5	2	10
R5P0	100	5	-	2	10
R5P2.5	100	5	2.5	2	10
R5P5	100	5	5	2	10
R7.5P0	100	7.5	-	2	10
R7.5P2.5	100	7.5	2.5	2	10
R7.5P5	100	7.5	5	2	10
R10P0	100	10	-	2	10
R10P2.5	100	10	2.5	2	10
R10P5	100	10	5	2	10

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Figure 3.1 Two-roll mill machine (model: LRM-S-110/3E)

3.3.2 Compression molding

The coarse PVC blends were compressed to form specimen shapes using compression molding (LP-S-50, Labtech Engineering, Thailand) as displayed in Figure 3.2. The compression conditions were as follows: preheat for 7 min, compression into sheet for 8 min at 185 °C with pressure of 50 bar and cooling to room temperature for 5 min. Then, the compressed sheets were cut into standard shape for characterization analysis and mechanical testing.

Figure 3.2 Compression molding machine (model: LP-S-50)

3.4 Characterizations

3.4.1 Fourier transform infrared spectroscope (FTIR)

Investigation of the PVC blend functional groups was carried out by Fourier transform microscope (Nicolet 6700, Thermo Fisher SCIENTIFIC, USA) as shown in Figure 3.3. The blend was dissolved in tetrahydrofuran (THF) solvent overnight. Then, the solution was cast onto pettidish and put into an oven at 70 °C to evaporate solvent. The FTIR spectrum of the blend prepared by KBr disk technique was achieved using transmission mode. The spectrum was recorded in the frequency in range of 400-4000 cm^{-1} with 64 scans.

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Figure 3.3 Fourier transform microscope (model: Nicolet 6700)

3.4.2 Scanning electron microscopy (SEM)

Scanning electron microscope (JSM-6610LV, JEOL, Japan) as presented in Figure 3.4 was employed to determine the dispersion of rubber particles and plasticizer in PVC matrix. Fracture surface of blennd samples obtained from impact and tensile testings were analyzed under an operating voltage of 15 kV. Sample preparation was carried out as follows: a specimen was subject to vaporized osmium tetroxide (OsO_4) overnight in the chamber containing 1% w/w OsO_4 solution. Osmium tetroxide vapor is capable of staining the rubber particles by oxidizing the rubber double bonds, appearing the holes which can be observed by SEM. The treated specimen was attached to the bar stub and coated with thin layer of gold.

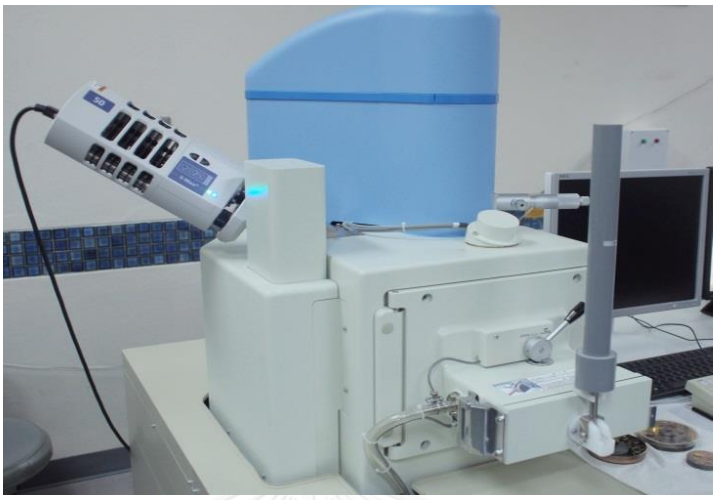

Figure 3.4 Scanning electron microscope (model: JSM-6610LV)

3.5 Mechanical testings

3.5.1 Impact strength

The notched Izod impact testing was carried out accordance to ASTM D256 using impact testing machine (GT-70-MDH, GOTECH, Taiwan) as shown in Figure 3.5 with hammer energy of 5.5 J. The dimensions of specimens were 12.7 × 60 × 3.2 mm (width × length × thickness) with 10 mm of notched deepness. The impact strength values were averaged from five samples testing.

Figure 3.5 Izod impact tester (model: GT-70-MDH)

3.5.2 Tensile properties

Tensile properties values, including Young's modulus, tensile strength and elongation at break were determined on universal testing machine (LLOYD LR 100K, LLOYD, United Kingdom) as shown in Figure 3.6 following ASTM D638 with dumbbell shaped samples (type IV) using load cell of 10 kN and crosshead speed of 50 mm/min at condition testing, ambient temperature (25 °C). The samples dimensions were 19 × 115 × 3 mm (width × length × thickness). The average values were measured from five specimens.

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Figure 3.6 Universal testing machine (model: LLOYD LR 100K)

3.5.3 Flexural properties

The flexural testing was performed by universal testing machine (LLOYD500, LLOYD/United Kingdom) as presented in Figure 3.7. The dimension samples were formed following ASTM D790 with 19 × 115 × 3 mm (width × length × thickness).

Figure 3.7 Universal testing machine (model: LLOYD LR 100K)

3.5.4 Hardness durometer shore (type D)

The shore hardness was investigated in accordance with ASTM D2240 using hardness durometer shore type D (CODE DR, The Shore Instrument & Mfg, USA) as displayed in Figure 3.8. The samples were formed in square dimension 50.8 × 50.8 mm (width × length) with thickness of 6 mm. Five values were recorded when the indenter was vertically pressed on surface of samples within 5 seconds.

Figure 3.8 Hardness durometer shore (model: CODE DR)

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3.5.5 Heat distortion temperature (HDT)

Heat distortion temperature of PVC blends was carried out using heat distortion tester (148-HD-PC, Yasuda Seiki Seisakusho, Ltd., Japan) as illustrated in Figure 3.9 following ASTM D648 standard. The dimension of samples was formed in 3 × 127 × 3 mm (width × length × thickness). Before testing, the samples were controlled in constant conditions of temperature at 23 ± 2 °C and relative humidity at 50 ± 5 % for 40 h and after that placed the samples in the oven with temperature at 70 °C for 24 h. The condition testing was used as follows: heating rate of 120 °C/h under the maximum bending stress of 0.455 MPa and displacement of 0.254 mm.

Figure 3.9 Heat distortion tester (model: 148-HD-PC)

3.6 Migration ability of plasticizer

3.6.1 Preparation of samples for migration study

Plasticized PVC, plasticized PVC/SMMA/SBR blend and polystyrene (PS) were prepared into sheet samples having the thickness of 1 mm by compression molding (LP-S-50, Labtech Engineering, Thailand) using the conditions as follows: preheating for 7 min, hot pressing for 3 min at 185 °C with pressure of 50 bar and cooling for 5 min to room temperature. PS sheet was prepared in a similar manner except the pressing temperature of 190 °C.

3.6.2 Migration testing

After forming the thin sheets of plasticized PVC, plasticized PVC/SMMA/SBR blend and PS (approximately 3 mm × 3 mm (width × length) and thickness was 1 mm. PS sheet was sandwiched between two plasticized PVC or plasticized PVC/SMMA/SBR blend sheets. The sandwiched sample was kept for a week in an oven set the temperature of 50 °C to allow the migration of plasticizer. Due to the migration ability of plasticizer, plasticized PS was anticipated. The plasticization of PS was evaluated by the determination of PS T_g using differential scanning calorimetry (DSC) method.

3.7 Determination of PS T_g by differential scanning calorimetry (DSC)

Migration of plasticizer was determined using differential scanning calorimeter (DSC 204 F1 Phoenix, LMS INSTRUMENTS, Germany) to follow the change in PS T_g as well as PVC T_g after migration test. Approximately 10 mg of polystyrene and PVC sheets was put into alumina crucible. The T_g was measured under condition as follows: heating range from 25 to 200 °C with 10 °C/min heating rate under a nitrogen flow rate of 20 ml/min. Differential scanning calorimeter shown in Figure 3.10 was employed for T_g determination.

Figure 3.10 Differential scanning calorimeter (model: DSC 204 F1 Phoenix)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterizations of materials

4.1.1 FTIR analysis

FTIR spectroscopy is a common technique to determine functional groups of polymeric materials. FTIR spectrum was recorded in the range between 400 and 4000 cm^{-1} with resolution of 4 cm^{-1}. The FTIR spectra of unplasticized PVC, diisononyl phthalate (DINP), plasticized PVC (R0P5), SMMA/SBR rubber and PVC/SMMA/SBR blends (R5P0) are shown in Figure 4.1. PVC blends are prepared using DINP content of 5 phr for R0P5 and SMMA/SBR rubber content of 5 phr for R5P0.

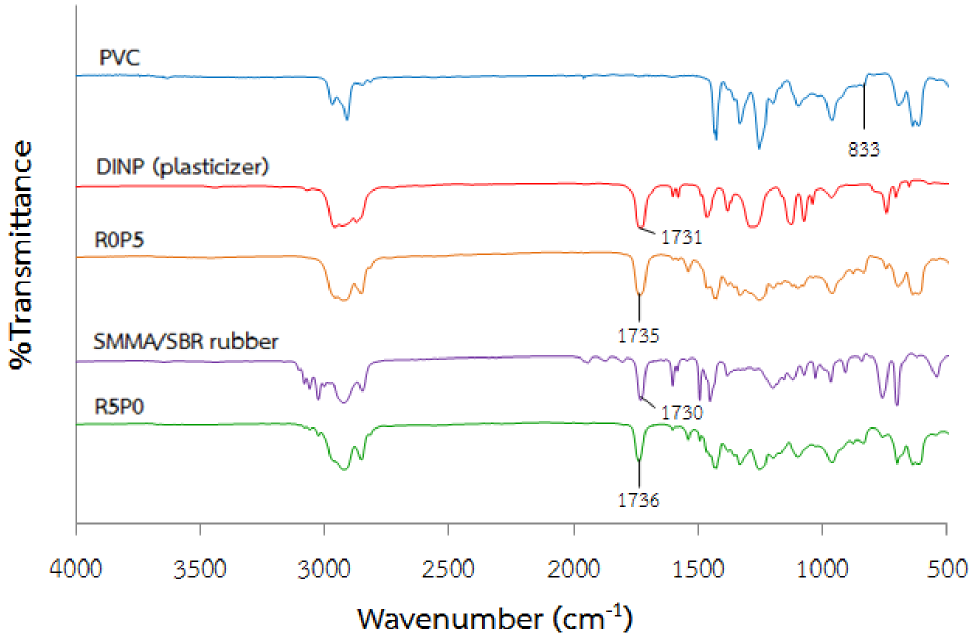

Figure 4.1 FT-IR spectra of unplasticized PVC, DINP, SMMA/SBR rubber and PVC blends

As seen, unplasticized PVC exhibits absorption peak at 2910 cm^{-1}, 1332 cm^{-1}, 1254 cm^{-1}, 960 cm^{-1}, 833 cm^{-1} and 614 cm^{-1} which correspond to –CH stretching, -CH$_2$ deformation, CH rocking, *trans* CH wagging, C-Cl stretching and *cis* CH wagging in PVC chain respectively. The absorption bands of DINP appear at 1731 cm^{-1} and 1464 cm^{-1}, corresponding to C=O stretching and CH$_3$ stretching, respectively. For DINP information (such as R0P5 formula), the carbonyl group is observed at 1735 cm^{-1} and believed to be DINP carbonyl group that slightly shifts from 1731 cm^{-1}. For the SMMA/SBR rubber, the absorption bands at 2923 cm^{-1}, 1730 cm^{-1}, 1452 cm^{-1}, 1198 cm^{-1} and 1601 cm^{-1} are assigned to -CH stretching, C=O stretching, CH$_3$ stretching, -OCH$_3$ stretching and C=C stretching (aromatic), respectively. The absorption peak of R5P0 carbonyl group is observed at higher wavenumber (1736 cm^{-1}) compared to the carbonyl group of SMMA/SBR rubber (1730 cm^{-1}) [9]. The significant shift of carbonyl peaks to higher wavenumber indicates that the interaction between two components occurs arising from intermolecular hydrogen bonding between carbonyl group (C=O) and hydrogen atom of CH-Cl in PVC, implying the compatibility between additives and PVC due to the specific interaction [43]. Ramesh and co-workers [35] explained that the shift of carbonyl absorption peak to higher wavenumber (from 1721 cm^{-1} to 1732 cm^{-1}) is indicative of the interaction between DINP carbonyl group (C=O) and PVC CH-Cl group. The functional groups and absorption bands of PVC and additives observed in this work are summarized in Table 4.1-4.3.

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Table 4.1 Functional groups and absorption peaks of PVC [35]

Functional groups	Wavenumber (cm^{-1})	Reference wavenumber (cm^{-1})
-CH stretching	2910	2890-2958
-CH_2 deformation	1332	1339
CH rocking	1254	1240-1257
trans CH wagging	960	961
C-Cl stretching	833	844
cis CH wagging	614	600

Table 4.2 Functional groups and absorption bands of DINP (plasticizer)

Functional groups	Wavenumber (cm^{-1})	Reference wavenumber (cm^{-1})
C=O stretching	1731	1655-1803
CH_3 stretching	1464	1444-1477

Table 4.3 Functional groups and absorption bands found in SMMA/SBR rubber [35]

Functional groups	Wavenumber (cm^{-1})	Reference wavenumber (cm^{-1})
-CH stretching	2923	2927-2986
C=O stretching	1730	1700-1744
CH_3 stretching	1452	1439
-OCH_3 stretching	1198	1195
C=C stretching (aromatic)	1601	1450-1650

4.1.2 Morphology analysis

Fracture surface morphology was observed using scanning electron microscope (SEM). Prior to morphological observation the fracture surface of testing specimens was exposed to vapor of OsO_4 solution in order to destroy rubber double bonds, resulting in the remaining holes in polymer.

4.1.2.1 Impact-fractured surface of PVC and plasticized PVC

The Izod impact-fractured surface morphology of PVC and plasticized PVC was observed by SEM technique. The plasticizer contents in PVC are 2.5, 5 and 10 phr. Figure 4.2 shows the impact-fractured surface of unplasticized PVC and plasticized PVC at ×5000 magnification.

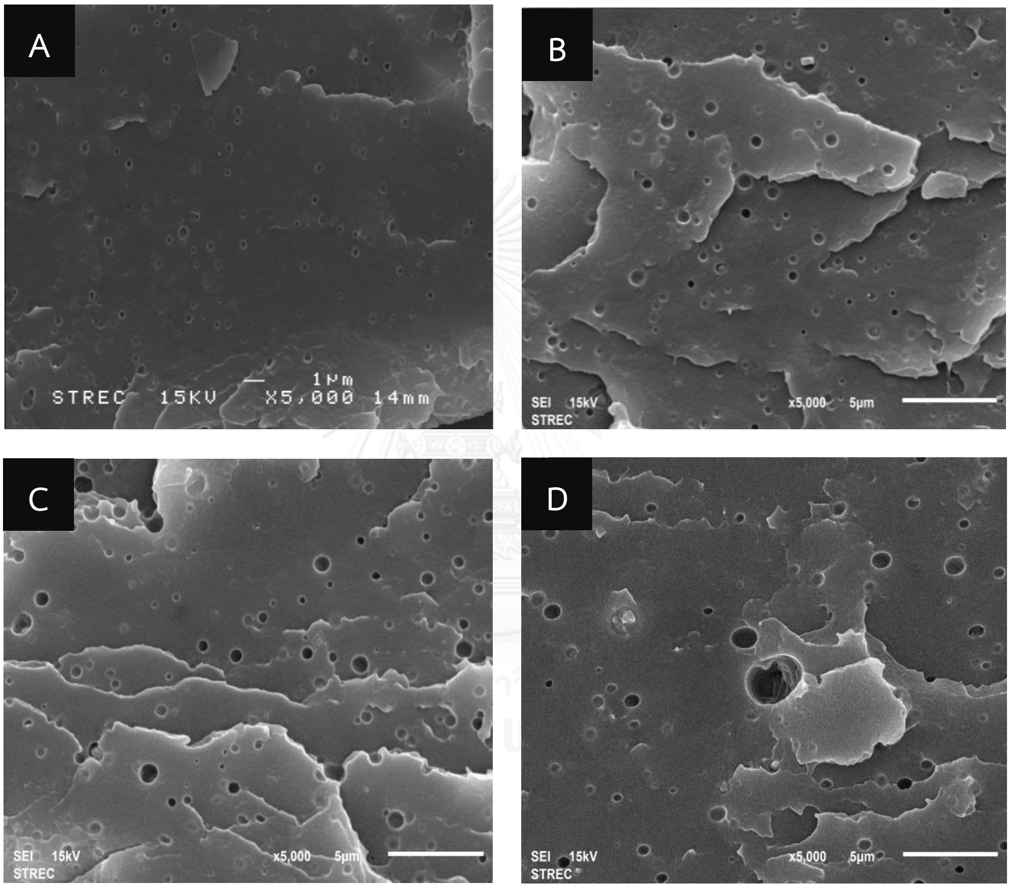


Figure 4.2 SEM micrographs of impact-fractured surface of (A) unplasticized PVC, plasticized PVC (B) R0P2.5, (C) R0P5 and (D) R0P10 (×5000 magnification)

Figure 4.2(A) shows that the impact-fractured surface of PVC exhibits a relatively smooth fracture surface, indicating typical brittle fracture characteristic of rigid materials including PVC [4, 5, 39, 44]. The morphology images of plasticized PVC containing 2.5, 5 and 10 phr of DINP are shown in Figure 4.2(B), 4.2(C) and 4.2(D), respectively. The surface morphology of plasticized PVC appears rougher with scattering holes and the fracture surface of plasticized PVC is broken after applied loading. It is believed that DINP is present in droplet form in PVC matrix, judged by an increase in the number of holes with an increase in DINP content.

4.1.2.2 Impact-fractured surface of PVC/SMMA/SBR blends

The impact-fractured surface of PVC/SMMA/SBR blends was observed by SEM technique. The SEM images of PVC blends consisting of SMMA/SBR rubber contents of 2.5, 5, 7.5 and 10 phr are shown in Figure 4.3. All figures are presented at magnification of 5000.

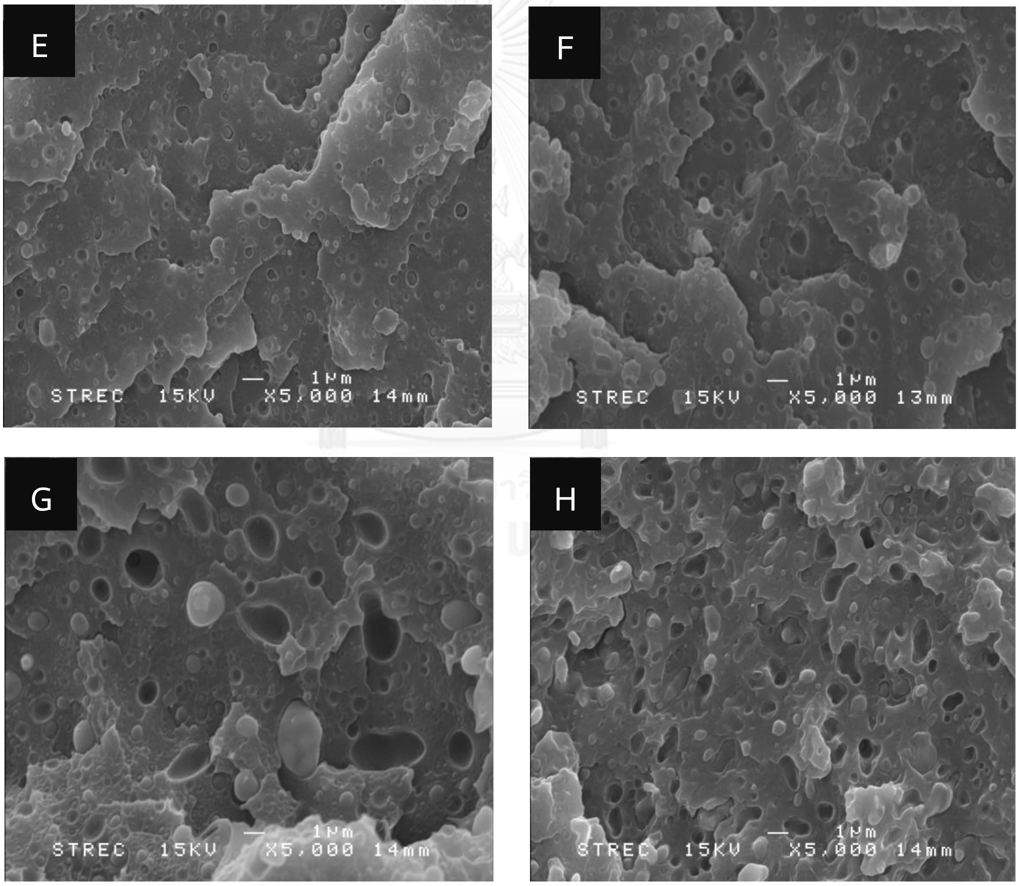
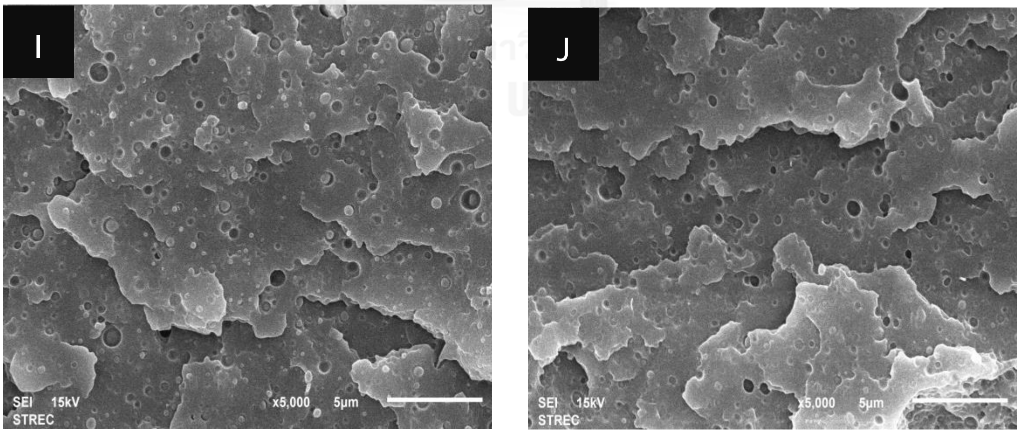


Figure 4.3 SEM micrographs of impact-fractured surface of PVC/SMMA/SBR blends of (E) R2.5P0 (F) R5P0 (G) R7.5P0 and (H) R10P0 (×5000 magnification)

From previous results, the impact-fractured surface of unplasticized PVC is smooth. In contrast, the impact-fractured surface of PVC/SMMA/SBR blends exhibits a relatively rougher surface containing numerous holes. It should be noted that the dark holes arose from the staining of rubber phase by OsO_4 vapor. The images of PVC/SMMA/SBR blends containing 2.5 and 5 phr rubber contents (Figure 4.3(E) and 4.3(F)), the fracture surface is rather bumpy surface with tiny spherical microvoids. In case of higher SMMA/SBR rubber contents such as 7.5 and 10 phr (Figure 4.3(G) and 4.3(H)), the dispersion of rubber particles seems to be homogenous and the fractured images appear in irregular spongy surface [5, 39]. Additionally, the morphology phases of 7.5 and 10 phr SMMA/SBR rubber present in elliptical shape with the bigger size of numerous holes due to higher rubber contents [3]. The SMMA/SBR rubber exhibits coarse fracture surface, pointing out the ductile failure behavior when subjecting to impact loading [4, 5].

4.1.2.3 Impact-fractured surface of plasticized PVC/SMMA/SBR blends



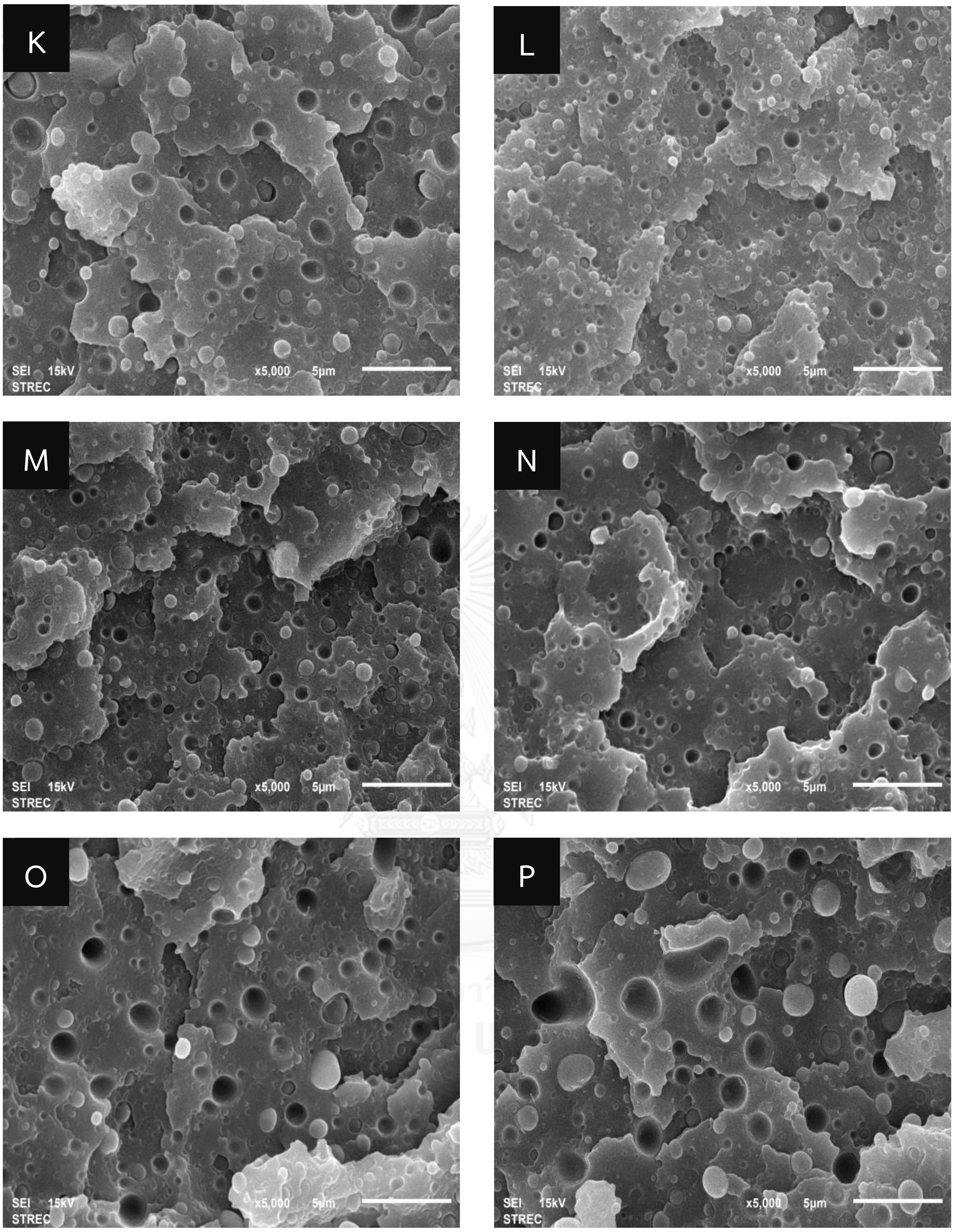


Figure 4.4 SEM micrographs of impact-fractured surface of (I) R2.5P2.5 (J) R2.5P5 (K) R5P2.5 (L) R5P5 (M) R7.5P2.5 (N) R7.5P5 (O) R10P2.5 and (P) R10P5 (magnification ×5000)

The morphological observation of impact-fractured surface of plasticized PVC/SMMA/SBR blends is presented in Figure 4.4. In details, the fracture surfaces of PVC containing various SMMA/SBR rubber to plasticizer ratios (2.5/2.5, 2.5/5, 5/2.5, 5/5, 7.5/2.5, 7.5/5, 10/2.5 and 10/5) are shown in Figure 4.4(I), 4.4(J), 44.4(K), 4.4(L), 4.4(M), 4.4(N), 4.4(O) and 4.4(P), respectively. The black holes represent both OsO_4 vaporized SMMA/SBR rubber particles and plasticizer droplets. As a result of oxidation reaction, double bonds containing compounds are stained and appeared with the holes. The black hole images provide information of size and shape of particles or droplets as well as their dispersibility in polymer matrix. The morphology of fracture surface shows roughness with an increase in the amount of SMMA/SBR rubber. The PVC containing lower amounts of SMMA/SBR rubber (Figure 4.4(I) and 4.4(J)) exhibits rather coarse fracture surface with tiny holes. Considering the plasticizer content of 2.5 phr, an increase in the amount of SMMA/SBR rubber from 5 to 10 phr (Figure 4.4(K), 4.4(M) and 4.4(O)), results in a larger number of black holes with bigger sizes distributing in coarser fracture surfaces. Furthermore, black holes uniformly dispersed in PVC matrix.

4.1.2.4 Tensile-fractured surface of plasticized PVC

The influence of plasticizer on fractured morphology was characterized by SEM. Specimens for SEM analysis including PVC containing 2.5, 5 and 10 phr DINP were obtained from tensile testing. Figure 4.5 shows the morphology of tensile-fractured surface of neat PVC and plasticized PVC at magnification ×2000.

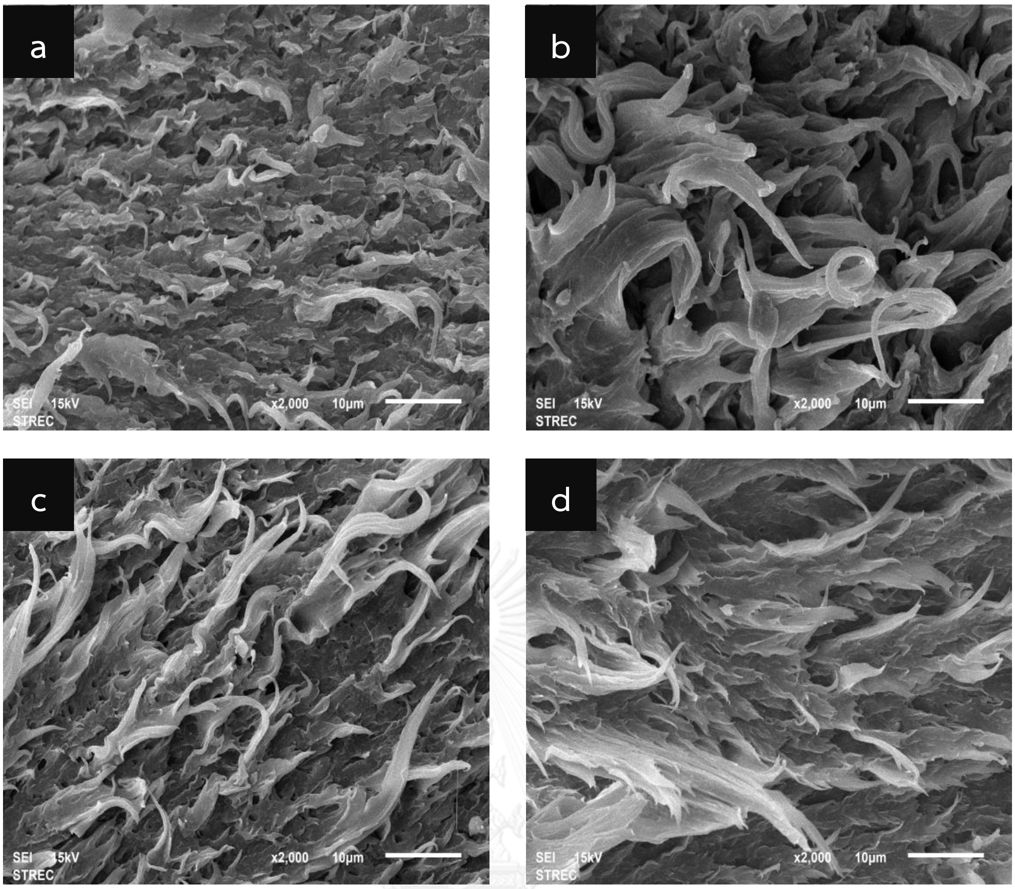


Figure 4.5 SEM micrographs of tensile-fractured surface of neat PVC and plasticized PVC containing (a) PVC (b) R0P2.5 (c) R0P5 and (d) R0P10 (magnification ×2000)

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The tensile-fractured surface of neat PVC exhibits roughness with short tentacles, implying the rigid characteristic of neat PVC [39]. An addition of plasticizer resulted in obvious roughness surface with relatively long tentacles. An increase in plasticizer content from 2.5, 5 to 10 phr resulted in an increase in the number of long tentacles as shown in Figure 4.5(b), 4.5(c) and 4.5(c), respectively. The long tentacle arisen from tensile testing is indicative of ductile PVC.

4.1.2.5 Tensile-fractured surface of PVC containing SMMA/SBR blend

The morphology of tensile-fractured surface of PVC containing SMMA/SBR rubber was observed with scanning electron microscope (SEM) after tensile testing. The SEM images at magnification ×2000 of PVC compounds having the content of SMMA/SBR rubber of 2.5, 5, 7.5 and 10 phr are illustrated in Figure 4.6.

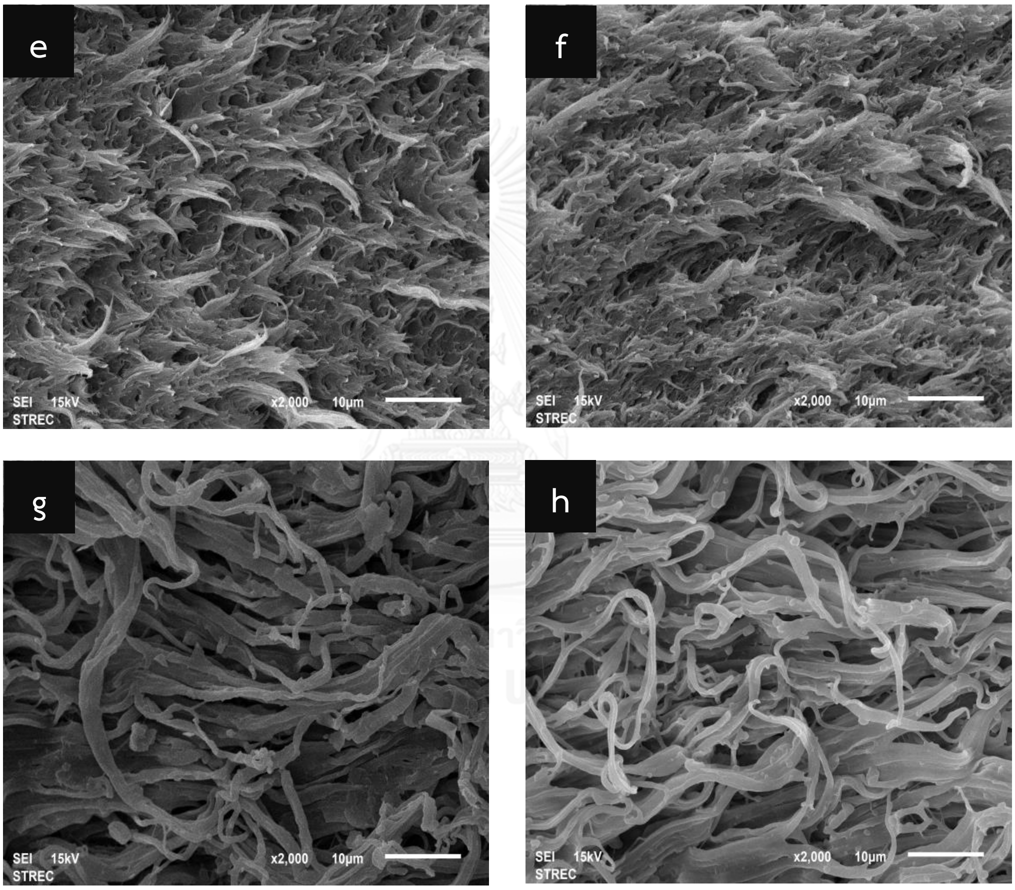
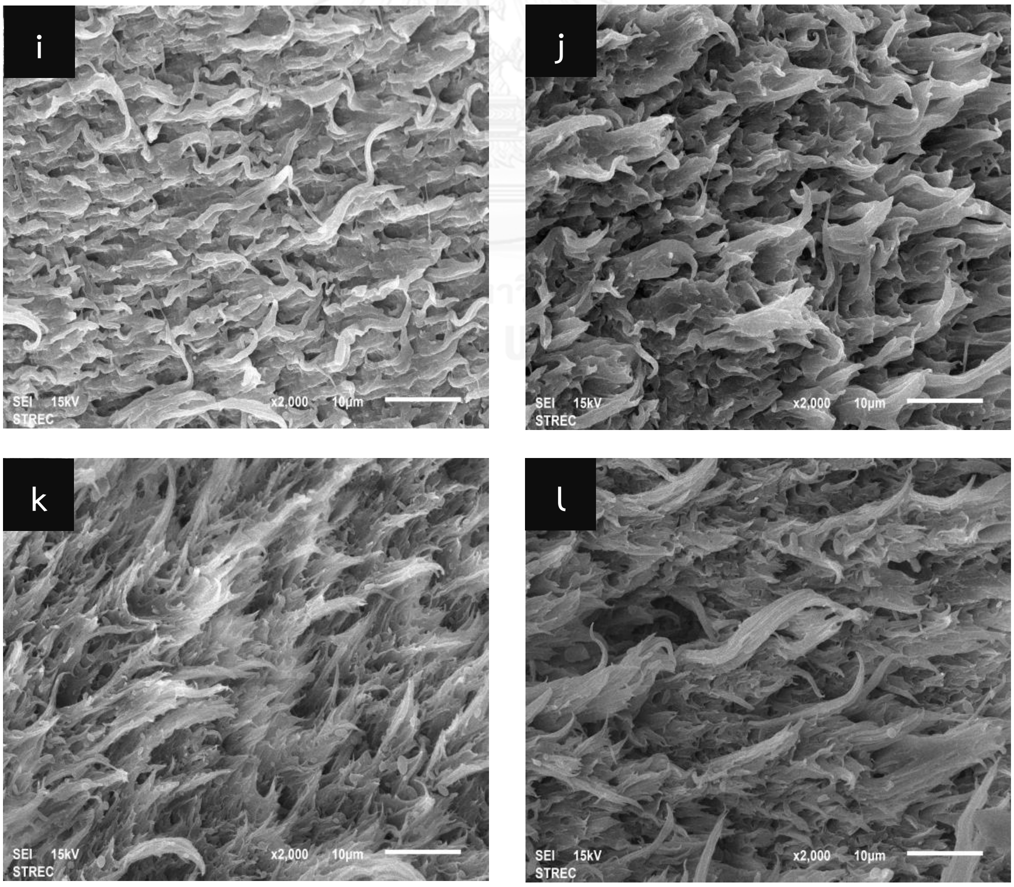


Figure 4.6 SEM micrographs of tensile-fractured surface of PVC blends containing (e) R2.5P0 (f) R5P0 (g) R7.5P0 and (h) R10P0 (magnification ×2000)

The SEM images of tensile-fractured surface of PVC blends containing 2.5, 5, 7.5 and 10 phr SMMA/SBR rubber are illustrated in Figure 4.6(e), 4.6(f), 4.6(g) and 4.6(h), respectively. The fracture surface of PVC/SMMA/SBR blends exhibits coarse surface with tentacles which were in similar manner to tensile-fractured surface of plasticized PVC (Figure 4.5(b-d)). The PVC blends having SMMA/SBR rubber contents of 2.5 and 5 phr are presented in Figure 4.6(e) and 4.6(f), respectively. Short tentacles on the fracture surface are observed whereas the fracture surface of PVC blends containing 7.5 and 10 phr SMMA/SBR rubber (Figure 4.6(g) and 4.6(h)), are completely deformed, indicating the flexible characteristic of SMMA/SBR rubber in PVC.

4.1.2.5 Tensile-fractured surface of plasticized PVC/SMMA/SBR blends

The tensile-fractured surface morphology of plasticized PVC/SMMA/SBR blends after tensile loading is presented in Figure 4.7 at magnification ×2000.



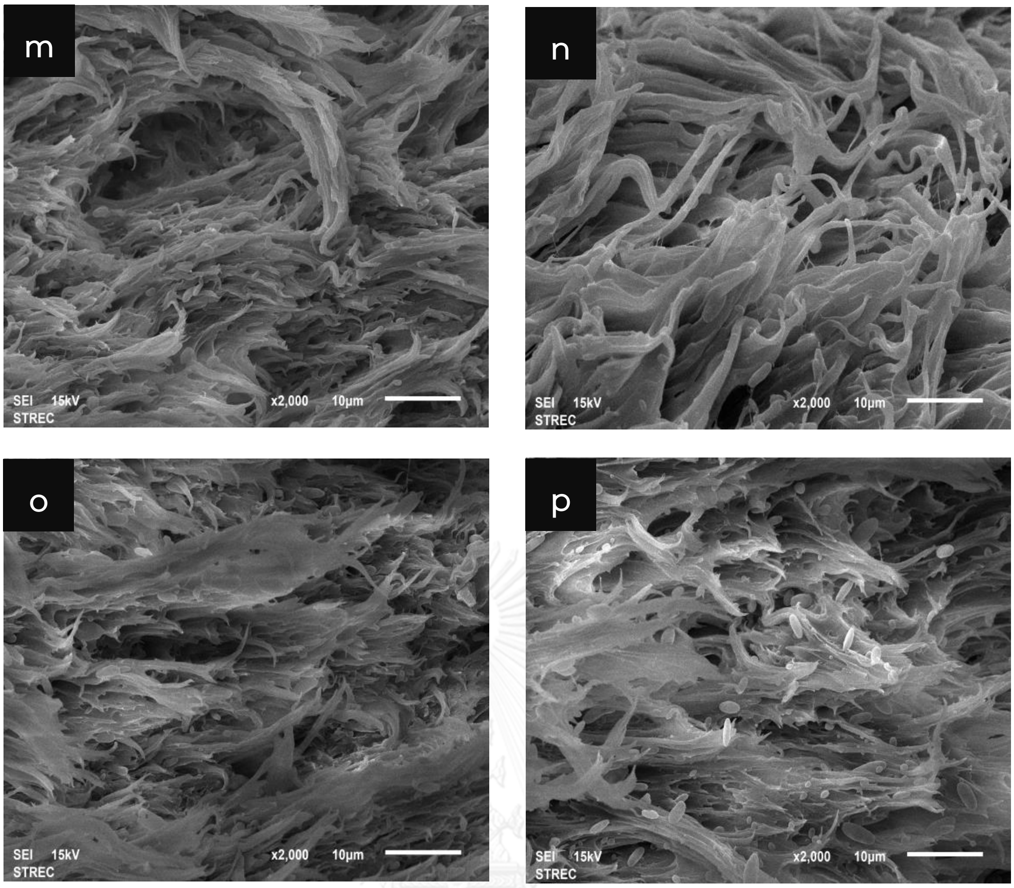


Figure 4.7 SEM micrographs of tensile-fractured surface of (i) R2.5P2.5 (j) R2.5P5 (k) R5P2.5 (l) R5P5 (m) R7.5P2.5 (n) R7.5P5 (o) R10P2.5 and (p) R10P5 (magnification ×2000)

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The morphological images of tensile-fractured surface of PVC blends having SMMA/SBR rubber/DINP ratios of 2.5/2.5, 2.5/5, 5/2.5, 5/5, 7.5/2.5, 7.5/5, 10/2.5 and 10/5 are shown in Figure 4.7(i), 4.7(j), 4.7(k), 4.7(l), 4.7(m), 4.7(n), 4.7(o) and 4.7(p), respectively. The morphology of plasticized PVC containing SMMA/SBR rubber is similar with plasticized PVC (Figure 4.5(b-d)) and PVC/SMMA/SBR blends (Figure 4.6(e-h)) discussed previously. An increase in SMMA/SBR rubber content resulted in a formation of the longer tentacles feature when compared to an increase in plasticizer content. The longer tentacles after tensile loading indicate the more ductile behavior for PVC blends.

4.2 Mechanical testing

4.2.1 Impact strength

The Izod impact testing in accordance with ASTM D256was employed to determine the impact strength for evaluation of the toughness of materials. The effect of plasticizer contents in PVC of 2.5, 5 and 10 phr and the amounts of SMMA/SBR rubber in PVC varied from 2.5 to 10 phr with 2.5 phr increments are studied.

4.2.1.1 Effect of plasticizer content

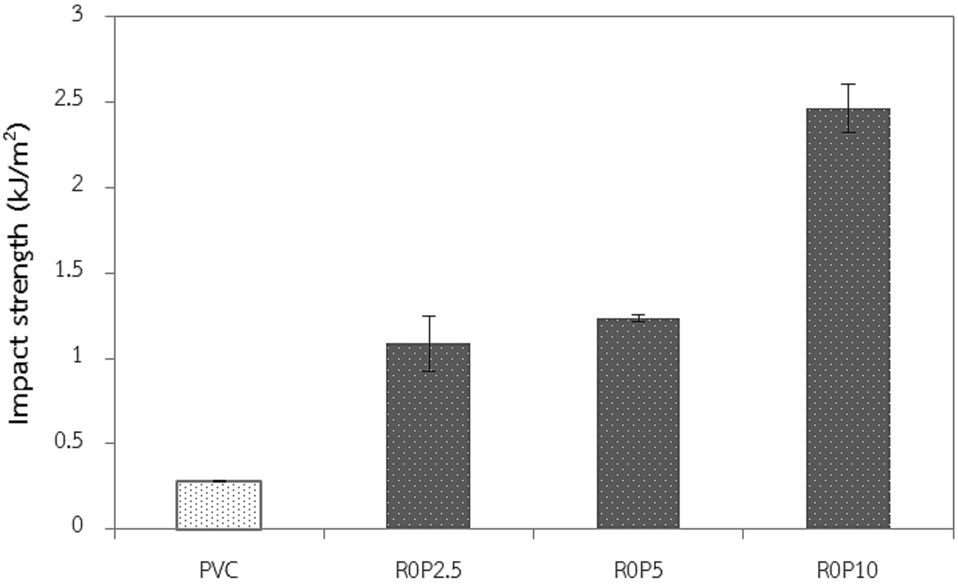

Figure 4.8 Impact strength of PVC and plasticized PVC prepared using various plasticizer contents.

Figure 4.8 shows the impact strength values of neat PVC and plasticized PVC. The Izod impact strength of PVC at ambience temperature (25 ^{o}C) indicated that PVC exhibiled low ductility, with impact strength of 0.28 kJ/m^2. The impact strength increases with an increase in the amount of plasticizer. Interestingly, the plasticizer content of 10 phr gave outstanding increment of impact strength. It is believed that plasticizer acted as an internal lubricant which enhanced the slipping of PVC polymer chain when force (impact loading) was applied. Therefore, an increase in plasticizer content resulted in an increase in the impact strength of the plasticized PVC.

4.2.1.2 Effect of SMMA/SBR rubber content

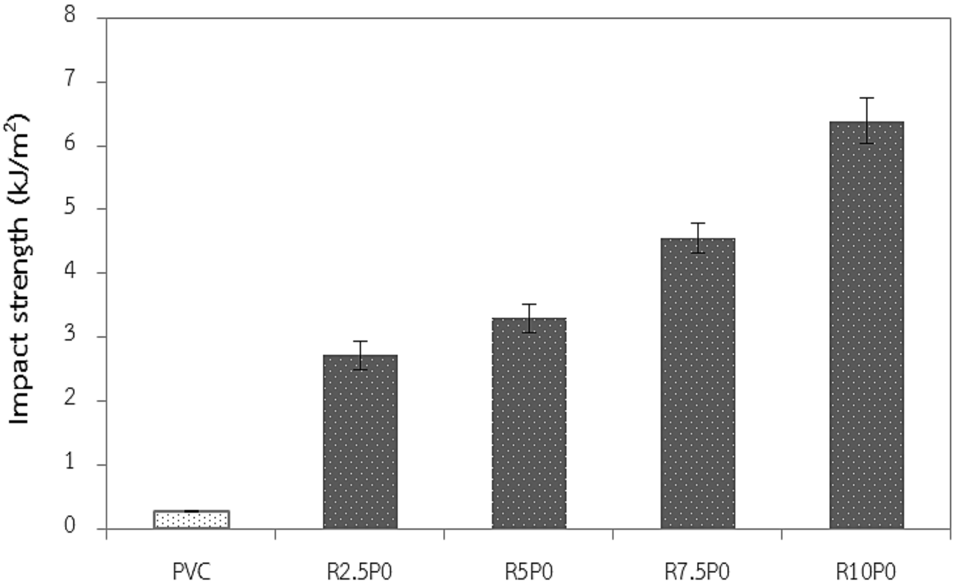

Figure 4.9 Impact strength of PVC and PVC/SMMA/SBR blends containing different amount of SMMA/SBR

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The improvement of impact strength of PVC by added SMMA/SBR rubber is illustrated in Figure 4.9. Obviously, the neat PVC exhibits poor toughness due to its rigidity. The impact strength of PVC containing SMMA/SBR rubber is found to be higher than neat PVC. A sighnificant increase in impact strength with an increase in the SMMA/SBR rubber content is due to the presence of rubber particles which are able to absorb impact energy under speedy action [39]. The impact strength of PVC containing 2.5, 5, 7.5 and 10 phr SMMA/SBR rubber contents are 2.53, 3.30, 4.55 and 6.38 kJ/m^2, respectively. The good dispersion of rubber particles in PVC (Figure 4.3) also are supportive of improved impact strength [45].

4.2.1.3 Effect of plasticizer content in PVC/SMMA/SBR blends

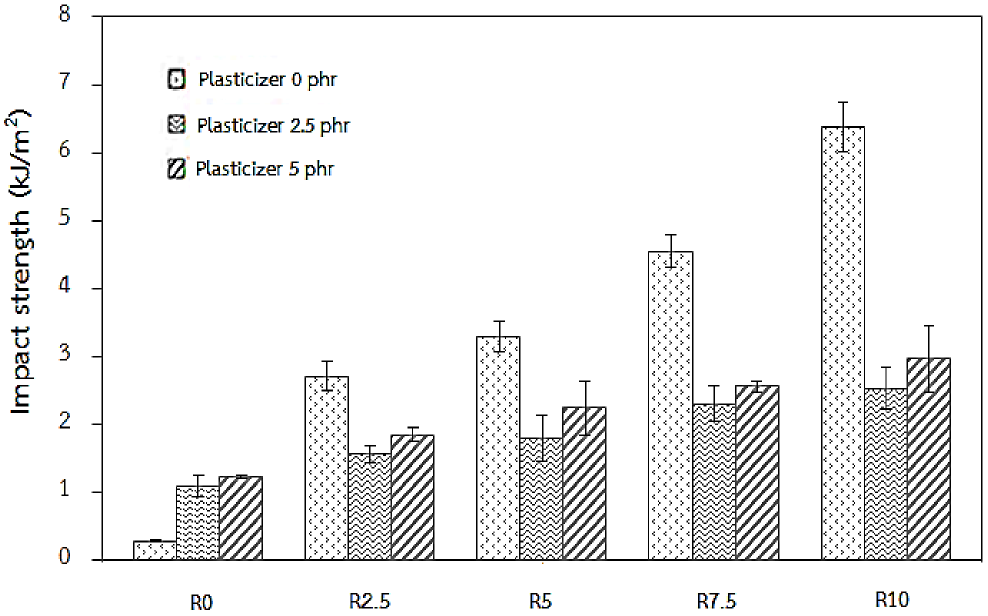

Figure 4.10 Impact strength of plasticized PVC/SMMA/SBR blends containing different amount of plasticizer

The effect of plasticizer contents in PVC/SMMA/SBR blends on impact property is shown in Figure 4.10. Previously, the presence of plasticizer or SMMA/SBR rubber in PVC helped improve the impact strength of PVC since the SMMA/SBR rubber acts as impact modifier for PVC. Regarding to the plasticizer which acts as internal lubricant for PVC but not an impact modifier, the addition the plasticizer into PVC/SMMA/SBR compound likely reduced the impact strength. Considering the PVC containing 10 phr SMMA/SBR rubber, its impact strength was 6.38 kJ/m^2. Then, an increase in DINP content from 2.5 to 5 phr in PVC/SMMA/SBR blends resulted in impact strength values of 2.53 to 2.97 kJ/m^2, respectively.

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4.2.2 Tensile properties

The tensile properties were investigated according to ASTM D680 standard method. The effects of plasticizer and SMMA/SBR rubber on tensile properties including Young' modulus, tensile strength and percent elongation at break were studied. The PVC blends consisting of plasticizer contents of 2.5, 5 and 10 phr and SMMA/SBR rubber amounts of 2.5, 5, 7.5 and 10 phr were tested.

4.2.2.1 Effect of plasticizer content

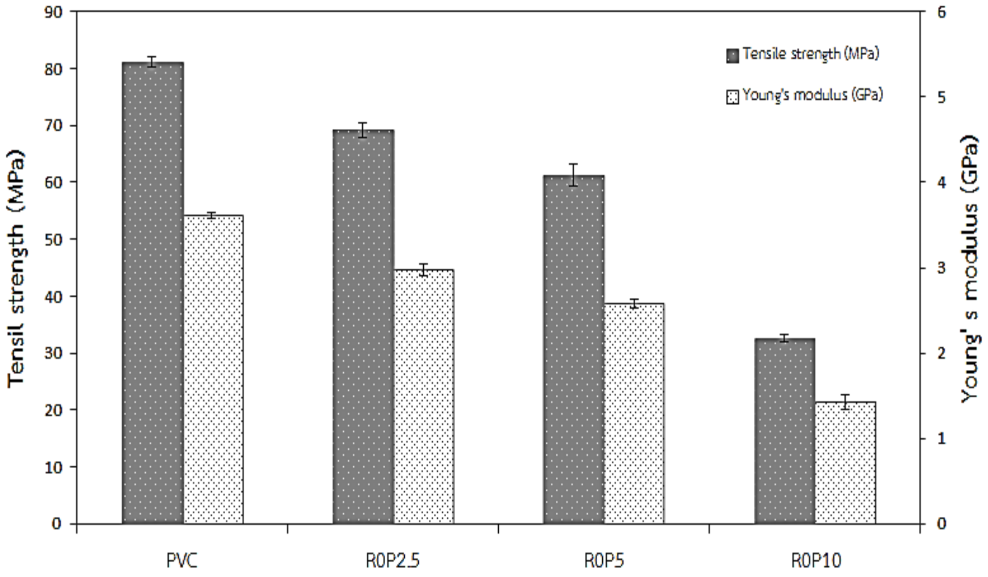

Figure 4.11 Tensile strength and Young's modulus of PVC and plasticized PVC prepared by using different content of plasticizer

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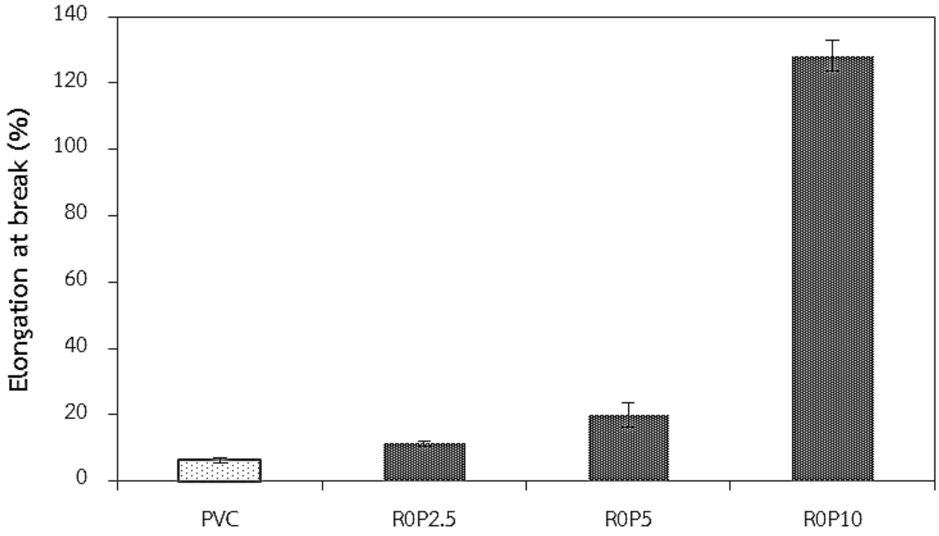

Figure 4.12 Elongation at break of PVC and plasticized PVC prepared by using different content of plasticizer

The effects of plasticizer on Young's modulus, tensile strength and elongation at break are shown in Figure 4.11 and 4.12, respectively. The Young's modulus and tensile strength of neat PVC are 3.62 GPa and 81.12 MPa, respectively, which are considered to be high due to high intermolecular force of chlorine atom [46]. On the other hand, the elongation at break of neat PVC is 6.31%. which, in contrast to Young's modulus, is considered to be poor due to the rigidity characteristic of PVC. Tensile strength continually decreases with an increase in plasticizer content due to the internal lubricancy effect [36]. Pita and co-workers [37] explained the addition of low-molecular-weight plasticizer into predominant PVC and plasticizer interfered the interaction force between PVC chains by reducing the dipolar force of PVC, subsequently causing the decreasing modulus as well as stress at yield point. Regarding to the elongation at break, the values significantly increases from 11.24% to 19.81% with addition of 2.5 and 5 phr of plasticizer, respectively and remarkably increases to 128.13% when 10 phr of plasticizer was employed. This was due to the increasing chain mobility with an increase in the plasticizer content.

4.2.2.2 Effect of SMMA/SBR rubber content

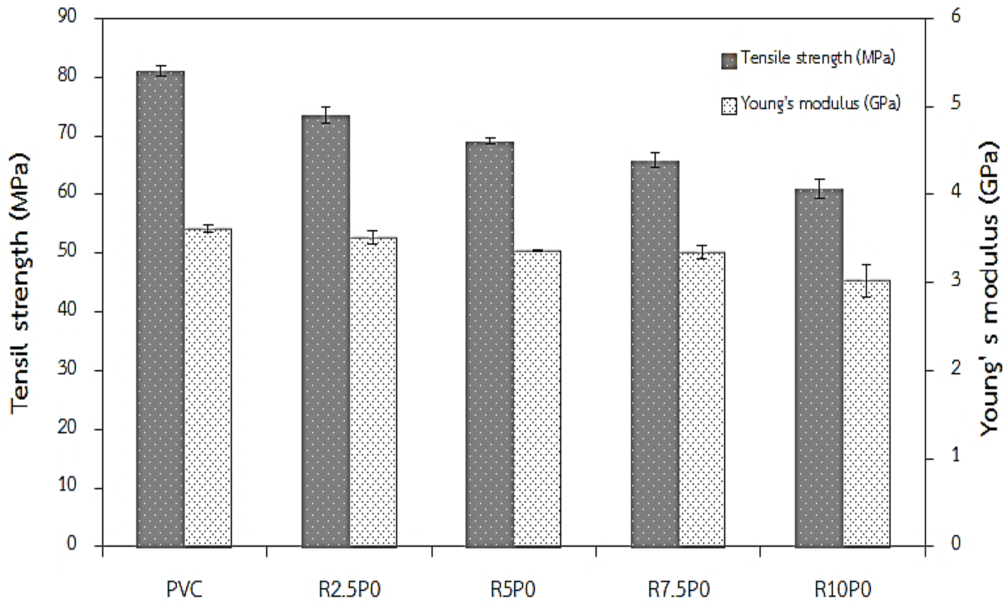

Figure 4.13 Tensile strength and Young's modulus of PVC and PVC/SMMA/SBR blends containing different amount of SMMA/SBR rubber

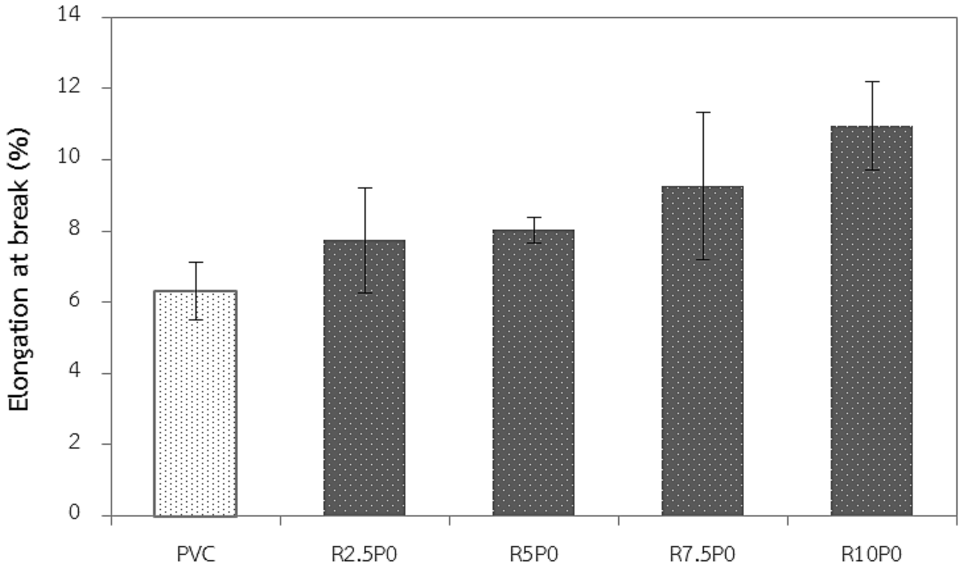

Figure 4.14 Elongation at break of PVC and PVC/SMMA/SBR blends containing different amount of SMMA/SBR rubber

Figure 4.13 and 4.14 present the effect of SMMA/SBR rubber on Young's modulus, tensile strength and elongation at break, respectively. Generally, the nature of PVC is stiff with high modulus and tensile strength. The addition SMMA/SBR rubber favored the decrease in those properties. The PVC samples containing 2.5, 5, 7.5 and 10 phr SMMA/SBR rubber show the Young's modulus of 3.52, 3.37, 3.34 and 3.02 GPa and tensile strength of 73.43, 69.15, 65.87 and 60.99 MPa, respectively. Young's modulus and tensile strength gradually decrease with an increase in the amount of SMMA/SBR rubber. Hosseinpour and co-workers [4] proposed that rubber particles acted as center of stress. Thus, the failure of samples occurred prematurely. On the contrary, an increase in SMMA/SBR rubber content led to an increase in the elongation at break (Figure 4.14), as a result of the presence of rubber phase [4].

4.2.2.3 Effect of plasticizer content in PVC/SMMA/SBR blends

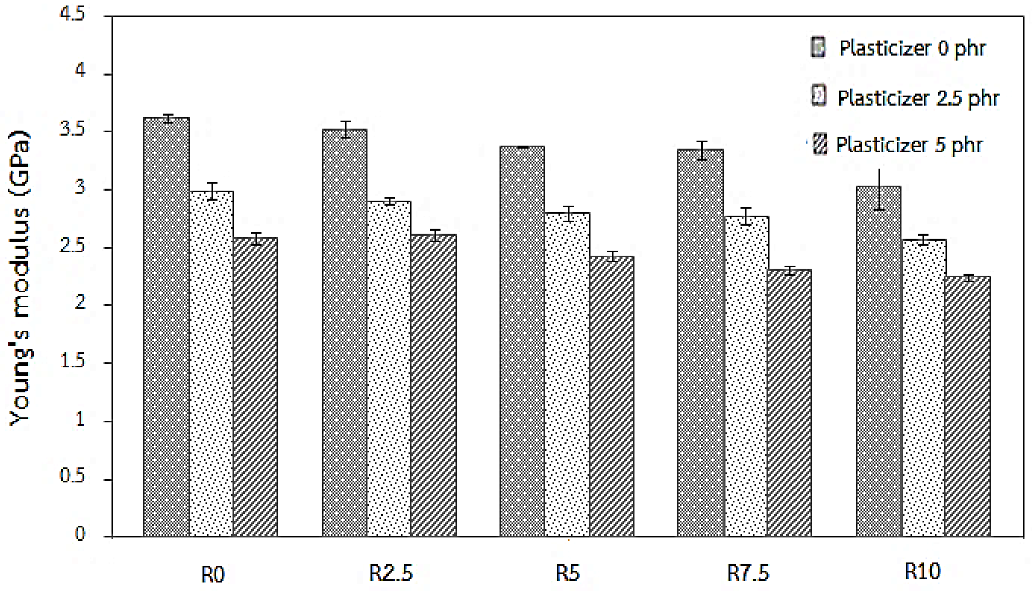

Figure 4.15 Young's modulus of plasticized PVC/SMMA/SBR blends containing different plasticizer content

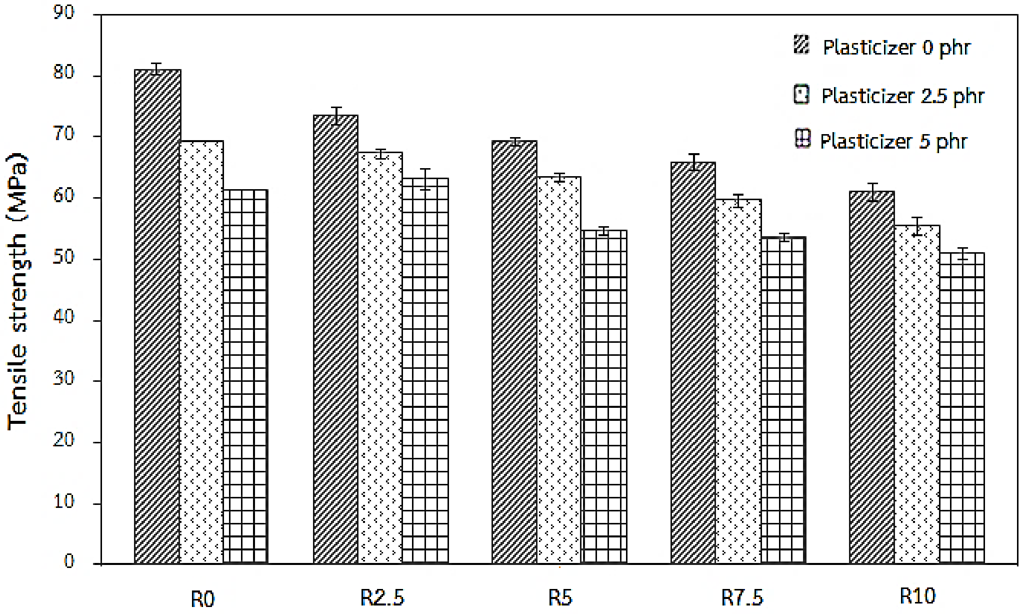

Figure 4.16 Tensile strength of plasticized PVC/SMMA/SBR blends containing different plasticizer content

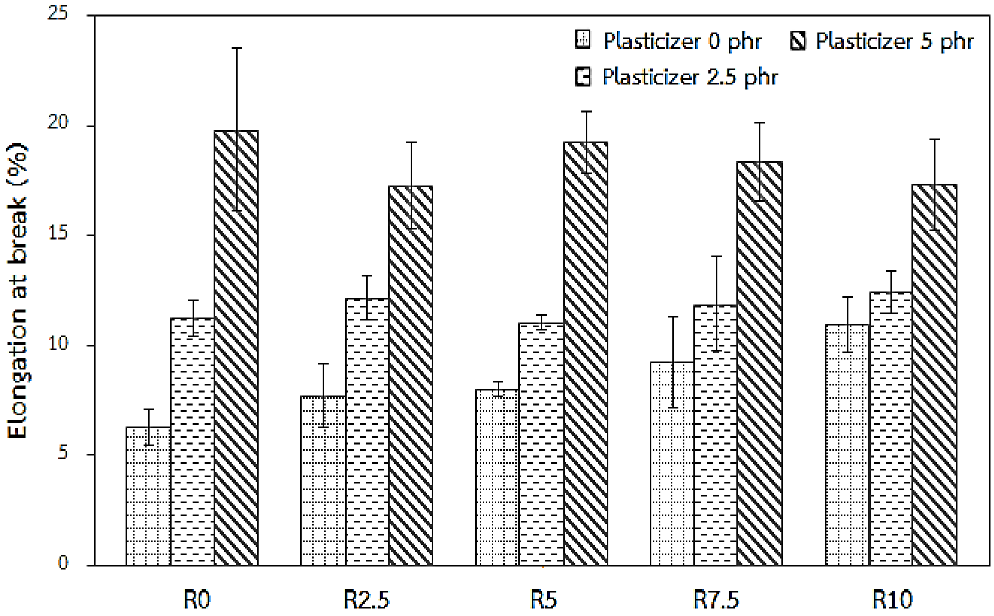

Figure 4.17 Elongation at break of plasticized PVC/SMMA/SBR blends containing different plasticizer content

The effects of plasticizer in PVC blends on tensile properties including Young's modulus, tensile strength and elongation at break are presented in Figure 4.15, 4.16 and 4.17. Previously, Young's modulus and tensile strength of PVC slightly decrease with an increase in the amount of plasticizer or SMMA/SBR rubber. As a result of the addition of 2.5 and 5 phr plasticizers into PVC/SMMA/SBR blends, the Young's modulus and tensile strength drastically decrease. Considering the SMMA/SBR rubber content of 10 phr, R10P0 shows tensile strength values of 60.99 MPa. An increase in plasticizer contents from 2.5 to 5 phr results a decrease in the tensile strength values of R10P2.5 and R10P5 from 55.35 to 50.91 MPa, respectively. The trend of the effect of plasticizer on Young's modulus of plasticized PVC/SMMA/SBR blends is in similar manner to tensile strength value. On the other hand, the elongation at break of plasticized PVC/SMMA/SBR blends increases significantly with an increase in the amount of plasticizer. In summary, the presence of plasticizer in PVC/SMMA/SBR blends caused severe effect on the modulus and tensile strength but, on the other hand, improved the flexibility of PVC.

4.2.3 Flexural properties

The samples for flexural strength testing were fabricated according to ASTM D790 standard method. The PVC blends are consisting 2.5, 5 and 10 phr plasticizer contents and 2.5, 5, 7.5 and 10 phr SMMA/SBR rubber contents.

4.2.3.1 Effect of plasticizer content

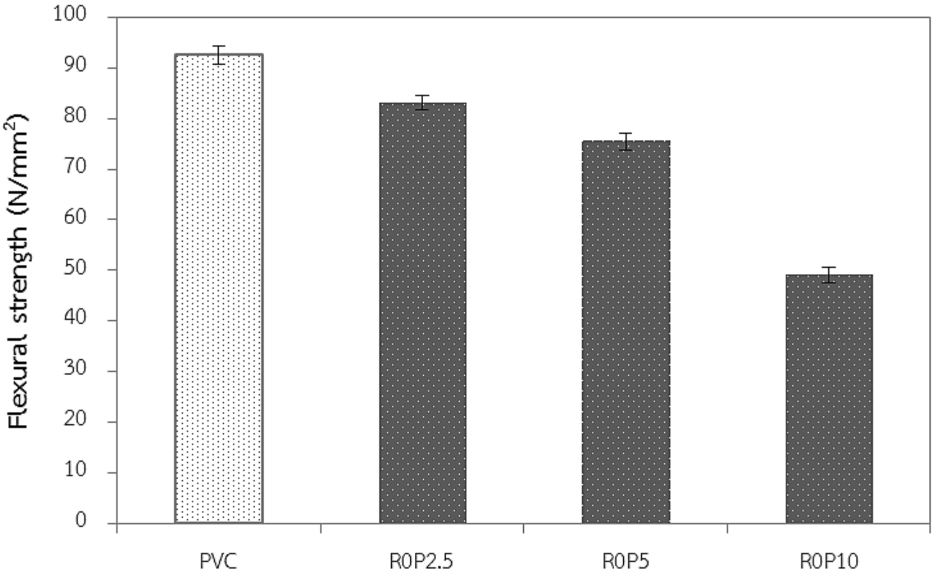

Figure 4.18 Flexural strength of PVC and plasticized PVC containing different plasticizer content

Figure 4.18 shows the flexural strength of products where DINP is introduced. The flexural strength of neat PVC is high with 92.54 N/mm^2 of value due to its stiffness arising from strong intermolecular force of chlorine atom in PVC. Thus, it is against in shape change and prone to be fragile under the applying force [46]. The effect of plasticizer on flexural strength decreases with an increase in the amount of DINP in similar manner to the tensile strength. The PVC with plasticizer contents of 2.5, 5 and 10 phr show 84.60, 82.00 and 73.21 N/mm^2 of flexural strength, respectively because the plasticizer disrupts the arrangement of PVC structure. Thus the movement of molecule chain of plasticized PVC is easier and it also easily change shape under flexural loading.

4.2.3.2 Effect of SMMA/SBR rubber content

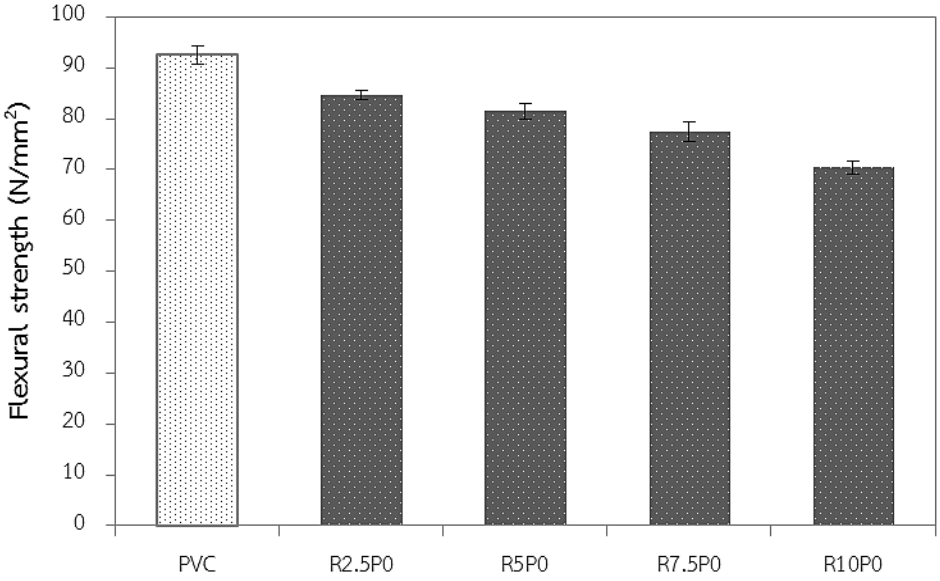

Figure 4.19 Flexural strength of PVC and PVC/SMMA/SBR blends containing different amount of SMMA/SBR rubber

Figure 4.19 illustrates the flexural strength of PVC and PVC/SMMA/SBR blends. In this work, neat PVC has a large value of flexural strength. The results from flexural testing, the PVC/SMMA/SBR blends containing SMMA/SBR rubber contents of 2.5, 5, 7.5 and 10 phr show the flexural strength values of 84.60, 81.38, 77.44 and 70.35 N/mm^2, respectively. An increase in the amount of SMMA/SBR rubber resulted in continueously decreases of the flexural strength due to the lower tensile strength compared with neat PVC. In addition, the SMMA/SBR rubber is consisting of rubber particles making the samples softer. Thus the changing shape under flexural loading is less resisted.

4.2.3.3 Effect of plasticizer content in PVC/SMMA/SBR blends

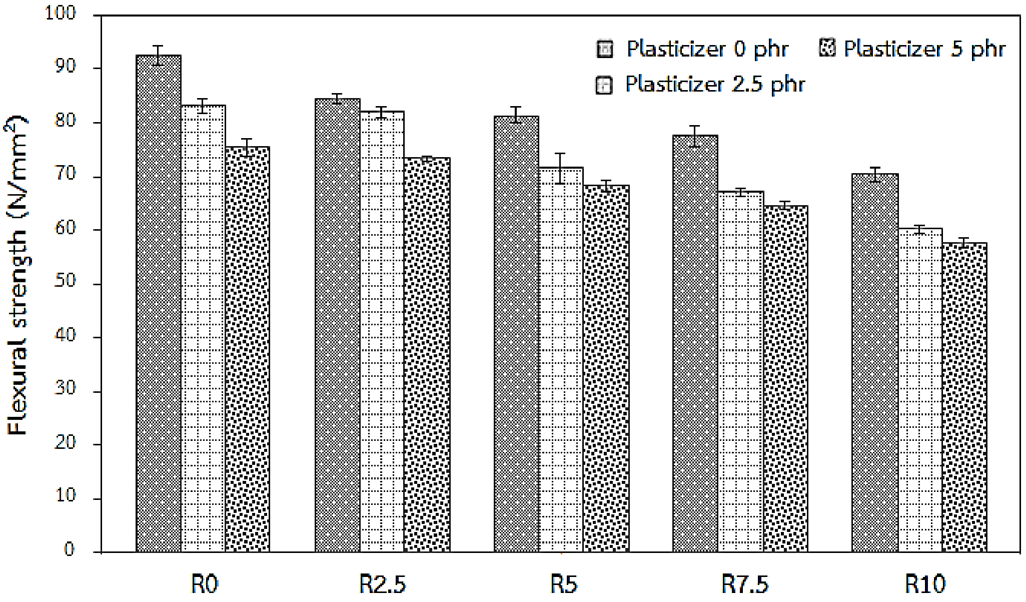

Figure 4.20 Flexural strength of plasticized PVC/SMMA/SBR blends containing different plasticizer content

The effect of plasticized PVC/SMMA/SBR blends on flexural properties is revealed in Figure 4.20. The effect of plasticizer on flexural strength is in the same trend with the effect of DINP and SMMA/SBR rubber in PVC. The flexural strength continuously decreases with increasing the amount of plasticizer. In this work, the flexural strength of R10P0 was 70.35 N/mm^2. PVC/SMMA/SBR blends with an incorporation of plasticizer content of 2.5 and 5 phr show the flexural strength at 60.10 and 57.59 N/mm^2, respectively. The presence of DINP and SMMA/SBR rubber in PVC resulted in a decrease in flexural strength due to the ease of PVC deformation caused by the combitnation of those additives; the more the amount of plasticizer the more the the decrease in flexural strength. These result imply that the addition of plasticizer is necessary but undesirable particular at the high content.

4.2.4 Hardness

The hardness was used to measure the degree of softening of samples following ASTM D790 using durometer shore type D. In this work, the PVC contains 2.5, 5 and 10 phr plasticizer contents and 2.5, 5, 7.5 and 10 phr SMMA/SBR rubber contents.

4.2.4.1 Effect of plasticizer content

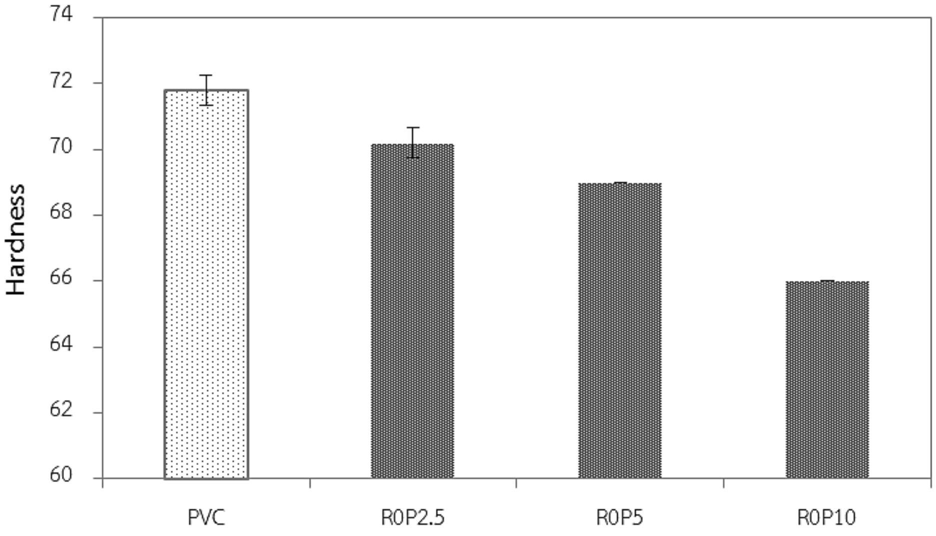

Figure 4.21 Hardness of PVC and plasticized PVC containing different plasticizer content

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The influence of plasticizer in PVC is demonstrated in Figure 4.21. The hardness used durometer shore type D for rigid material. Normally, the nature of PVC is to have rigid surface. This grade of PVC has a hardness value of 71.8. An increase in plasticizer content in PVC from 2.5, 5 and 10 phr leads to the decrease in hardness values of 70.2, 69.0 and 66.0, respectively due to the mechanism action of plasticizer. Acting as spacer between PVC molecule chains, plasticizer causes an increase in the free volume of polymer chains and polymer linkage of PVC is debilitated [38]. Elgozali and co-workers [36] adduced that the dipolar interaction between chlorine atom of PVC and carbonyl of ester group in molecule of plasticizer caused weaker interaction between in polymer chains and the larger free volume in polymer matrix increased. In summary, in the presence of the plasticizer, polymer becomes softer resulting in lowering the hardness value.

4.2.4.2 Effect of SMMA/SBR rubber content

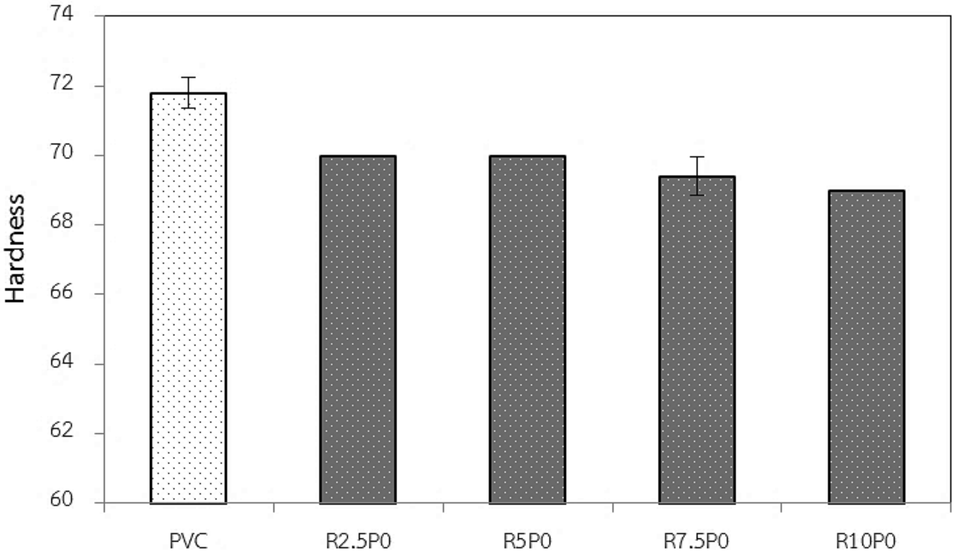

Figure 4.22 Hardness of PVC and PVC/SMMA/SBR blends containing different SMMA/SBR content

Figure 4.22 shows the influence of SMMA/SBR on hardness property of PVC/SMMA/SBR blends. As the results of 2.5, 5, 7.5 and 10 phr of SMMA/SBR rubber in PVC, the hardness of 70, 70, 69.4 and 69 are observed, respectively. The component of SMMA/SBR rubber is consisting of polybutadiene rubber that acts as a soft particle causing a slight decrease of the hardness with the rise of rubber components in PVC compound.

4.2.4.3 Effect of plasticizer content in PVC/SMMA/SBR blends

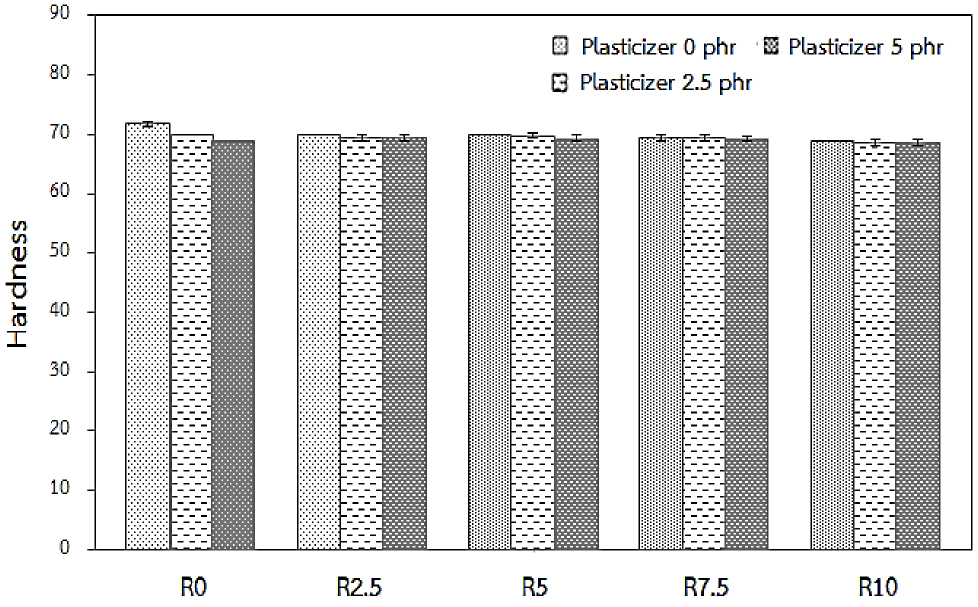

Figure 4.23 Hardness of plasticized PVC/SMMA/SBR blends containing different plasticizer content

The influence of plasticizer on hardness property of PVC/SMMA/SBR blends is disclosed in Figure 4.23. The neat PVC exhibits rigid surface. When introduced the plasticizer or SMMA/SBR rubber in PVC, the hardness slightly decreases with increasing amount of plasticizer or SMMA/SBR rubber. It is likely that plasticizer is a major effect on the hardness property deterioration.

4.2.5 Heat distortion temperature (HDT)

Heat distortion temperature testing was to estimate heat resistance of PVC blends. The heat distortion temperature of samples is determined in accordance with ASTM D648. The PVC contains 2.5, 5 and 10 phr plasticizer contents and 2.5, 5, 7.5 and 10 phr of SMMA/SBR rubber.

4.2.5.1 Effect of plasticizer content

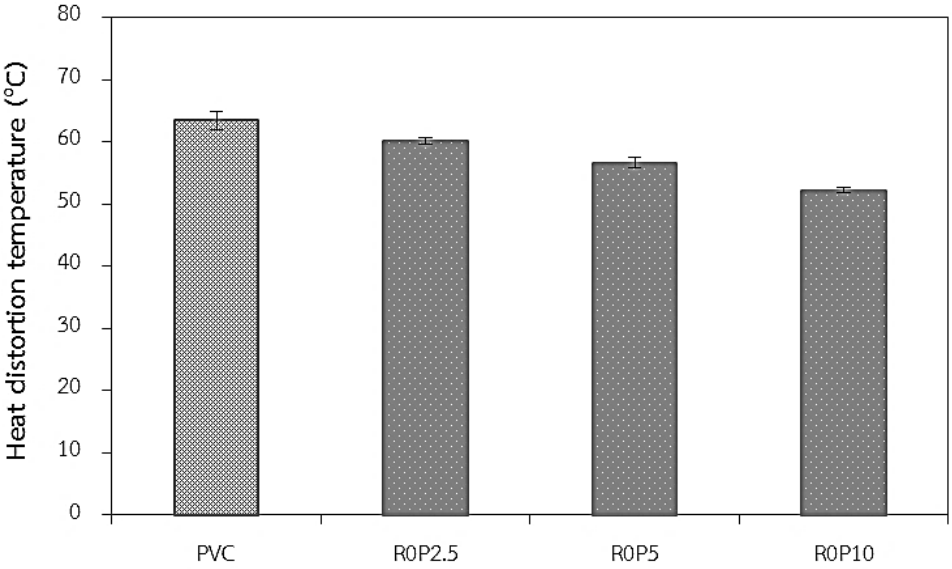

Figure 4.24 Heat distortion temperature of PVC and plasticized PVC containing different plasticizer content

The effect of plasticizer on heat distortion temperature (HDT) of PVC is shown in Figure 4.24. The HDT value of neat PVC in this work under the maximum bending stress of 0.455 MPa was 63.4 °C. HDT values of PVC containing 2.5, 5 and 10 phr of plasticizer are 60.1, 56.6 and 52.2 °C, respectively and the HDT values significantly decrease with the increase of plasticizer content. The mechanism of plasticizer concerns the interpolation of plasticizer between amorphous phases of PVC which causes the rise in the free volume of PVC whereas the glass transition temperature (T_g) is reduced [40].

4.2.5.2 Effect of SMMA/SBR rubber content

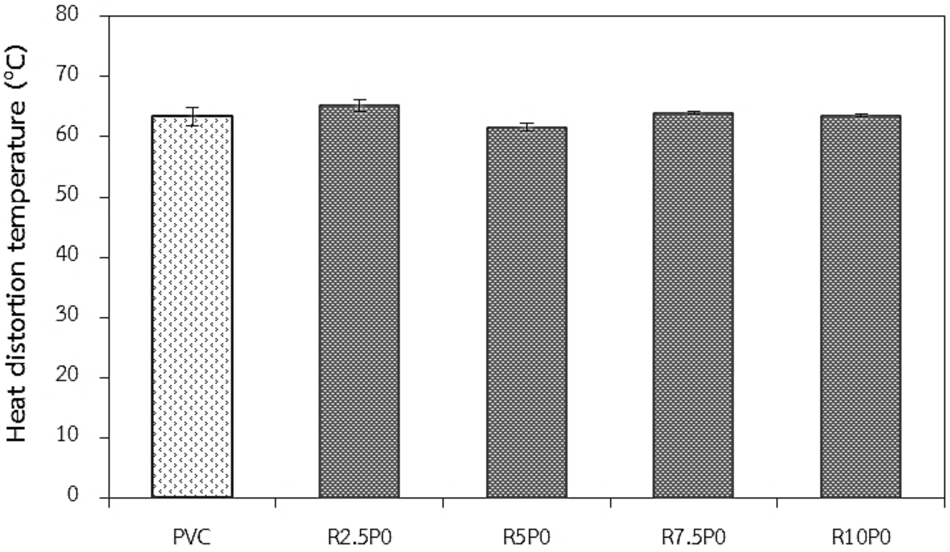

Figure 4.25 Heat distortion temperature of PVC and PVC/SMMA/SBR blends containing different SMMA/SBR content

The influence of SMMA/SBR rubber can be seen from Figure 4.25. Previously, PVC exhibits the HDT value of 63.4 °C. Considering the PVC containing 2.5, 5, 7.5 and 10 phr of SMMA/SBR rubber content, the observed HDT values are 65.2 °C, 61.6 °C, 64.0 °C and 63.3 °C, respectively. The incorporation of SMMA/SBR rubber in PVC matrix trends to cause a very little change in the heat distortion temperature. The effect of SMMA/SBR rubber may be elucidated that its steric effect in the part of methyl group of methyl methacrylate interrupts the chain mobility of PVC compound [40].

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4.2.5.3 Effect of plasticized PVC/SMMA/SBR blends

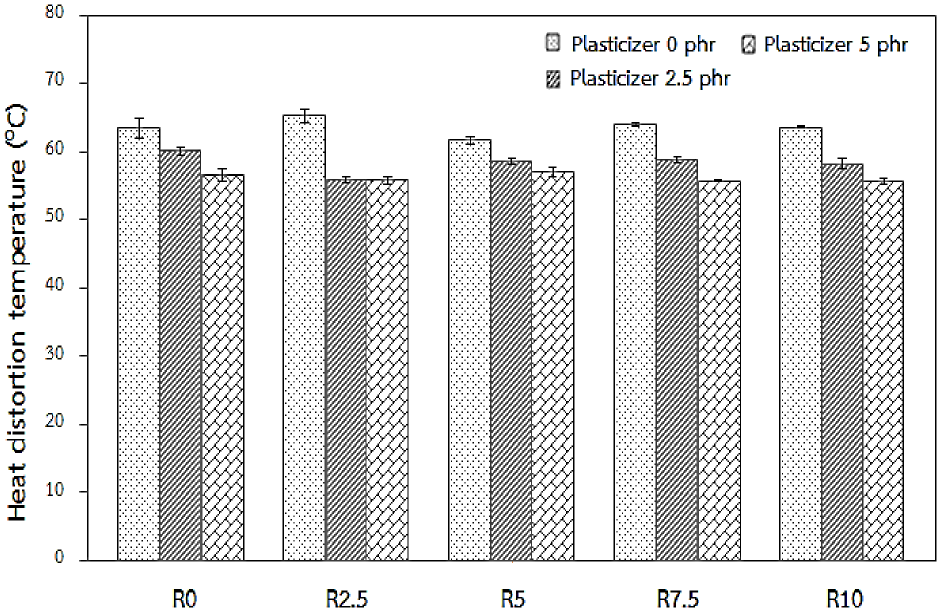

Figure 4.26 Heat distortion temperature of plasticized PVC/SMMA/SBR blends containing different plasticizer content

The heat distortion temperature (HDT) of plasticized PVC/SMMA/SBR blends is presented in Figure 4.26. An increase in the content of plasticizer in PVC leads to a decrease in the heat distortion temperature under the maximum bending stress of 0.455 MPa. The products are softer because of the presence of plasticizer in PVC. In addition, plasticizer may also reduce the value of T_g as discussed by Zhen Zhang and co-workers [40, 47]. They demonstrated that HDT decreased following the diminishing of T_g in the amorphous polymers.

4.3 Migration ability of plasticizer

Migration of plasticizer (DINP) from plasticized PVC was detected by using differential scanning calorimeter (DSC) on first scan cycle. Polystyrene (PS) contained the released plasticizer was used to determine the amount of releasing of plasticizer from PVC. The plasticized PVC of R0P5, R5P5 and R5P10 were investigated.

During migration testing, plasticizer slowly migrated from PVC to PS, resulting in plasticized PS. As a result, T_g of plasticized PS shifted to lower temperature which was determined by DSC [48].

4.3.1 Determination of PS T_g by differential scanning calorimetry (DSC)

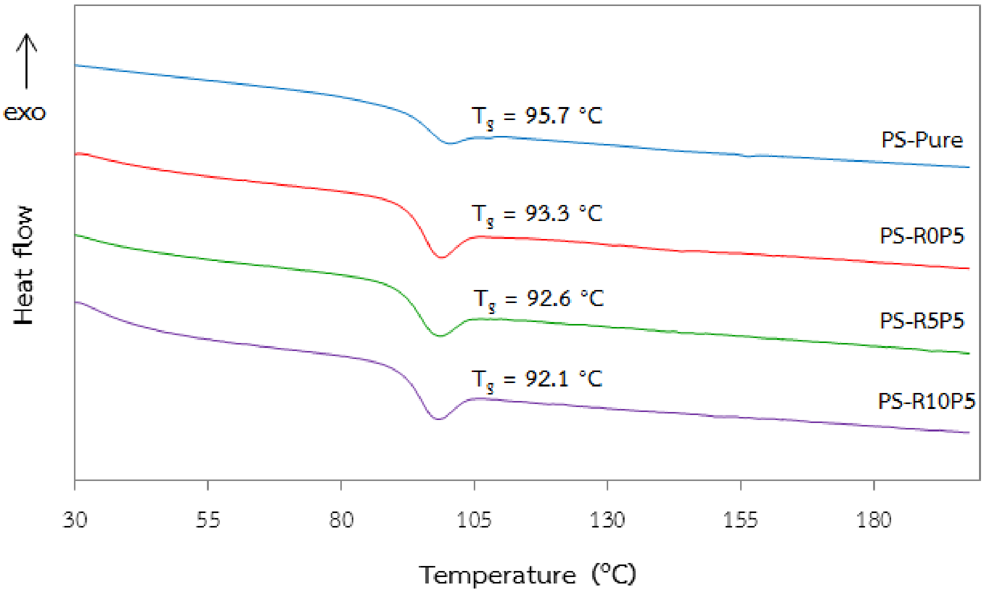

Figure 4.27 DSC thermogram of plasticized PS

Figure 4.27 shows T_g of PS with various SMMA/SBR contents. The T_g of neat PS is found at 95.7 °C. For plasticized PS, T_g values of PS-ROP5, PS-R5P5, and PS-R10P5 are 93.3 °C, 92.6 °C, and 92.1 °C, respectively. Compared to plasticized PVC, the migration ability of DINP in PVC containing SMMA/SBR rubber is relatively faster. This is due to the fact that DINP migration ability in the interphase is faster than those DINP in PVC matrix. Therefore, the usage amount of DINP addition into PVC/SMMA/SBR blend should be kept as low as possible without the compromise of processing difficulty.

CHAPTER V
CONCLUSIONS

5.1 Conclusions

In this work, the PVC blend reinforced with SMMA/SBR rubber was prepared. The rubber contents of 2.5, 5, 7.5 and 10 phr along with the addition of DINP plasticizer ranging from 2.5, 5 to 10 phr were studied. The effects of SMMA/SBR rubber on mechanical properties, including impact strength, tensile properties, flexural strength, hardness and heat distortion temperature were evaluated by standard tests. Furthermore, plasticizer migration ability was investigated. The conclusion results are summarized as follows:

5.1.1 FTIR analysis of SMMA/SBR rubber containing PVC samples showed the absorption band at 1732 cm^{-1} (C=O stretching), 3025 cm^{-1} (=C-H stretching) and 636.8 cm^{-1} (C-Cl band). The slightly shift of absorption peak of carbonyl group (C=O) of methyl methacrylate from 1730 to 1736 cm^{-1}, corresponding to hydrogen bonding between these carbonyl groups and PVC which is indicative of the interaction between the additives and PVC matrix.

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5.1.2 The impact strength of SMMA/SBR rubber containing PVC increased significantly with an increase in the SMMA/SBR content (ex. SMMA/SBR 5 phr and 10 phr produced impact strengths of 3.30 and 6.38 kJ/m^2 respectively), resulting from the action of SMMA/SBR rubber phase as impact modifier as revealed by SEM images.

5.1.3 The modulus, tensile strength, flexural strength and hardness gradually decreased with an increase in the amount of SMMA/SBR rubber whereas the elongation at break increased due to the weak interfacial adhesion between PVC matrix and rubber phase, for example, PVC blends containing SMMA/SBR rubber contents of 2.5, 5, 7.5 and 10 phrs resulted in tensile strengths of 73.43, 69.15, 65.87

and 60.99 MPa, respectively percent elongation at break values of 7.74%, 8.03%, 9.26% and 10.95%, respectively.

5.1.4 The heat distortion temperature very little change with higher content of SMMA/SBR rubber due to the fact that methyl group in PMMA inhibited PVC chain mobility. (ex. SMMA/SBR 5 phr and 10 phr resulted in HDT values of 64.00 °C and 63.60 °C, respectively).

5.1.5 The migration ability of DINP in PVC containing SMMA/SBR rubber was relatively faster than those in neat PVC due to the fact that DINP migration ability in the interphase was faster than those DINP in PVC matrix. It is, therefore recommended that the usage amount of DINP addition into PVC/SMMA/SBR blend should be kept minimum as low as possible without the compromise of processing difficulty.

5.2 Suggestions

5.2.1 PVC having K-value above 65 should be employed for this study. Such PVC is considered to be rigid PVC which exhibits the impact strength suitable for piping applications. The addition of SMMA/SBR rubber is likely to enhance the impact strength which is expected to be higher than the standard rigid PVC.

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APPENDIX

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APPENDIX A

Thermogravimetric analysis

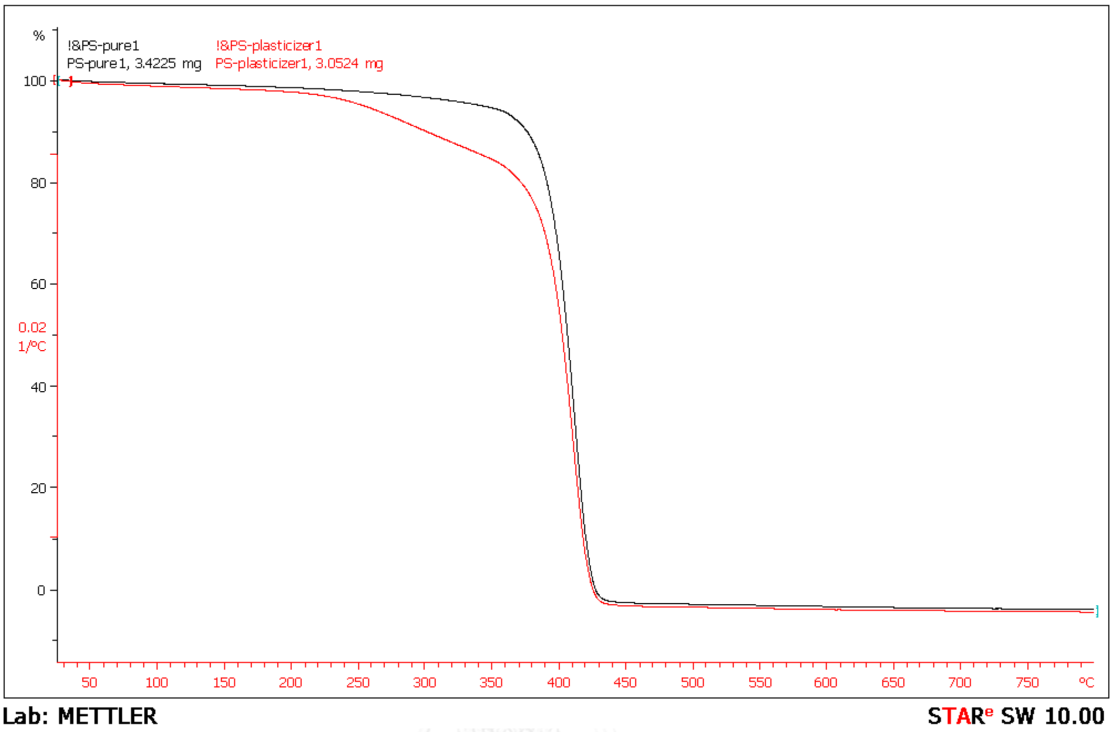

Figure A1 TGA thermogram of polystyrene and plasticized polystyrene

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VITA

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