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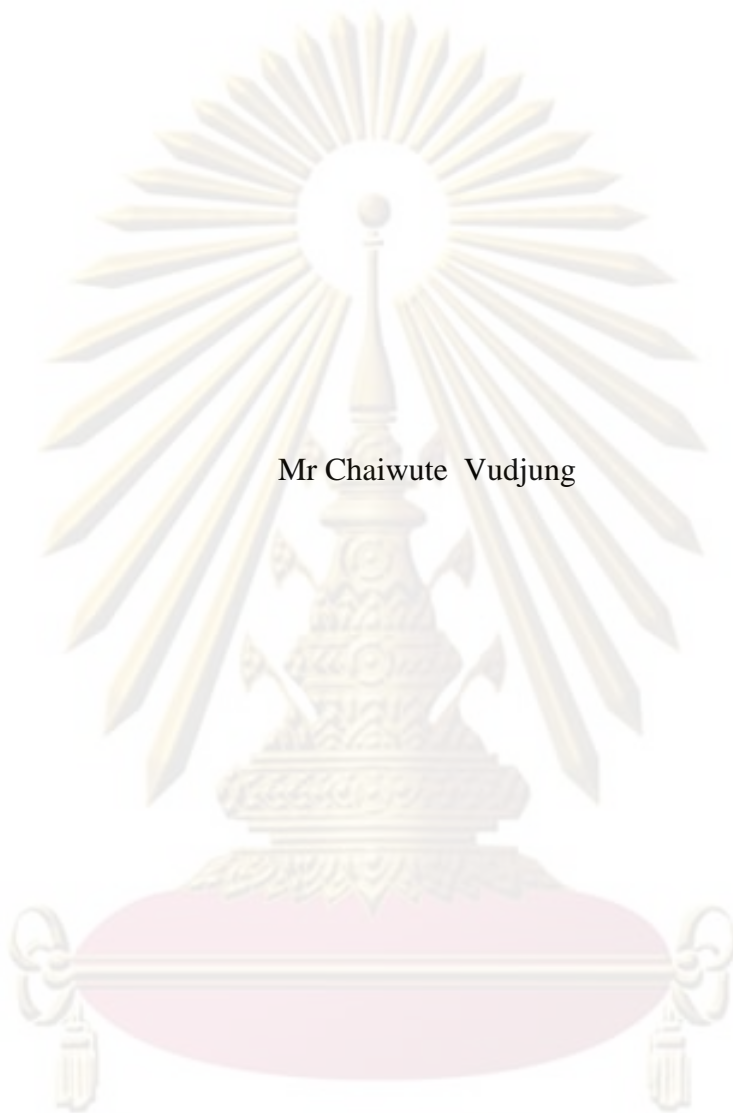
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PROPERTIES AND STABILITY OF ACRYLIC SHEET CONTAINING SILICA AND
POLY (METHYL METHACRYLATE) -g- DEPROTEINIZED NATURAL RUBBER



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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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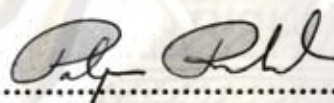
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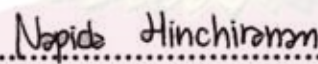
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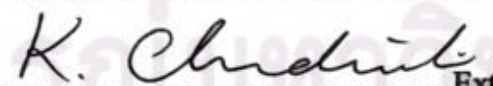
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ชัชวดี วัคจ้ง : สมบัติและเสถียรภาพของแผ่นอะคริลิกที่มีซิลิกาและยางธรรมชาติโปรตีนต่ำกราฟต์ด้วยพอลิเมทิลเมทาคริเลต. (PROPERTIES AND STABILITY OF ACRYLIC SHEET CONTAINING SILICA AND POLY (METHYL METHACRYLATE)-g-DEPROTEINIZED NATURAL RUBBER) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. คร.นพิตา หิญาธิระนันท์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: อ.ดร.ฉันททิพ คำนวนทิพย์, 86 หน้า.

แผ่นพอลิเมทิลเมทาคริเลต (Polymethyl methacrylate, PMMA) หรือแผ่นอะคริลิกที่มีกราฟต์โคพอลิเมอร์ของพอลิเมทิลเมทาคริเลตบนยางธรรมชาติโปรตีนต่ำ (GDPNR) เตรียมด้วยกระบวนการบัลค์พอลิเมอไรเซชัน โดยใช้เบนโซอิลเปอร์ออกไซด์และสารประกอบเอไซเป็นตัวริเริ่มปฏิกิริยา และเตรียมกราฟต์โคพอลิเมอร์ของพอลิเมทิลเมทาคริเลตบนยางธรรมชาติโปรตีนต่ำ (deproteinized natural rubber, DPNR) และน้ำยางข้น (concentrated natural rubber latex, NR) ด้วยกระบวนการอิมัลชันโคพอลิเมอไรเซชัน ตัวแปรที่ทำการศึกษาในขั้นตอนนี้ ได้แก่ เวลาในการทำปฏิกิริยา พบว่าเวลาในการทำปฏิกิริยามีผลต่อสมบัติการกราฟต์ โดยเวลาในการทำปฏิกิริยาที่ให้ประสิทธิภาพการกราฟต์ในการเตรียม GDPNR สูงสุด คือ 3 ชั่วโมง ขณะที่การเตรียมกราฟต์จากยาง NR พบว่ากราฟต์ที่ได้มี ประสิทธิภาพการกราฟต์ต่ำกว่ากราฟต์ที่เตรียมจาก DPNR สำหรับการนำยาง GDPNR ไปประยุกต์ใช้ในงานอะคริลิกนั้น งานวิจัยนี้ศึกษาผลของชนิดและปริมาณของยางกราฟต์ที่เติมลงในแผ่นอะคริลิกต่อสมบัติเชิงกลและสมบัติทางกายภาพก่อนและหลังการบ่มเร่งด้วยความร้อนและแสงอัลตราไวโอเลตของแผ่นอะคริลิก จากการศึกษาพบว่า สมบัติเชิงกลเป็นฟังก์ชันกับปริมาณยางกราฟต์ สมบัติการทนทานต่อแรงกระแทกของแผ่นอะคริลิกที่มี GDPNR เพิ่มขึ้นตามปริมาณการเติม GDPNR โดยให้ค่าสูงสุดที่ 150 กิโลจูล/ตารางเมตร เมื่อเติม GDPNR ในแผ่นอะคริลิกที่ 10% โคนน. อย่างไรก็ตามการเติม GNR ลงไปในแผ่นอะคริลิกสามารถทำได้เพียงเล็กน้อยเนื่องจาก GNR มีปริมาณการกราฟต์น้อยกว่า GDPNR และ NR ยังมีน้ำหนักโมเลกุลสูงกว่า DPNR ทำให้ยากต่อการละลายในมอนอเมอร์เมทิลเมทาคริเลตในขั้นตอนการเตรียมแผ่นอะคริลิก นอกจากนี้ยังพบว่าแผ่นอะคริลิกที่มี GDPNR มีเสถียรภาพต่อความร้อนและแสงอัลตราไวโอเลตมากกว่าแผ่นอะคริลิกที่มี DPNR การเติมซิลิกาลงในแผ่นอะคริลิกที่มี GDPNR เพื่อปรับปรุงเสถียรภาพต่อความร้อนและแสงอัลตราไวโอเลต พบว่าเมื่อเติมซิลิกาในแผ่นอะคริลิกมากขึ้นทำให้เสถียรภาพต่อความร้อนและแสงอัลตราไวโอเลตดีขึ้น

สาขาวิชา..ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์.. ลายมือชื่อนิสิต.....

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ลายมือชื่อ.ที่ปรึกษาวิทยานิพนธ์ร่วม.....

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CHAIWUTE VUDUNG: PROPERTIES AND STABILITY OF ACRYLIC SHEET CONTAINING SILICA AND POLY(METHYL METHACRYLATE)-g-DEPROTEINIZED NATURAL RUBBER. THESIS ADVISOR: ASSIST. PROF. NAPIDA HINCHIRANAN, Ph.D., THESIS CO-ADVISOR: CHUNTIP KUMNUANTIP, Ph.D., 86 pp.

The poly(methyl methacrylate) (PMMA) or acrylic sheets containing graft copolymer of PMMA on deproteinized natural rubber (DPNR) (GDPNR) were prepared by bulk polymerization using benzoyl peroxide and azo-compounds as initiators. GDPNR and graft copolymer of PMMA on concentrated natural rubber latex (GNR) were produced via emulsion copolymerization. The effect of reaction time was the important factor to study for preparation of graft copolymer step. It was found that the reaction time at 3 h gave the maximum value of grafting efficiency for production of GDPNR; while the preparation of GNR presented the lower grafting efficiency. The influence of type and content of graft rubbers on the mechanical and physical properties of the modified acrylic sheets before and after ageing with heat and ultraviolet was also investigated. The results showed that mechanical properties of the modified acrylic sheet were a function of amount of grafted rubbers. The impact resistance of the acrylic sheet containing GDPNR increased with increasing GDPNR content. The highest impact strength of the modified acrylic sheet was *ca.* 150 kJ/m² at 10 wt% GDPNR content. However, the addition of GNR into the acrylic sheet was limited due to the lower level of grafting efficiency compared to GDPNR and the higher molecular weight of NR which caused the difficulty to be dissolved in methyl methacrylate monomer during preparation of PMMA sheet. Moreover, the heat and UV stability of the GDPNR-modified acrylic sheet was higher than that of the acrylic sheet containing DPNR. Silica was used as a thermal and UV stabilizer for acrylic sheets. The results indicated that the increase in the silica content improved the thermal and UV stability of the modified acrylic sheets.

Field of study...Petrochemistry and Polymer Science...Student's signature.....*Chaiwute Vudjung*

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ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

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LIST OF ABBREVIATIONS

ABVN	: 2,2'-Azobis-(2,4-dimethylvaleronitrile)
b.p.	: Boiling point
BPO	: Benzoyl peroxide
°C	: Degree Celsius
DPNR	: Deproteinized natural rubber
DRC	: Dry rubber content
EB	: Elongation at break
FT-IR	: Fourier-Transform Infrared Spectrometer
GDPNR	: Grafted deproteinized natural rubber
GE	: Grafting efficiency
GNR	: Grafted natural rubber
h	: Hour (s)
LPE	: Light petroleum ether
min	: Minute (s)
MMA	: Methyl methacrylate
NR	: Natural rubber
phr	: Part per hundred
SEM	: Scanning Electron Microscope
TS	: Tensile strength
wt	: Weight
wt%	: % by weight

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CHAPTER I

INTRODUCTION

1.1 Purpose of Investigation

Poly(methyl methacrylate) (PMMA) or acrylic plastics mainly prepared from bulk polymerization of methyl methacrylate (MMA) by casting process have advantages of clarity, light weight and high resistance to outdoor environment. Consequently, it is used in a wide variety of applications such as aircraft window, car components, laminated glass, laminated roof, protective coating, etc. However, it is brittle and has a low impact strength [1]. There are many attempts to improve the mechanical properties of brittle materials such as poly(vinyl chloride) (PVC) and PMMA by blending with elastic polymers such as butadiene rubber, styrene-butadiene rubber, ethylene-vinyl acetate copolymer and natural rubber (NR) etc. used as impact modifiers [2].

Thailand is the world largest producer of NR and the biggest exporter of NR latex [3]. NR consists of ca. 94% rubber hydrocarbon and 6% non-rubber components such as proteins, lipids, sugars and ash [4]. Proteins in latex which are carried over into the medical glove by inadequate manufacturing process, may pose a risk of provoking allergic reaction in some patients and medical workers. To prepare the unallergenic gloves, it is necessary to remove the proteins from NR latex which it has been known as deproteinized natural rubber (DPNR) latex. DPNR is lightness when it is compared to NR. Therefore, DPNR has potential to be used as impact modifier for acrylic sheets requiring high clarity with high impact strength. Unfortunately, the direct blends of rubbers and PMMA normally exhibit poor mechanical properties due to their high incompatibility and immiscibility. Graft copolymerization is one of chemical modification for properties improvement of diene-based elastomers. Graft copolymer can enhance compatibility and impact properties of thermoplastic elastomers [5].

Normally, acrylic sheets also suffer from some defects such as poor heat resistance, weak mechanical surface etc. [6, 7]. The way to improve the thermal

stability of acrylic sheet is to introduce silica into the acrylic sheet [8]. Therefore, the objective of this research was to prepare graft copolymer of PMMA on DPNR by emulsion polymerization initiated by potassium persulfate. The modified acrylic sheets were prepared by bulk polymerization of MMA with a small amount of graft rubber and/or silica and then casted in a two-glass plate mold. The mechanical and physical properties including morphology of the modified acrylic sheets before and after thermal and ultraviolet ageing were investigated.

1.2 Research Objectives

The objectives of this research could be summarized as follows:

1. To prepare the graft copolymer of PMMA on DPNR latex at various reaction time to achieve the desired grafting levels.
2. To investigate the mechanical and physical properties including morphology before and after thermal and ultraviolet ageing of the modified acrylic sheets containing various graft rubber and/or silica contents.

1.3 Scope of Investigation

For the preparation of graft rubbers, the effect of rubber types (NR and DPNR) on the grafting properties was investigated. Subsequently, the graft rubbers were added into MMA monomer for preparing the modified acrylic sheets. The effect of the concentration of graft rubbers and silica on the mechanical and physical properties including the morphology of the modified acrylic sheet was examined before and after thermal and ultraviolet ageing. The step experiments are as followed:

1. Literature survey and in-depth study of this research work.
2. Preparation of graft copolymer of PMMA on DPNR by emulsion copolymerization using potassium persulfate as an initiator.
3. Structure characterization of the graft DPNR.
4. Preparation of the modified acrylic sheets containing various contents of rubbers (NR, DPNR, GNR and GDPNR) and silica by bulk polymerization.

5. Investigation of the effect of the rubber concentration and silica content on the mechanical and physical properties of the modified acrylic sheets before and after thermal and ultraviolet ageing.
6. Summary of results.



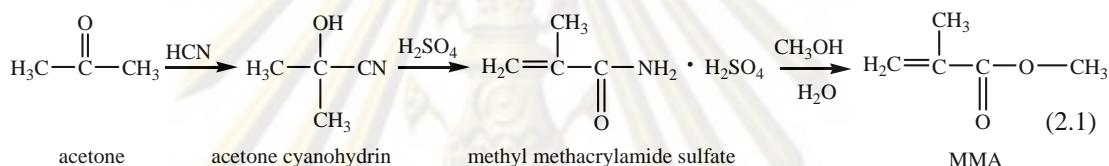
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CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Methyl Methacrylate and Poly(methyl methacrylate) [1]

Methyl methacrylate (MMA) is a chemical compound mostly known as the monomer for the production of the transparent plastic poly(methyl methacrylate) (PMMA). Generally, MMA is synthesized from acetone and hydrogen cyanide as shown in eq. 2.1.



In a typical process, acetone is treated with hydrogen cyanide at 40°C in the presence of ammonia used as a catalyst to produce acetone cyanohydrin. Then, the acetone cyanohydrin is treated with concentrated sulfuric acid at 100°C to form methyl methacrylamide sulfate which is directly fed into an aqueous methanol to produce MMA. The MMA product is separated by steam and purified by distillation. The MMA or acrylic monomer is colorless liquid with a characteristic sweet odor. Its boiling point is ca. 100.5°C. For shipping and storage, hydroquinone or *p*-methoxyphenol is commonly used as an inhibitor for MMA monomer to inhibit the self-polymerization of MMA.

The first acrylic polymer commercially produced was poly(methyl acrylate) (PMMA). Its production was begun in 1927 by Rohm and Haas AG in Germany. In about 1930, Hill of Imperial Chemical Industries Ltd. (UK) prepared acrylic or MMA sheets which are potentially useful material. However, the high raw material cost prohibited the commercial development. At that time, MMA was obtained by dehydrogenation of hydroxyisobutyric ester. In 1932, Crawford synthesized MMA based on cheap raw materials: acetone and hydrogen cyanide. Thus, PMMA became a feasible proposition and commercial production in 1934. The acrylic sheets were used

during the Second World War for aircraft glazing. According to the war, the acrylic sheets have been used in various applications such as display signs, lighting fittings and bathroom fittings. PMMA can be melted by heat that can replace the casting process in order to increase the cost effective means. PMMA is also extensively used for the production of dentures.

The polymerization of MMA is readily accomplished by bulk, solution, suspension and emulsion techniques. Among these methods, bulk and suspension polymerization methods are mainly used for the production of the homopolymer. The production of cast sheet, rods and tubes is carried out by bulk polymerization, starting in most cases with syrup of partially polymerized MMA with a convenient viscosity for handling. In addition, the shrinkage and heat evolution during polymerization are reduced by the use of syrup. PMMA sheets are commonly made by extrusion. Alternatively, they may be casted in cells consisting of two glass sheets separated by a coated rubber gasket. The cell is filled with syrup and sealed. The polymerization is carried out at 60-70°C in an air oven or water bath, with a finishing treatment at 100°C. Normally, peroxide or azo initiators may be applied as an initiators. PMMA prepared by free radical polymerization is amorphous because of its lack of complete stereoregularity and its bulky side groups. It is therefore soluble in aromatic hydrocarbons, chlorinated hydrocarbons, and esters. However, it has very good resistance to water, alkalis, aqueous inorganic and most dilute acids. PMMA has much resistance to hydrolysis than poly(methyl acrylate), probably by virtue of the shielding presented by the α -methyl group.

PMMA is a linear, hard, polar and rigid transparent thermoplastic with a higher softening point, better impact strength, and better weatherability than polystyrene. The typical properties of PMMA are given in Table 2.1. An outstanding property of PMMA is its clarity. Thus, the transmission of normal incident light through a sheet of the polymer is about 92%. A further outstanding property of PMMA is the good outdoor weathering. After several years under tropical conditions, the color change is extremely small. The mechanical and thermal properties of the polymer such as tensile strength, impact strength, etc. are also good. Electrical properties are good but not outstanding. A limitation of the optical uses of the material is its poor abrasion resistance compared to glass.

Table 2.1 Typical properties of poly(methyl methacrylate) [8]

Property	Value
Density, g/cm ³	1.15-1.19
Water absorption, %	0.3-2
Hardness, Rockwell M	63-97
Young's modulus, GPa	1.79-3.38
Tensile strength, MPa	55-85
Elongation at break, %	1-30
Charpy Impact, J/cm ²	0.2-0.4
Specific heat capacity, J/(g·K)	1.46-1.47
Thermal conductivity, W/(m·K)	0.19-0.24
Glass temperature, °C	100-105
Melting point, °C	130-140
Vicat Softening Point, °C	47-117
Transmission, %	80-93
Refractive index	1.49-1.498

Despite considerable effort, the attempts to improve the scratch resistance or surface hardness of PMMA have so far been accompanied by deterioration in other properties, such as impact strength.

2.2 Bulk Copolymerization [9-11]

Bulk or mass polymerization of a pure monomer is the simplest process with a minimum contamination in the resulting product. Monomer, polymer and initiator are the only components in the bulk polymerization. Polymerization apparatus is shown in Figure 2.1. However, the bulk polymerization of vinyl monomer is more difficult, since the reactions are highly exothermic. The usual thermally decomposed initiators proceeds at a rate which is strongly dependent on temperature. Thus, the problem of coupled heat transfer is normally incurred because of the viscosity development at the early stage of reaction, resulting to difficulty in control [1]. The advantages and disadvantages of the commercial polymerization systems are shown in Table 2.2.

In the bulk copolymerization, the monomers and initiators are mixed in a reactor consisting of heating or cooling unit. Many reactions are carried out by charging one monomer into the reactor and/or slowly adding the second monomer. Additional, reaction is often too exothermic for the bulk process resulting to the requirement of careful temperature control. Therefore, the special steps must be taken to remove heat during polymerization.

It can be differentiated between quiescent and stirred bulk polymerization. Both methods are applied to system which polymer is stable in monomer and progressively increases viscosity with conversion. In quiescent systems, gel formation, corresponding to infinite viscosity, can occur. However, the reaction rate of this system is difficult to be control due to the released heat during polymerization.

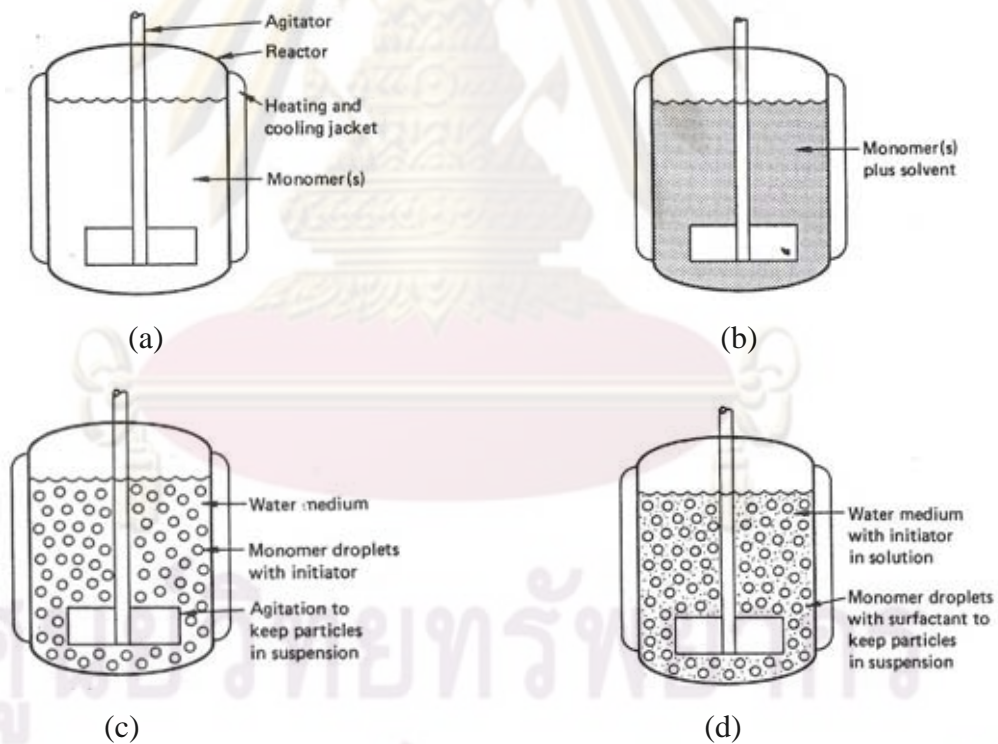


Figure 2.1 Diagrams of polymerization apparatus: (a) bulk, (b) solution, (c) suspension and (d) emulsion polymerization [10].

Table 2.2 Commercial polymerization systems [12]

Type	Advantage	Disadvantages
Bulk: batch	<ul style="list-style-type: none"> • Minimum contamination • Simple equipment for making castings 	<ul style="list-style-type: none"> • Strongly exothermic • Broadened molecular weight distribution at high conversion • Complex if small particles required
Bulk: continuous	<ul style="list-style-type: none"> • Lower conversion per pass leads to better heat control and narrower molecular weight distribution 	<ul style="list-style-type: none"> • Requirement of agitation, material transfer, separation, and recycling
Solution	<ul style="list-style-type: none"> • Ready control of heat of polymerization 	<ul style="list-style-type: none"> • Not useful for dry polymer because of difficulty of complete solvent removal
Suspension	<ul style="list-style-type: none"> • Ready control of heat of polymerization • Suspension or resulting granular polymer may be directly usable 	<ul style="list-style-type: none"> • Requirement of continuous agitation • Contamination by stabilizer • Requirement of washing and drying processes
Emulsion	<ul style="list-style-type: none"> • Rapid polymerization to high molecular weight and narrow distribution with ready heat control 	<ul style="list-style-type: none"> • Contamination with emulsifier, etc., almost inevitable, leading to poor color and color instability • Requirement of stability washing and drying process

2.3 Casting Process

Casting is a manufacturing process and involves the pouring of a liquid resin into a mold and allowing it to harden with little or no pressure. The liquid may consist of a melted or dissolved thermoplastic, thermosetting resin, or thermoplastic monomer. Hardening takes place by cooling, evaporation of solvent or chemical reaction [10]. Casting method requires simpler machines for making products with more economical practice of small quantities. It is also lower expenses for molds [11]. The configuration of the conventional mold for preparing the general thermoplastics is shown in Figure 2.2.

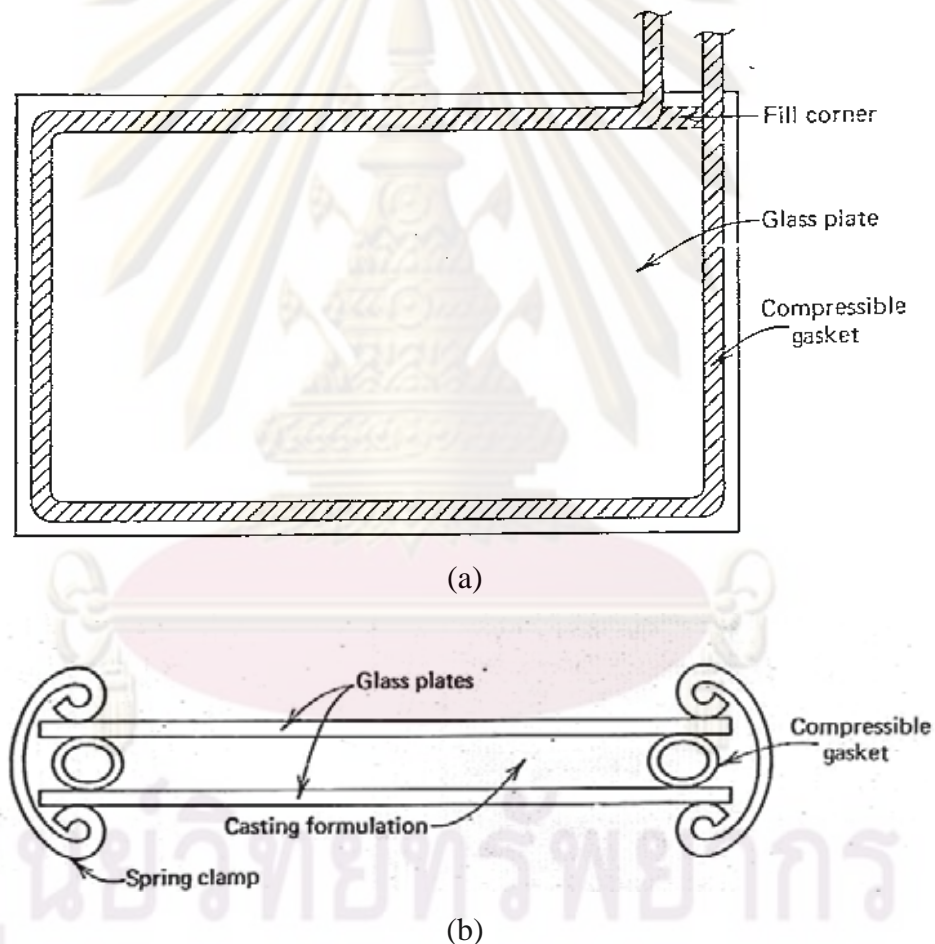


Figure 2.2 Conventional cell casting mold configuration: (a) face view and (b) edge view [10].

2.4 Impact Modifier [13-14]

In the early days of the thermoplastics industry, the commercial polymers such as polystyrene, rigid PVC and PMMA exhibited low impact strength in their homopolymer forms. In the case of polystyrene and styrene-acrylonitrile (SAN), rubbers such as polybutadiene (PBD) or NR are incorporated to such polymers during polymerization in order to increase their toughness.

2.4.1 Effect of Secondary Glass Transitions Temperature

The impact resistance of the brittle polymers is correlated to the presence of a secondary glass transition temperature of polymer. This temperature locates below the primary glass transition temperature. The secondary transition temperature is associated with motion of the polymer backbone, not pendant side-chain groups. This is effective to improve the impact resistance. Because our definition of impact strength is the ability of the material to undergo massive yielding at impact speeds, the main-chain motions that can be activated at impact speed are expected to correlate with impact strength. Thus, a low secondary glass transition temperature is an indication of chain segments that possess some degree of mobility at impact speed. This mobility can be translated into large-scale deformation of the polymer chains.

2.4.2 Interaction of Additive Impact Modifier and Polymer Matrix

There are relatively few polymers, such as polycarbonate, that manifest the secondary glass transition temperature that is significant enough to yield high impact strength with maintaining a sufficiently high primary glass transition temperature for acceptable engineering properties. Polymers which have a secondary transition at low temperature are PVC and polyphenylene oxide. These require impact modifiers to yield high impact resistance. However, some polymers, such as polystyrene, has no secondary transition temperature. Consequently, this concept providing a secondary glass transition temperature in the materials for impact strength is achieved in practice by addition of rubber impact modifiers having a low glass transition temperature.

In general, rubbery materials can be used as impact modifiers due to their shear stresses that arise at the rubber-matrix boundaries. When the large numbers of microscopic rubbery phases inclusions are distributed throughout the matrix, this matrix deformation is delocalized throughout the sample and large amounts of energy can be absorbed. The systems that have been the best characterized are the vinyl polymers such as high impact polystyrene and acrylonitrile butadiene styrene copolymer. Whereas, graft copolymers containing identical segments to the blend components can be applied as compatibilizer to increase the miscibility between the copolymer segments and the corresponding blend components. In most cases, the compatibilizer possibly affects the final products such as reduction of the interfacial tension during melt mixing resulting to a finer dispersed phase which increases the adhesion at phase boundaries. This gives the improved stress transfer with strengthening the interface in the solid state and stabilization of the dispersed phase by reducing the rate of domain coalescence during melts processing and annealing [14].

2.5 Natural Rubber [2-3]

Natural rubber (NR), a white milky fluid, is produced by specialized cells in a variety of plants, throughout the world, in totally unrelated families, including the *Compositae* and *Moraceae* as well as the *Euphorbiaceae*. Although in the past many different species have been used for obtaining crops of latex, the principal source of NR today is *Hevea Brasiliensis* which is a native of a tropical rain forest in the Amazon Basin in Brazil. Nowadays, most of NR comes from South East Asia, mainly Thailand, Malaysia, and Indonesia.

Hevea Brasiliensis, the commercial rubber tree, is a tall tree which naturally grows up to forty metres (130 feet) and lives for one hundred years or more. *Hevea Brasiliensis* requires temperatures of 20-30°C, at least 2,000 mm of rainfall per year, and high atmospheric humidity. This naturally occurring polymer has chemical structure as *cis*-1,4-polyisoprene which is presented in Figure 2.3.

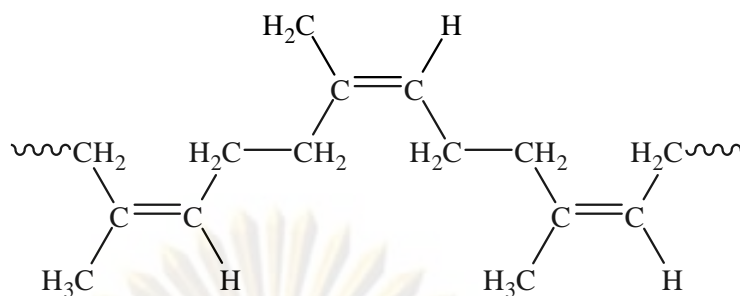


Figure 2.3 *cis*-1,4-polyisoprene [15].

2.5.1 Natural Rubber Latex [16]

NR products are derived from *Hevea brasiliensis* latex, a milky fluid obtained by tapping the bark of *Hevea* tree as shown in Figure 2.4. Like all plant materials, the latex contains growth-related substances such as proteins, carbohydrates, and other organic and inorganic components. The rubber latex consists of hydrocarbon particles (the elastic component sought in all NR products) ca. 25% to 45%. The non-rubber substances constitute only a small percentage of the latex system. When the rubber latex is subjected to ultracentrifugation, latex can be separated into 3 main fractions (Figure 2.5) such as top rubber hydrocarbon particle phase, ambient C-serum in which all latex particles are suspended and denser bottom fraction of nonrubber particles, particularly lutoids which contain another serum (B-serum). This NR latex is composed with 1-5% of proteins which are distributed into the rubber phase (27%), C-serum (48%) and the bottom fraction (25%). A study of these proteins with sodium dodecylsulfate-polyacrylamide gel electrophoresis revealed that there are two major surface-bound proteins of 14 - 24 kd in the rubber particle phase. Although the soluble proteins in C-serum are in the range of 7 - 133 kd, those in the B-serum showing a narrower molecular weight range, is varied from less than 14 - 45 kd.

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Figure 2.4 NR latex collected in a cup after skillful tapping of a *Hevea brasiliensis* [14].

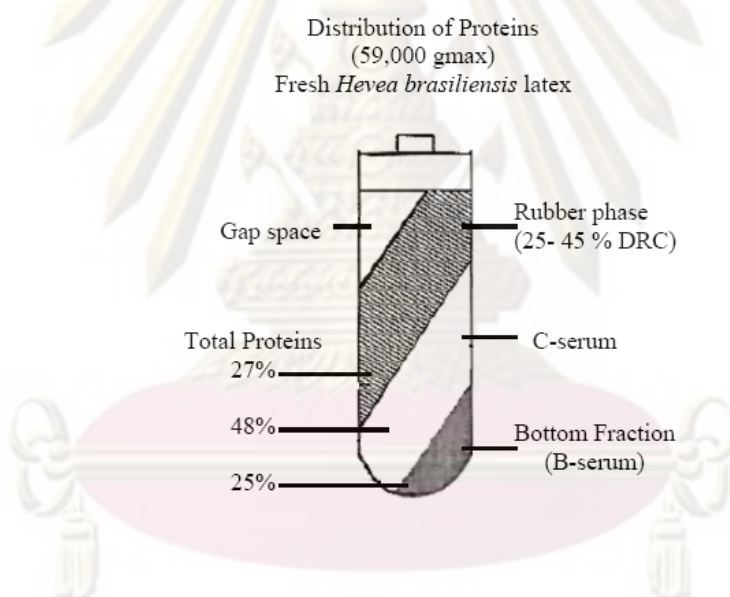


Figure 2.5 Three main fractions of *Hevea brasiliensis* latex obtained from ultracentrifugation [16].

The bulk of these proteins is removed when the latex is in production process. Only a small fraction of proteins still remains in the products as the residual extractable proteins (EPs) resulting to allergy reactions. Although about 10 proteins have been identified as potential allergens in latex, it is doubtful whether all of them could survive the stringent manufacturing processes and serum part of an extractable fraction in latex products. Information regarding the status of allergenic proteins in latex product is presently incomplete.

2.5.2 Natural Rubber Products [16]

NR latex is usually converted into two major types: the concentrated rubber latex and solid dry rubber.

For the preparation of the concentrated NR latex, the latex collected from the rubber tree is generally concentrated by centrifugation to remove part of unwanted serum. The rubber content in the concentrated NR latex is 60% (v/v). The concentrated NR latex is preserved by adding ammonia to inhibit bacterial growth after it is tapped and centrifuged. The concentrated NR latex is the starting material for NR latex products. The limits, specified for centrifuged NR latex, are shown in Table 2.3. For the production of dry rubber, the NR latex is coagulated, creped, crumbled, extensively washed and dried at 100°C. This raw material is available in forms of solid bales and sheet (e.g. ribbed smoked sheet grades).

Table 2.3 Natural rubber latex concentrate specifications [3]

	High ammonia- content lattices	Low ammonia- content lattices
Total solids content (% m/m, min)	61.5	61.5
Dry rubber content (% m/m, min)	60.0	60.0
Non rubber solids (% m/m, max)	2.0	2.0
Alkalinity (% m/m on latex)	0.6 min	0.29 max
Mechanical stability time (s, min)	650	650
Coagulum content (% m/m, max)	0.05	0.05
Copper content (mg/kg on total solids)	8 max	8 max
Manganese content (-do-)	8 max	8 max
Sludge content (% m/m, max)	0.10	0.10
Volatile fatty acid no. (max)	0.20	0.20
KOH no. (max)	1.0	1.0

The concentrated NR latex is mixed with various compounding chemicals before producing gloves, condoms, balloons, catheters, baby soothers or dental dams. Production methods may involve dipping, foaming or extrusion as an elastic thread.

For dipped products, the desired shape formers (molds) are dipped into the compounded NR latex for doing a thin film. Dipping can be done either in the presence or absence of destabilizing chemicals. The product is generally washed (the “wet-gel” or “procure” leach) to remove the excess chemicals before vulcanization in ovens at 100 - 120°C. Leaching is also done after vulcanization. For the protein allergy problem, emphasis is now placed on the application of optimized leaching protocols to remove as much as possible of the soluble allergenic proteins. Since gloves with high residual extractable proteins content may irritate sensitized users, many manufacturers, especially in Malaysia, attempt to reduce the protein content in the rubber products to achieve sufficiently low level. In fact, new and improved technologies to protein removal of NR latex are now listed below:

- Proper optimized “procure” and “postcure” leaching protocols
- Chemical or enzymatic deproteinization
- Chlorination (powder-free)
- Polymer coating (powder-free)
- Use of low-protein lattices (specially processed raw lattices)

2.5.3 Deproteinized Natural Rubber [3]

Deproteinized natural rubber (DPNR) is produced from fresh field latex by treatment with a proteolytic enzyme. This technique can decrease the protein content in NR latex from 3% to maximum at 0.15%. This grade has low water affinity and it is suitable for various applications such as cable insulation and engineering uses which require low creep characteristics.

The preparation of low-protein lattices involves the protein reduction during the liquid latex stage or reduction at the source. There are several ways for doing this, but the two approaches often adopted are physical means and enzymatic treatment.

- Physical means: latex concentrate (raw or prevulcanized) is diluted and further re-centrifuged to remove the soluble proteins in the serum phase. Alternatively, a creaming process with a creaming agent can be used.

- Enzymatic treatment: *Hevea* field latex or latex concentrate is treated with a proteolytic enzyme, after which the treated latex is centrifuged to remove the broken-down proteins in the serum phase. In such a preparation, a suitable stabilizing system, usually involving a surfactant, is required to maintain the colloidal stability of the latex. Otherwise, the latex could produce poor-quality film products. The mechanical properties of DPNR glove are shown in Table 2.4.

2.6 Graft copolymerization of Natural rubber

NR has been modified in many ways, since the establishment of a continuous supply of plantation rubber. Modification highly affects its physical properties. Moreover, thermoplastic or resinous materials can be obtained by a modification of rubber [18].

The Natural Rubber Research Organizations of Malaysia has investigated processes for grafting polymers to NR using free radical chemistry. Materials contained both plastic and rubber constituents and Heveaplus-MG (a graft copolymer of NR and PMMA) become commercially available.

Table 2.4 Properties of rubber glove production from DPNR latex and concentrated NR latex (Low ammonia-content lattices) [3]

	DPNR latex	Concentrated natural rubber latex
Before ageing		
Tensile strength (MPa)	27.35 ± 1.25	30.20 ± 1.90
500% Modulus (MPa)	2.50 ± 0.25	3.24 ± 0.22
Elongation at break (%)	890 ± 25	850 ± 20
After ageing (70°C, 166 h)		
Tensile strength (MPa)	20.25 ± 0.85	21.25 ± 1.24
500% Modulus (MPa)	4.20 ± 0.20	4.45 ± 0.26
Elongation at break (%)	720 ± 20	680 ± 20

2.6.1 Graft Copolymers

In graft copolymerizations, side chains of polymer are formed and attached to macromolecules with different chemical composition. The simplest case of graft copolymer can be represented by the following structure (Figure 2.6), where a sequence of monomer units (A) is referred as the main chain or backbone. The sequence of B units is the side chain of graft, and X is the backbone to which the graft is attached [18]. Graft copolymer could be produced by using a post polymerization of vinyl monomers such as styrene, acrylonitrile, MMA.

2.6.2 Graft Copolymerization Methods [20-21]

The synthesis of graft copolymers is much more diverse, but it can be divided into groups of related processes:

a) Chain Transfer

In a free radical polymerization, chain transfer is an important reaction. The chain transfer to a monomer, solvent, mercaptan, or other growing chain can take place. When the chain transfer reaction to another chain takes place, it creates radicals which act as sites for further chain growth and grafting. The simplest technique is to dissolve the polymer in the appropriate solvent and initiate with the peroxide initiator

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Figure 2.6 Model of graft copolymer [18].

which abstracts a hydrogen radical and generates a radical on the polymer chain as the grafting sites for the fresh monomer. In many cases, when latex grafting has been used, the product has usually been targeted toward thermoplastic applications.

b) Copolymerization via Unsaturated Groups

In NR, a few such groups per molecule are always presented and these undoubtedly participate during normal grafting. By carrying out the reaction to about 4% of the available double bonds in a solvent such as toluene at low temperature followed by a nitrogen purge, grafting can be effected by addition of monomer to form of two monomer chains attached to the oxygens of the opened -O-O-bridge. This technique could be applied for isoprene and butadiene copolymers.

Redox polymerization is the most popular techniques for grafting reactions. A hydroperoxide or similar group is reduced to a free radical plus an anion, while the metal ion is oxidized to a higher valency state. At the same time, a monomer is added. When the reducible group is attached to a polymeric chain, the free radical grafting sites formed on the macromolecular backbone act as initiators for graft copolymerization. Hydroxy polymers can be grafted by redox polymerization by using water insoluble peroxide, such as hydrogen peroxide in conjunction with ferrous ions. The hydroxyl radicals produced abstract hydrogen atoms from the hydroxy groups in the polymer giving free radical grafting sites on the backbone. The advantage of this reaction lies in the fact that only hydroxyls on the polymer are converted into R-O radicals, so that no homopolymer can be produced and pure graft is obtained.

c) High-Energy Reaction Techniques

During high-energy irradiation in vacuo e.g., from a ^{60}Co source, some main chain degradation of NR and other polyisoprene occur. The irradiation of NR in the presence of a vinyl monomer leads primarily to synthesize graft copolymers, but some block copolymer is certainly always presented. The irradiation syntheses may be carried out in solution, either in contact with liquid monomer (with or without a diluent) or in contact with monomer in the absence of air to produce free suspension.

The rubber may be preirradiated in the absence of air to produce free radicals for later monomer addition, but the life of these radicals is short as a result of mobility within the rubber matrix. The irradiation at very low temperature is possible process to use the trapped radicals technique for a variety of natural and synthetic rubbers. Latex phase grafting generally favored for its simplicity: NR grafts with MMA, styrene, acrylonitrile, and vinyl choride have been made in this way.

d) Photochemical Synthesis

Macromolecules containing photosensitive groups which absorb energy from ultraviolet frequencies are often degraded by free radical processes. The degradation processes as a rule is fairly slow, but by the addition of photosensitizer, such as xanthone, benzyl, benzoin, and 1-chloroanthraquinone, the art can be speeded up to enable graft copolymerization to take place in the presence of monomers. This can be done in the case of NR in the latex phase with reasonably high yields of graft copolymer.

e) Metallation Using Activated Organolithium with Chelating Diamines

Unsaturated elastomers can be radily metallated with activated organolithium compounds in the presence of chelating diamines or alkoxides of potassium or sodium. They can also be grafted with ionically polymerizable monomers to produce comblike materials.

Although graft copolymerizations are widely practiced with vinyl monomers and polymers, especially for improving compatibility, impact, and low temperature properties of thermoplastics, the technology has been based more upon art than upon science. Often small proportions of actual grafting have been sufficient to give worthwhile modification of properties. If grafting does not give directly the properties desired, it may improve morphology or compatibility with specific added polymers or plasticizers that impart the desired effect. In addition, these graft copolymers have been mixed with other resins such as poly(vinyl chloride) to improve compatibility, impact strength, and low temperature properties of thermoplastics.

2.7 Silica [23]

The most of silica and silicate minerals (ca. 95%) are produced from the earth's crust. Silica is available in many forms, each having various properties to be used in different industries. The major commercial markets for silica are ceramics, glass, chemicals, foundry uses, paint, paper, ink, rubber, plastic, pharmaceuticals, cosmetics, greases, and catalyst supports. There are two types of silica: natural (ground) silica and synthetic silica.

2.7.1 Applications [24]

a) Polyvinyl Chloride (PVC)

Silica is used for a various application of PVC. Because of the high abrasivity of natural silica (Mohs hardness of 7 for quartzite), the synthetic silica are preferred in order to minimize machine wear on mixing and extrusion equipment. The crystalline silica also imparts unfavorable high brittleness to most thermoplastic composites.

In soft PVC, silica is used to control thixotropy, improve dielectric properties, and prevent plate-out, antiblocking and flatteing properties. Fumed silica is used to modify the rheological properties of PVC, particularly in PVC plastisols, that are used for synthetic leather and automobile undercoatings. Surface-treated grades that are terminated with methyl groups reduce the rate of viscosity increase, resulting to lessen the thickening behavior.

Synthetic silica is a poor conductor of heat and electricity. Therefore, it can be only used in low-voltage PVC insulation applications. Both the dielectric constant and the dielectric loss factor of PVC insulation are reduced by the addition of 1.5-2% fumed silica. At room temperature, the loss factors, $\tan \delta$ and $\epsilon \times \tan \delta$, have similar values with and without the addition of fumed silica.

In PVC films, films, fumed and gel silica are used for antiblocking, antislip, and plate-out properties. Blocking usually occurs with thin films, while slip is more prevalent between surfaces of packing foils. For the high-surface-area silica, its dosage between 0.4% and 1.5% significantly reduces the tendency of the films to stick together. Silica resists blocking by absorbing plasticizers that can cause tack,

rather than the desired “dry touch.” Also, the silica textures the film’s surface to decrease the areas of close contact between films.

b) Polyolefins, Styrenics, and Thermoplastic Elastomers

Silica is primarily used as special additives instead of reinforcing fillers in these resin systems. Normally, silica is used as reinforcing filler for rubber rather than plastics. However, silica can be applied for polyethylene and polyethylene blown film to antiblocking free-flow purposes.

The previous work showed the effect of silica on the coefficient of traction of low-density polyethylene (LDPE) film surfaces. When the coefficient of friction decreases, one would expect to improve the antiblocking properties. The addition of 0.1% fumed silica dropped the friction coefficient by 50% over LDPE film without the addition of silica. Silica is also used to reduce plate-out in polyethylene and polystyrene resin. Levels between 0.1% and 1.5% of precipitated silica are usually used to improve the surface printability of the plastic.

The rubber applications are major market for silica. However, its usefulness has not extended into the thermoplastic elastomers. It can be used at levels from 2.5% to 25% in elastomers to give reinforcing properties. It is believed that the fumed silica has high reinforcement by increasing the formation of a network structure of silica. Such structures are common used as adhesives and sealant applications.

2.8 Literature Reviews

2.8.1 Graft Copolymerization of Natural Rubber

Nakason et al. [25] prepared DPNR latex by the incubation of fresh NR latex with a proteolysis enzyme. The DPNR latex was used to prepare a graft copolymer with MMA. High ammonia concentrated NR latex (HA) was also used to prepare a graft copolymer with MMA for comparison. The appropriate reaction time was 3 h at 50°C. The results indicated that DPNR gave the higher monomer conversion, grafting efficiency and graft product content with larger average particle size when it was compared to the graft copolymerization of MMA onto HA system. The difference

between the reaction of the DPNR and HA lattices was attributed to the removal of proteins, which acted as free-radical scavengers to terminate the free-radical species during the graft copolymerization.

Eawsuwan et al. [26] studied the graft copolymerization of styrene and MMA onto NR using cumene hydroperoxide and tetraethylene pentamine as redox initiators. Statistical analysis, two-level factorial design, was used to study the influence of initiator concentration, reaction temperature, ratio of styrene to MMA, and ratio of monomer to NR on the grafting efficiency. The two-level factorial experimental design showed that the initiator concentration, reaction temperature, and ratio of monomer to NR had a significant effect on grafting efficiency. Reaction temperature and ratio of monomer to NR had a significant effect on percentage of graft copolymer. The graft NR product could be used as an impact modifier for PVC. The impact strength of PVC was improved by addition of the grafted NR product. The good mechanical properties was obtained at 10 phr of graft NR. For PVC modified with 10 phr graft NR, the impact strength of PVC was increased ca. 118% and tensile strength was decreased ca. 20% from unmodified PVC.

Pukkate et al. [27] studied the nano-matrix structure of graft copolymer of styrene on urea-deproteinized natural rubber (U-DPNR) latex by using FT-IR spectroscopy, $^1\text{H-NMR}$ spectroscopy and transmission electron microscopy. Conversion and grafting efficiency of styrene were higher than 90% under the best condition of the graft- copolymerization. From the transmission electron micrograph of film specimen stained by OsO_4 , it was found that the NR particles with 0.5 μm in diameter were dispersed in polystyrene matrix with 15 nm in thickness. The conversion and grafting efficiency of graft copolymerization of styrene onto U-DPNR was compared with those for a control sample prepared from enzymatic deproteinized NR (E-DPNR).

Man et al. [28] studied the effect of monomer concentrations on grafting efficiency, thermal and mechanical properties of graft copolymer of styrene and MMA on DPNR latex. The synthesized graft copolymers were characterized by ^1H NMR. The highest grafting efficiency was found at 20 wt% monomer concentration.

At low monomer concentration (10 wt %), the grafting efficiency was not significant. At 30 wt% of monomer concentration, the grafting efficiency was slightly decreased. The thermal properties of graft copolymers were analyzed using differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA). The degradation temperature (T_{deg}) of copolymer increased with increasing the monomer concentration showing the improvement of thermal stability. The DSC results showed the miscibility of the component phases when the monomer concentration increased. The mechanical properties of gum and filled modified NR were also investigated in terms of tensile strength, tensile modulus and elongation at break. The results showed that the tensile strength and elongation at break of the specimens decreased with increasing the monomer concentration.

2.8.2 Modification of Acrylic sheet

Cheng et al. [29] studied transparent EVA/PMMA sheets produced via *in situ* polymerization of MMA. In the presence of the EVA-graft-PMMA (EVA-g-PMMA) prepared by using *tert*-butyl peroctoate (*t*-BO) as an initiator in the EVA/PMMA, EVA can be well dispersed in the PMMA matrix. Both tensile fracture energy and Izod impact strength of the EVA/PMMA blends were higher than those of the neat PMMA. This was confirmed by using Scanning Electron Microscopy (SEM). Copolymer also prevented the dispersed EVA particles from pulling out the fracture surface. The strength of the EVA/PMMA blends were investigated at room temperature over the four strain rates of decadence (from 1.6×10^{-4} to 0.16 s^{-1}). It had an obvious transition, whereas the neat PMMA remained the brittleness over the entire range of strain rates.

Mansour et al. [30] prepared copolymer films of styrene (ST) and MMA with different percentage. Differential scanning calorimeter showed a single transition at 50/50 ST/MMA. Thermogravimetry technique was used to compare the thermal stability of the copolymer and homopolymers. The copolymers degradation occurred at higher temperatures than pure PMMA indicating the higher stabilization of the copolymer. FTIR spectroscopy was used to give information on the structural changes consequent upon exposure. This indicated that the copolymerization of ST and

PMMA modifies the photo degradation behavior of polystyrene. The optical absorption (α) and the band gap (E_g) of film were determined before and after exposure to ultraviolet (UV) radiation. The optical transmission and reflection data for 50/50 ST/MMA copolymer were also analyzed to evaluate the refraction index (n) and extinction coefficient (k) before and after exposure to UV radiation.

Hinchiranan et al. [31] reported the improved properties of modified acrylic sheet via addition the graft NR. The mechanical properties of a modified acrylic sheet prepared by bulk copolymerization of MMA and styrene were improved by the addition of a small amount of graft NR (GNR). The graft copolymerization of MMA and ST onto NR latex was carried out by emulsion polymerization using potassium persulfate as an initiator. The properties of the modified acrylic sheet containing GNR with 22.5 wt% graft copolymer were investigated as a function of GNR content. The results indicated that the impact strength, tensile strength and elongation at break of the modified acrylic sheet increased with increasing the amount of GNR in the range of 0.5–4 parts. From the stress–strain behavior, the characteristics of the modified acrylic sheet shifted from brittle to ductile when the amount of GNR was increased. The scanning electron micrographs of the modified acrylic sheets showed the relatively smooth fracture surface with relatively few small cracks. This implies that the GNR could be used as an impact modifier for acrylic plastics.

Thawornwisit et al [2] studied the properties of copolymer sheets containing ST, MMA and modified NR prepared by bulk copolymerization using benzoyl peroxide and 2,2'-azobis-(2,4-dimethylvaleronitrile) as initiators. The modified NRs were prepared by graft copolymerization and hydrogenation. The graft NR prepared by emulsion copolymerization using redox initiator consisted of 66.1 wt% NR-g-(MMA-co-ST), 26.9 wt% free rubber and 7.0 wt% of free copolymers. The hydrogenation of NR catalyzed by $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)$ was carried out at 140°C and 400 psig, to obtain the hydrogenation level as 56.5%. The effect of ST, rubber and monomer contents on the mechanical and physical properties including morphology of the modified acrylic sheets was investigated. The results showed that the better mechanical properties of modified acrylic sheet were obtained from the addition of 2 wt% of graft NR and 1 wt% of hydrogenated NR. The optimum content

of ST in the modified acrylic sheets for improving the mechanical properties was 20 wt%. Moreover, the modified acrylic sheet containing the hydrogenated NR the superior thermal resistance. The tensile fracture surface examined by SEM showed the relatively smooth surface with few relatively small cracks. It implied that the modified NR could be used as an impact modifier for acrylic cast sheet.

2.8.3 Silica as stabilizer for acrylic sheet

Wang et al. [32] prepared nanocomposites containing PMMA, silica (SiO_2) and zirconia (ZrO_2) using a novel non-hydrolytic sol-gel process. Silica acid and zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) were used as the precursors of SiO_2 and ZrO_2 , respectively. FT-IR and SEM results showed that nanometer-scaled $\text{SiO}_2/\text{ZrO}_2$ particles were uniformly distributed and covalently bonded to the PMMA host matrix without macroscopic organic-inorganic phase separation. This was also confirmed by solvent extraction experiments. It was found that the transmittance of the nanocomposite films in the visible region remained above 95% at 20 wt% of inorganic content. It also proportionally increased with decreasing the inorganic content. The thermal stability and the thermal decomposition kinetics of the composition were studied. The results indicated that the activation energy (E_a) of the thermal decomposition of PMMA main chains in the composites was increased due to the addition of inorganic moieties. This kind of composite material might have the potential for application in optical devices.

Garcia et al. [33] prepared nanocomposites consisting of PMMA and 12 nm silica particles by casting. The composites still remained the homogeneous dispersion when the silica content was lower than 35 wt%. Twelve nanocomposites containing silica in the range of 1-35 wt% were prepared to investigate their properties by using SEM, FT-IR, DSC, TGA and Isothermal Chemiluminescence (IC). The thermal stability of dramatically specimens increased when 1 wt% of silica was added into PMMA. The two main processes occurring in degradation of PMMA were the radical formation at labile chain ends and the random chain scission. The former disappeared when composites contained 3 wt% of silica. This means that the higher thermal stabilization of these polymer composites resulted from the blocking of the PMMA

chain end by the silica particle. At the same time, the viscous flow at 300°C of these composites progressively decreases when the silica content was increased to 20 wt%. The concomitant decrease of viscous flow and the increase in the low temperature thermal stability strongly shifted the temperature range of application of these composites.

Li et al. [7] studied the properties of transparent inorganic UV-filter/epoxy nanocomposites with high photo-stabilization properties. Firstly, inorganic UV-filter ZnO, core-shell structural silica-titania (S-T) and silica-titania-silica (S-T-S) nanoparticles were synthesized. The transparent inorganic UV-filter/epoxy (ZnO/epoxy and S-T-S/epoxy) nanocomposites were subsequently prepared from the transparent epoxy via *in situ* polymerization method. Optical properties of inorganic UV-filter/epoxy nanocomposites were examined by using the light-emitting diode (LED). The lifetime test results showed that the photo-stabilization effect of inorganic UV-filter on the lifetime of LED lamp obeyed the following sequence: ZnO > S-T-S > S-T. To compared with the UV-LED lamps encapsulated with pure epoxy, the lifetime of UV LED lamps encapsulated with ZnO/epoxy, S-T-S/epoxy and S-T/epoxy nanocomposites was improved by 76%, 54% and 33%, respectively.

Katsikis et al. [34] studied the thermal stability of PMMA filled with silicon dioxide particles by means of rheological tests. The change in the storage modulus G' was measured to detect molecular changes in polymers. The long-term thermal stability of the composites was dependence on the melting temperature size of the silica particles (nano- to micrometers), and the volume fraction of the filler. At high temperatures and a large surface area of the silica particles, the behavior of the composites significantly differed from that of the pure polymer. Pure PMMA degraded at high temperatures, which correlated to a decrease in G' . In contrast an increase in G' with increasing temperature and filler surface was measured for the composite materials. This behavior was explained by chemical reactions of the PMMA molecules with the silica particles. However, this phenomenon was not found for silica-filled polystyrene.

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

The high ammonia NR latex containing ca. 62% DRC and the high ammonia DPNR latex containing ca. 61.12 % DRC were obtained from Inter Rubber Latex Co.,Ltd (Surachthani, Thailand). The properties of DPNR and NR latex are shown in Appendix A. The commercial grade methyl methacrylate monomer (MMA) and 2,2'-azobis-(2,4-dimethylvaleronitrile) (ABVN) supplied by Pan Asia Industrial Co., Ltd (Bangkok, Thailand). Benzoyl peroxide (BPO) (humidified with ~25% of H₂O PS) was obtained from PANREAC QUIMICA. Sodium hydroxide (NaOH) was obtained from Merck. The AR grade of potassium hydroxide (KOH) was obtained APS Ajax Finechem. The AR grade of sodium dodecyl sulfate (SDS), anhydrous sodium sulfate (Na₂SO₄) and the AR grade of Oleic acid were received from Fischer Scientific (Leicestershire, UK). Potassium persulphate (KPS) was purchased from Asia Pacific Specialty Chemical. The AR grades of light petroleum ether (LPE) and acetone were obtained Fisher Scientific (Leicestershire, UK). The commercial grade of methanol was the product of Reagent Chemical Industry. Nitrogen gas with 95% purity was manufactured by TIG (Chachoengsao, Thailand).

3.2 Glasswares

Figure 3.1 shows the apparatus for synthesis of graft copolymer via emulsion polymerization. The components of the experimental apparatus are listed below:

1. 4-Necked round bottom reactor, 500 cm³ capacity
2. Condenser
3. Nitrogen gas tube
4. Stainless steel stirrer
5. Water bath
6. Thermometer



Figure 3.1 Apparatus for emulsion graft copolymerization.

3.3 Grafted Deproteinized Natural Rubber Preparation

3.3.1 Purification of Monomer [8]

The MMA monomer (bp. 98°C/760 mmHg) contained a trace amount of hydroquinone as an inhibitor for self-polymerization of MMA. The inhibitor was removed by washing with 1.0% NaOH solution. The MMA was then washed with distilled water until neutral and followed by washing with anhydrous Na₂SO₄. The dried MMA monomer was distilled under reduced pressure (40°C, 20 mmHg). The purified MMA monomer was stored in the refrigerator.

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3.3.2. Preparation of Grafted Deproteinized Natural Rubber

The graft copolymer of PMMA onto DPNR and NR were prepared by using emulsion copolymerization. The high ammonia DPNR latex (150 g) was introduced into a round bottom reactor along with 100 ml of distilled water. KOH (1 phr) and SDS (1 phr) used as a buffer and emulsifier, respectively were then added while stirring. The mixture was deoxygenated by bubbling the nitrogen gas for approximately 15 min at room temperature. The stabilizer, Oleic acid (10 phr), was added after 15 min of stirring. The MMA monomer was then added, continually while stirring for 30 min to allow the latex particles to attain swelling. The mixture was warmed up to 70°C. 2 phr of the initiator (KPS) was then added. The reaction was then allowed to proceed for desired reaction time under continuous stirring to complete the polymerization and then the reaction was stopped. The product latex was discharged into ethanol and the polymer product was precipitated. The gross polymer was recovered and dried to a constant weight in vacuum pump. The standard recipe used for graft copolymerization is shown in Table 3.1.

Table 3.1 Recipe for preparation of GDPNR and GNR [28]

Item	Value
DPNR or NR (phr) ¹	100
Water (phr)	200
Oleic acid (phr)	10
KOH (phr)	1
SDS (phr)	1
Rubber:MMA weight ratio	90:10
Potassium persulfate (phr)	2
Reaction temperature (°C)	70
Reaction time (h)	2 - 6

¹phr = parts per hundred of rubber by weight

3.4 Determination of Properties of Grafted Deprotienized Natural Rubber

3.4.1 Determination of Monomer Conversion and Grafting Efficiency

The degree of conversion was determined by the percentage increase of rubber weight. The amount of grafted rubber, free rubber, free homopolymer and free copolymer in the product could be determined by soxhlet extraction. The free rubber was extracted by light petroleum ether (60-80°C) for 24 h, while free copolymer was extracted in acetone for 24 h. The data obtained from all steps were used to calculate the grafted rubber and grafting efficiency. The details of all calculations are presented as eq. 3.1-3.5.

$$\text{Total conversion (\%)} = \frac{\text{Weight of polymer formed} - \text{weight of rubber}}{\text{Weight of monomer charged}} \times 100 \quad (3.1)$$

$$\text{Grafting efficiency (\%)} = \frac{\text{Weight of monomer grafted}}{\text{Weight of monomer polymerized}} \times 100 \quad (3.2)$$

$$\text{Free NR (\%)} = \frac{\text{Weight of free rubber}}{\text{Weight of gross polymer products}} \times 100 \quad (3.3)$$

$$\text{Free homopolymer (\%)} = \frac{\text{Weight of free homopolymer}}{\text{Weight of gross polymer products}} \times 100 \quad (3.4)$$

$$\text{Graft copolymer (\%)} = \frac{\text{Weight of graft copolymer}}{\text{Weight of gross polymer products}} \times 100 \quad (3.5)$$

3.4.2 Characterization of Grafted Natural Rubber Product

After the soxhlet extraction, the structure of GDPNR was characterized by using Fourier-transform infrared spectroscopy (Thermo 470 FT-IR spectroscopy). The grafted rubber was dissolved in toluene (2 %w/v) and then casted as a film on the NaCl cell.

3.5 Procedure of Modified Acrylic Sheet

3.5.1 Preparation of Modified Acrylic Sheet Containing Grafted Rubber

The modified acrylic sheet containing graft rubber were prepared by bulk polymerization using casting process. The graft rubber was weighed and dissolved in MMA monomer. The mixture was stirred overnight to obtain the homogeneous solution. 0.1 wt% of BPO was added as a first initiator while stirring. The mixture was heated up to 85°C. The prepolymerization of MMA with graft rubber was performed under continuous stirring for 30 minutes. When the mixture was appropriately viscous, it was cooled down to room temperature. Then, 0.03 wt% of ABVN was added as a second initiator while stirring. The bubble of the mixture was removed by a vacuum pump. Then, the mixture was filled into glass mold and cured in a water bath at 60°C until the sheet hardened. In order to complete polymerization, the sheet was placed in an oven at 120°C for 2 h. The finished sheet was taken off from the glass mold after cooling at room temperature. The sheet was cut into the standard specimens according to the ASTM test method. The standard recipe and condition used for bulk polymerization of MMA with graft rubber is shown in Table 3.2.

Table 3.2 Recipe for casting modified acrylic sheets

	wt%
MMA	100
BPO	0.1
ABVN	0.03
NR	0.25
DPNR	0.25 – 2.0
GNR	0.25 – 1.5
GDPNR	0.5 – 10.0

3.5.2 Preparation of Modified Acrylic Sheet Containing Silica and GDPNR

The mixture from polymerization of MMA containing GDPNR at 2% w/w was appropriately viscous for the studying in this section. Then, 0.03 % w/w of ABVN and silica at various contents were added as a second initiator and filler respectively, while continuously stirring. When the bubble of the mixture was removed by a vacuum pump, the mixture was filled into glass mold and cured in a water bath (60°C) and then placed in an oven at 120°C for 2 h. The finished sheet was taken off from the glass mold after cooling at room temperature. The sheet was cut into the standard specimens according to the ASTM test method. The standard recipe used for preparation acrylic sheet containing GDPNR and silica is shown in Table 3.3

Table 3.3 Recipe for casting modified acrylic sheets containing silica and GDPNR

	wt%
MMA	100
Benzoyl peroxide (BPO)	0.1
2,2'-azobis-(2,4-dimethylvaleronitrile) (ABVN)	0.03
GDPNR	2
Silica	0.25, 0.75, 1.25

3.6 Mechanical Testing

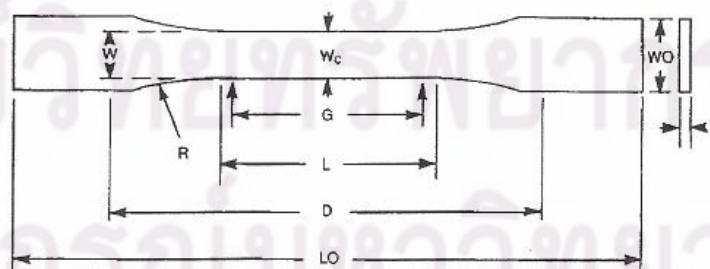
The mechanical properties of the modified acrylic sheets containing various contents of NR, DPNR, GNR or GDPNR were measured by following the ASTM test methods.

3.6.1 Tensile Properties (ASTM D 638)

Tensile properties of samples were measured at 25°C and humidity of 60% using dumbbell-shaped test pieces (Type I) as illustrated in Figure 3.2. The specimens were cut from a 3.0 mm thick sheet. The testing were performed on a Universal testing machine (LLOYD Instrument LR 10K Plus) with a crosshead speed of 500 mm/min.

3.6.2 Hardness

The methods for hardness testing followed ASTM D 2240. The hardness of specimen was measured using Durometer Hardness Test Shore D model 475 PTC. The specimen was placed on a hard and horizontal surface. The presser was held on a vertical position with the point of the indenter at least 12 mm from any edge of the specimen. The loading weight was 5 kg for applied to the specimen. After the presser foot was in firm contact with the specimen, scale reading was taken within 30 s.

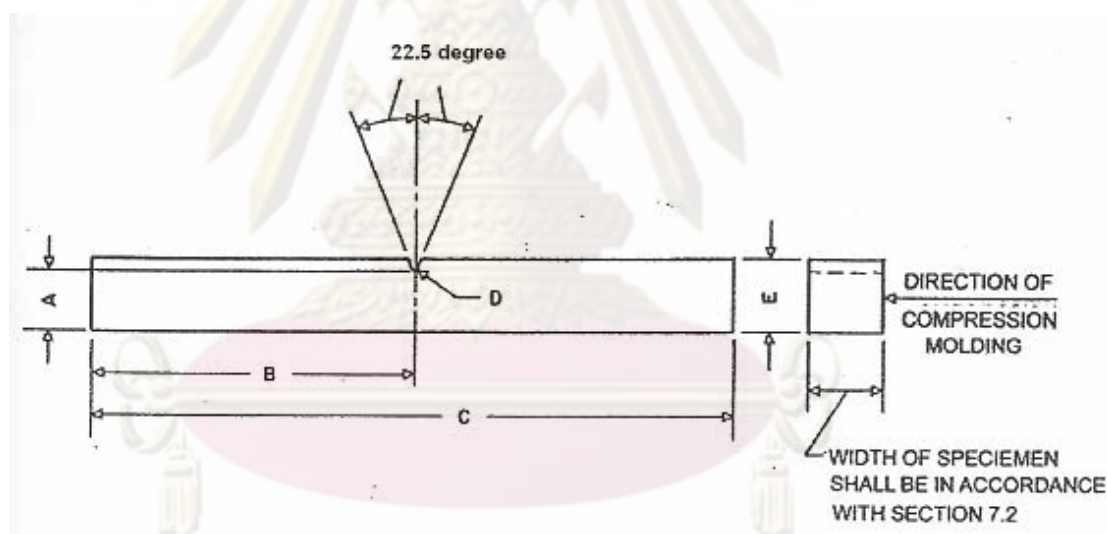


W : 13 mm WO : 19 mm G : 50 mm R : 76 mm
L : 57 mm LO : 165 mm D : 1155 mm T : 4 mm or under

Figure 3.2 Schematic diagram of tensile test specimen (Type I).

3.6.3 Impact Strength (ASTM D 256)

The test specimens conformed to the dimensions and geometry of Figure 3.3. The machine used in the present investigation was Izod Impact Tester (Impact tester GOTECH GT 7045). The width of each specimen was measured in the region of the notch with a micrometer caliper and recorded its average width along with it would be impacted edgewise at its center on the face opposite the notch for notched specimens. The breaking energy of specimen was estimated and the weight hammer with 2 J was applied for the specimens. The pendulum was released and an excess energy remaining in the pendulum was recorded after breaking the specimen, together with a description of the appearance of a broken specimen. The average impact energy was calculated in the group of specimens.



Unit: mm

A: 10.16 ± 0.05

D: 0.25 ± 0.05

B: 32.00 max, 31.50 min

E: 12.70 ± 0.05

C: 80 ± 0.2

Figure 3.3 Dimensions of simple beam, Izod type, impact test specimen.

3.7. Physical Testing

3.7.1 Transparent Properties

Transparent properties were reported in term of opacity of specimens by using color measurement (Gretagmacbeth Instrument color i5).

3.7.2 Ultraviolet Resistance

The physical and mechanical properties of the modified acrylic sheets (5 x 10 x 0.3 cm) after UV ageing were investigated. They were placed in the Ultraviolet box (The Q.PANEL company model Q.U.V) with the UV wavelength at 320 nm for 7 days at room temperature. The impact strength and tensile properties of the modified acrylic sheets after UV ageing were compared to untreated sample.

3.7.3 Thermal Resistance

The physical and mechanical properties of the modified acrylic sheets (5 x 10 x 0.3 cm) after thermal ageing were investigated. They were placed in an ageing oven (GT-7017 GOTECH) at 165°C for 25 min. The impact strength and tensile properties of the modified acrylic sheets after thermal ageing were compared to untreated sample.

3.8 Scanning Electron Microscopy (SEM)

The morphology of tensile fracture surface of the modified acrylic sheets obtained from the tensile properties test was investigated using a JEOL model JSM-6400 scanning electron microscopy at 15 kV. The specimens were mounted on a SEM stub using a double-side tape and the fracture surface of specimens was coated with gold.

CHAPTER IV

RESULTS AND DISCUSSION

The graft copolymers of PMMA onto DPNR were prepared by emulsion polymerization using potassium persulphate as an initiator. The effect of DPNR latex on the conversion, grafting efficiency, percentage of free rubber, percentage of homopolymer and percentage of graft copolymer was recorded as a function of time. The graft product was also characterized by Fourier-Transform Infrared Spectroscopy (FTIR). The graft DPNR (GDPNR) was added into the MMA syrup during the stage of bulk polymerization. The acrylic sheet could be prepared by casting process. The mechanical properties, optical properties and morphology of the modified acrylic sheets before and after ageing with heat and ultraviolet (UV) were investigated. Silica used as a stabilizer was also added during preparation of modified acrylic sheet. The properties of the silica-modified acrylic sheets were also reported.

4.1 Preparation and Grafting Properties of Graft Deproteinized Natural Rubber and Graft Natural Rubber

The GDPNR was prepared by emulsion graft copolymerization. The optimum reaction condition was reported by Nakason and Man [25, 28] as shown in Table 3.1. The graft product was extracted by light petroleum ether (LPE) for 24 h by using Soxhlet extraction for removing free rubber content and then dried to constant weight. To remove free homopolymer, the dried residue was extracted by acetone for 24 h. The data obtained from all steps were used to calculate the percentage of conversion, grafting efficiency (GE) and grafting properties. The details of all calculations are shown in Appendix B. The properties of GDPNR after extraction are shown in Table 4.1. This was also compared to the graft copolymerization of MMA onto natural rubber (NR) latex.

Table 4.1 Properties of GDPNR and graft NR (GNR)

Expt.	Reaction time (h)	Total conversion (%)	Free rubber (%)	Free homopolymer (%)	Graft copolymer (%)	GE (%)
GDPNR1	2	44.7(0.39) ¹	56.2 (0.70)	5.6 (0.91)	38.1 (1.62)	41.7 (0.05)
GDPNR2	3	65.9 (0.53)	28.0 (0.14)	6.1 (0.02)	65.8 (0.11)	49.2 (1.53)
GDPNR3	4	65.8 (0.21)	28.1 (0.41)	6.3 (0.49)	65.3 (0.91)	43.8 (1.14)
GDPNR4	5	67.6 (0.55)	28.7 (0.59)	6.7 (0.62)	64.4 (0.03)	38.4 (9.02)
GDPNR5	6	67.9 (0.22)	28.3 (0.18)	7.3 (0.11)	64.4(0.07)	38.5 (0.31)
GNR1	3	60.5 (0.66)	57.4 (1.92)	8.2 (0.89)	34.3 (1.07)	25.2 (3.76)

¹ The standard deviation is in a parenthesis

For GDPNR preparation (Table 4.1), the results indicated that %total conversion and %GE increased with increasing the reaction time. At 3 h, the %GE reached a maximum value at 49.2 % and thereafter, the grafting efficiency decreased. At the longer reaction time, there were no new generated active grafting sites generated on the rubber molecules. After 3 h, the amount of the free rubber and graft copolymer was slightly changed. Whereas, the PMMA homopolymer content was higher at a long reaction time. Thus, the appropriate reaction time for the preparation of GDPNR with highest %GE was 3 h at 70°C.

For GNR preparation at the same reaction condition for GDPNR preparation, it was found that the graft copolymerization of MMA onto NR gave the lower value of both %GE and %graft copolymer with higher free rubber and homopolymer content. This means that the removal of proteins in NR structure increased the levels of %GE and %total conversion. It was believed that proteins played a significant role for inhibition of free-radical polymerization by termination during graft copolymerization [25].

4.2 Structure Characterization of Graft Deproteinized Natural Rubber and Graft Natural Rubber

The structures of GDPNR and GNR obtained after soxhlet extraction were confirmed using FTIR spectroscopy. The FTIR spectra of DPNR and the GDPNR are shown in Figure 4.1 and FTIR spectra of NR and the GNR are shown in Figure 4.2. The FTIR spectra of DPNR exhibited the characteristic absorption bands of C=C stretching vibration at 1664 cm^{-1} and C-H vibration at 2997 , 1473 and 1376 cm^{-1} and C=C bending vibration at 853 cm^{-1} . The new signals of GDPNR appeared at 1732 cm^{-1} attributed to stretching vibration of C=O group, C-O stretching vibration at 1140 cm^{-1} . These confirmed that PMMA was grafted onto DPNR.

The spectra of NR and GNR exhibited the same characteristic as those of DPNR and GDPNR. The difference between NR and DPNR is the protein content. The protein impurities in the NR latex are >N-H and >N-C=O which are shown via the weak transmittance bands at 3280 and 1530 cm^{-1} , respectively [5]. They were slightly presented in FTIR spectra of DPNR and GDPNR.



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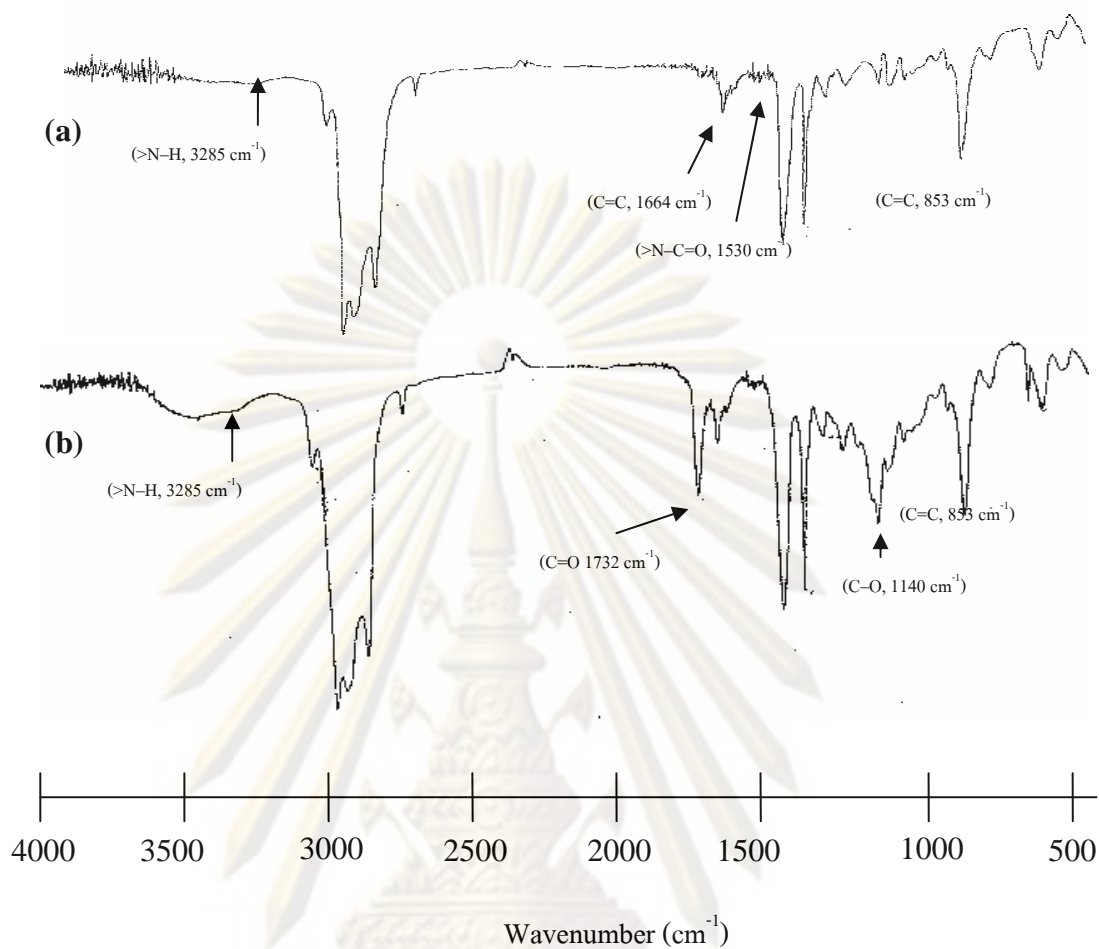


Figure 4.1 FTIR spectra of (a) DPNR and (b) GDPNR after soxhlet extraction.

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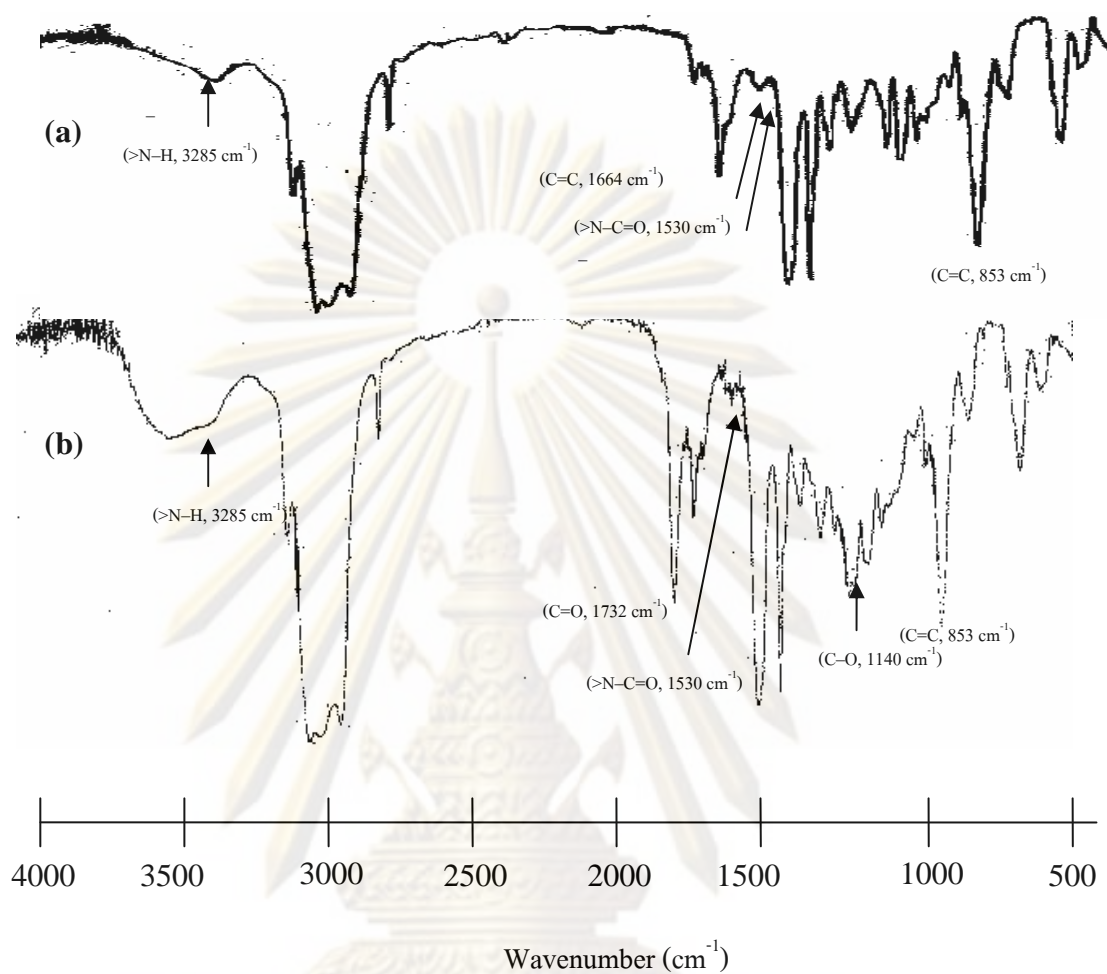


Figure 4.2 FTIR spectra of (a) NR and (b) GNR after soxhlet extraction.

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4.3 Physical and Mechanical Properties of Modified Acrylic Sheet Containing Grafted Copolymers

In this section, the physical and mechanical properties of the modified acrylic sheets containing GDPNR (49.2% GE) were investigated. This result was also compared to the addition of GNR (25.17% GE), NR and DPNR.

4.3.1 Color of MMA Syrup and Modified Acrylic Sheets Containing Various Rubber Types and Concentrations

The color of the MMA syrup containing various rubber types and concentrations was summarized in Table 4.2 and Figure 4.3. It was found that the MMA syrup containing NR (Figure 4.3b) was higher than that of MMA syrup containing DPNR (Figure 4.3c) at the same rubber concentration (0.25 wt %). At 1.5 wt% of rubber content, the opaque and yellowish white of MMA syrup containing GNR (Figure 4.3e) was higher than that of MMA syrup containing DPNR (Figure 4.3d) and GDPNR (Figure 4.1f), due to the high level of protein and non-rubber in NR structure. Similar behavior was also observed in the rubber glove fabrication from DPNR latex [37]. The opaque and yellowish of MMA syrup containing GDPNR increased with increasing GDPNR contents due to the cumulative residual protein and non-rubber contents in DPNR structure. In the preparation step for casting the modified acrylic sheets, the GDPNR content dissolved in the MMA syrup was in the range of 0.5 – 10.0 wt% while the modified acrylic sheet containing NR, GNR and DPNR used the lower level of rubber contents at 0.25, 1.5 and 2.0 wt%, respectively. This was dependent on the ease of handle for casting preparation. Due to the higher molecular weight of NR compared to DPNR [36], its concentration was limited for dissolving in the MMA syrup. For GDPNR, it was found that the graft copolymer of MMA onto DPNR enhanced the solubility of DPNR in the MMA syrup. Thus, the concentration of GDPNR in the MMA syrup could be increased up to 10 %w/w.

Table 4.2 Color of MMA syrup containing various rubber types and concentrations

Rubber type	Rubber content (wt%)	Solution appearance
-	-	clear
NR	0.25	clear, colorless
DPNR	0.25	clear, colorless
	0.5	clear, colorless
	1.0	clear, white
	1.5	quite clear, yellowish white
	2.0	opaque, yellowish white
GNR	0.25	clear
	0.5	clear, white
	1.0	quite clear, yellowish white
	1.5	opaque, yellowish white
GDPNR	0.5	clear
	1.0	clear, white
	1.5	clear, white
	2.0	clear, yellowish white
	4.0	quite clear, yellowish white
	6.0	opaque, yellow
	8.0	opaque, brownish yellow
10.0	opaque, brownish yellow	

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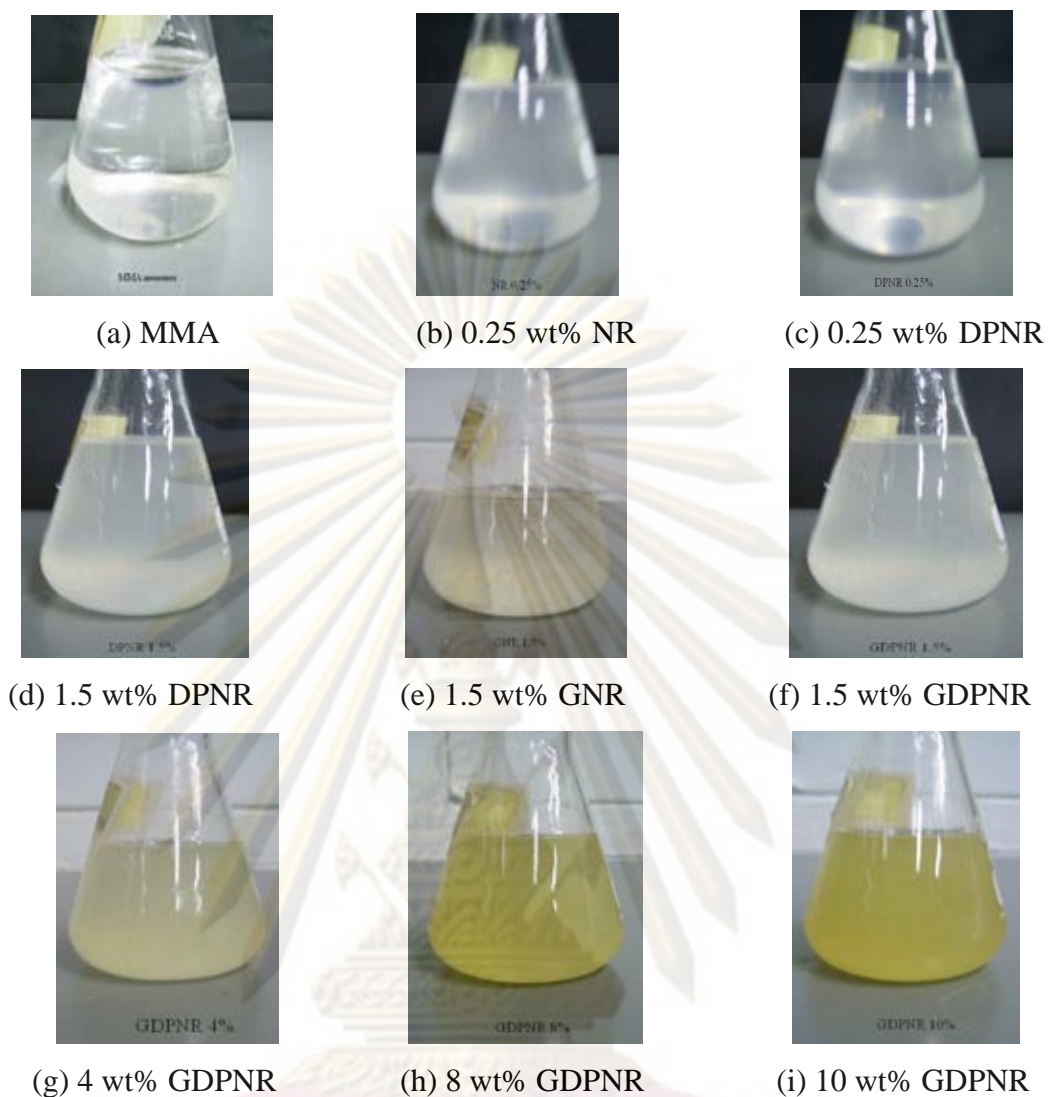


Figure 4.3 Color of MMA syrup before and after dissolving various rubber types and concentrations.

For the modified acrylic sheets, Table 4.3 and Figure 4.4 indicated the color of the modified acrylic sheets containing various rubber types and concentrations. It was found that the modified acrylic sheet was transparent when DPNR content was in the range of 0.25 – 1.0 wt%. Above 1.0 wt% of DPNR content, the modified acrylic sheet showed a little opaque. For the addition of GNR, the modified acrylic sheet was transparent in the range of 0.25 – 0.5 wt% of GNR content. When the GNR content was above 0.5 wt%, the modified acrylic sheet was little opaque. For the addition of GDPNR, the modified acrylic sheet was transparent when the GDPNR content was in the range of 0.5 – 1.0 wt%. Above 1.0 wt%, the modified acrylic sheet was also little

opaque. The opacity of the modified acrylic sheets increased with increasing GDPNR contents (Figure 4.4f–i). The modified acrylic sheet containing 0.25 wt% of NR and DPNR was transparent. For comparison between the addition of GNR and GDPNR, it was found that the modified acrylic sheet containing 1.5 wt% (Figure 4.4f) was higher transparent than that containing GNR at the same rubber concentration (Figure 4.4e). It was due to the higher proteins and non-rubber contents in the GNR structure.

Table 4.3 Color of modified acrylic sheets containing various rubber types and concentrations.

Rubber types	Rubber content (wt%)	Sheet appearance
-	-	transparent
NR	0.25	transparent
DPNR	0.25	transparent
	0.5	transparent
	1.0	transparent
	1.5	little opaque
	2.0	quite opaque
	GNR	0.25
GDPNR	0.5	transparent
	1.0	transparent
	1.5	little opaque
	2.0	little opaque
GDPNR	4.0	quite opaque
	6.0	opaque
	8.0	opaque
	10.0	opaque

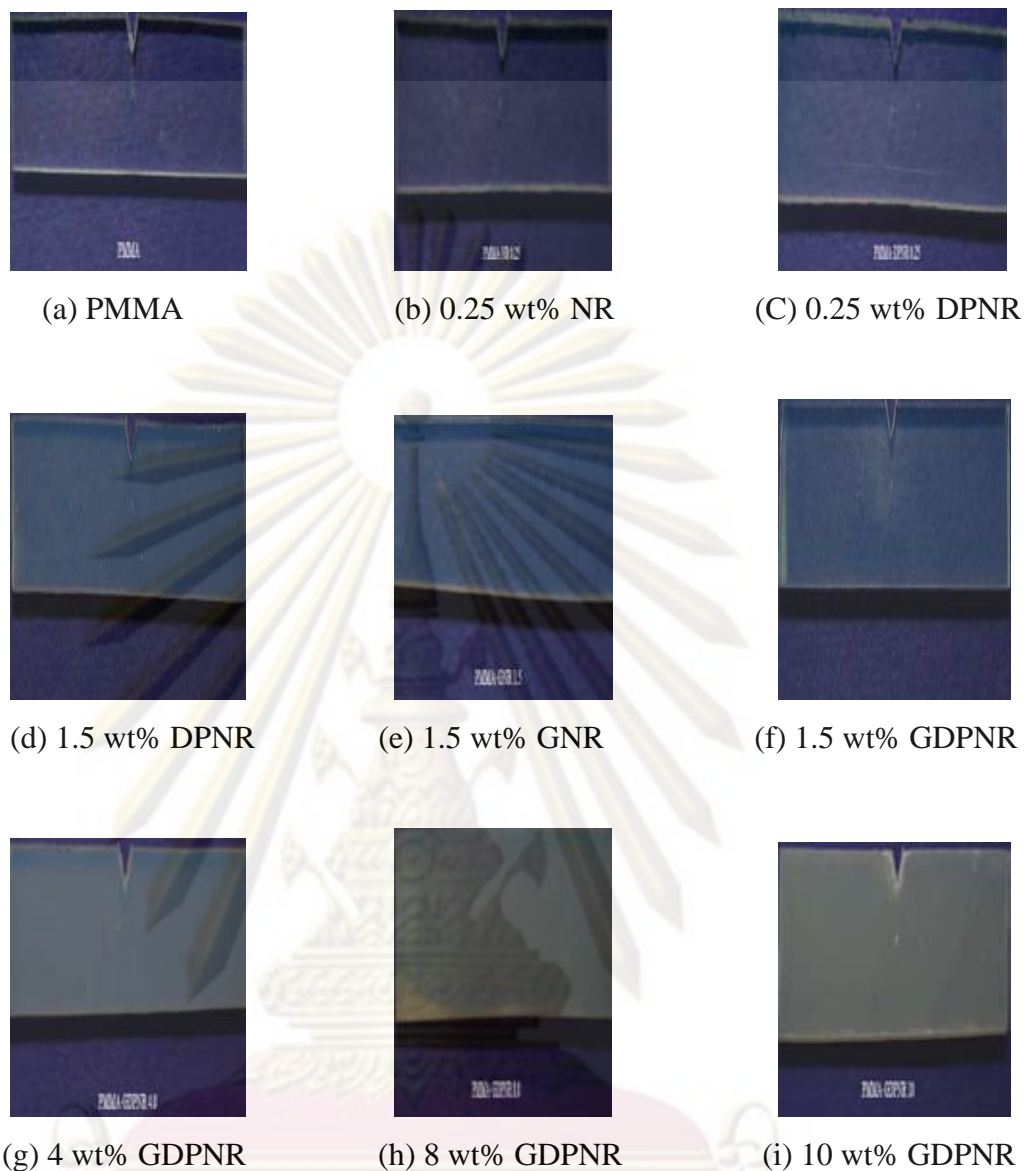


Figure 4.4 Color of modified acrylic sheets containing various rubber types and concentrations.

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4.3.2 Mechanical Properties of the Modified Acrylic Sheets

The influence of the rubber type and concentration on the mechanical properties of the modified acrylic sheets was investigated. The results of the Izod impact strength of the modified acrylic sheets are shown in Table 4.4. The impact strength of acrylic sheets without the addition of rubber was 44.7 kJ/m^2 . The addition of rubber tended to increase the impact resistance of the acrylic sheets. The impact strength of the modified acrylic sheets containing 0.25 wt% of NR increased up to 50 kJ/m^2 . For the addition of DPNR, the impact strength of the modified acrylic sheet increased with increasing the rubber contents and reached to the maximum value at 86.1 kJ/m^2 at 1.5 wt% of DPNR. At 0.25 wt%, the impact strength of modified acrylic sheet containing NR was higher than that containing DPNR due to good mechanical properties of NR. Similar behavior was also observed in the rubber glove fabrication from DPNR Latex [35]. For the addition GNR and GDPNR, the impact strength of the modified acrylic sheets increased with increasing graft rubber contents. This property was higher than that of ones containing DPNR and NR of the same rubber concentration. It indicated that the GDPNR and GNR provided the better compatibility with PMMA. This means that the graft copolymerization of rubber particles was essential for attaching the rubber particles to the surrounding glassy matrix resulting to the better compatibility and dispersion between phases. This allowed the energy transfer to the rubber particles to dissipate the impact energy. Similar behavior was also observed in the NR grafted with styrene/MMA which was used as an impact modifier for polyvinyl chloride [26]. However, the addition of GNR into the acrylic sheets was limited due to the lower level of grafting efficiency compared to GDPNR. The higher molecular weight of NR also caused the difficulty for dissolving in MMA syrup during the preparation of acrylic sheet. The lower molecular weight of DPNR caused the Izod impact resistance of modified acrylic sheet containing 1.5 wt% GDPNR lower than that containing GNR at the same concentration.

The tensile properties of the modified acrylic sheet containing various types and concentration of rubber are also shown in Table 4.4. It was found that the modified acrylic sheet without the addition of rubber had low tensile strength (TS)

Table 4.4 Effect of grafted rubber content on impact strength, tensile strength (TS), elongation at break (EB), hardness and opacity of modified acrylic sheet.

Rubber type	Rubber Content (wt%)	Impact Strength (kJ/m ²)	TS (MPa)	EB (%)	Hardness (Shore D)	Opacity (%)
-	-	44.7 (2.81) ¹	48.9 (1.90)	4.4 (0.15)	78.8 (0.78)	10.9 (0.01)
NR	0.25	50.2 (0.56)	62.3 (0.91)	4.5 (0.35)	78.6 (0.69)	11.2 (0.01)
DPNR	0.25	47.1 (2.28)	50.0 (0.92)	4.4 (1.37)	79.0 (0.84)	13.4(0.02)
	0.5	55.7 (1.45)	51.4 (7.33)	4.7 (0.16)	78.9 (0.87)	17.0 (0.01)
	1.0	70.4 (3.49)	52.4 (3.12)	4.8 (0.57)	79.0 (0.81)	22.6(0.01)
	1.5	86.1 (1.52)	63.7 (1.65)	5.3 (0.35)	77.2 (0.78)	26.6 (0.01)
	2.0	81.8 (1.73)	56.4 (1.45)	5.5 (0.61)	76.9 (0.99)	57.9 (0.03)
GNR	0.25	48.6 (0.56)	52.6 (2.04)	4.5 (0.23)	78.8 (0.78)	13.3 (0.03)
	0.5	70.0 (1.67)	63.1 (1.21)	4.7 (0.15)	78.4 (0.69)	16.0 (0.11)
	1.0	87.5 (0.9)	61.9 (3.48)	6.4 (0.32)	76.6 (0.84)	21.2 (0.01)
	1.5	94.9 (1.34)	56.5 (0.8)	5.3 (0.39)	76.1 (0.99)	33.8 (0.03)
GDPNR	0.5	56.9 (0.97)	45.7 (3.23)	4.6 (0.11)	79.2 (0.78)	14.8 (0.01)
	1.0	78.3 (2.28)	50.7 (4.39)	4.6 (0.57)	80.9 (0.56)	19.2 (0.01)
	1.5	87.6 (1.41)	55.2 (2.49)	6.0 (0.16)	77.4 (0.84)	30.3 (0.02)
	2.0	90.5 (3.0)	55.9 (2.94)	6.1 (0.44)	76.5 (0.70)	41.4 (0.01)
	4.0	101.5 (5.13)	63.3 (2.14)	6.5 (0.50)	75.7 (1.41)	60.8 (0.05)
	6.0	124.5 (3.81)	33.2 (1.30)	7.2 (0.34)	72.8 (1.47)	63.4 (0.02)
	8.0	125.4 (6.34)	29.4 (1.36)	7.2 (0.12)	70.1 (1.10)	83.6 (0.07)
	10.0	152.8 (6.58)	25.1 (2.10)	7.1 (0.39)	70.1 (0.73)	84.7 (0.01)

¹The standard deviation is in a parenthesis.

ca. 48.9 MPa. The TS of modified acrylic sheet increased with increasing rubber content and reached to a maximum value at 1.5 wt% DPNR, 0.5 wt% GNR modifiers and 4wt% GDPNR modifiers. It was anticipated that the NR portion of the graft product could promote the superior tensile strength of the modified acrylic sheets. Furthermore, the compatibility between PMMA of graft rubber and PMMA of the acrylic sheet matrix also increase the tensile properties of modified acrylic sheets. Above 4 wt% of GDPNR and 0.5 wt% of GNR, the TS of the acrylic sheet tended to decrease and then level off at *ca* 30 MPa and 50 MPa, respectively. The decrease in TS might be due to the interfacial saturation of graft rubber in the thermoplastic components. Similar behavior was also observed in the NR/PMMA blends with graft

copolymer of maleic anhydride onto NR as the compatibilizer [4]. The maximum TS of modified acrylic sheets containing only 0.5 wt% of GNR was observed. The TS was drastically decreased when GNR content was increased due to lower level of grafting efficiency (27.49 %) of GNR. This means that the GNR had high percentage of free NR fraction (57.75 %). This was more difficult to completely dissolve the high NR content in the modified acrylic solution. Consequently, this led the heterogeneous mixture during casting the sheet resulting to the reduction of the TS value.

From Table 4.4, the elongation at break (EB) of the acrylic sheet with or without the addition of NR (0.25 wt %) was *ca.* 4.4 - 4.5%. For the addition of DPNR, GNR and GDPNR, the EB of the modified acrylic sheets increased with increasing the rubber content and reached to a maximum value at 2 wt% DPNR, 1 wt% GNR and 8 wt% GDPNR. This phenomenon was opposite to the TS of the modified acrylic sheets. This could be explained that the higher rubber content in the PMMA matrix in the acrylic sheet could inhibit the progress of polymerization during casting process resulting to the lower TS with higher EB.

The stress-strain behavior of the modified acrylic sheets is shown in Figure 4.5. The stress-strain curve of the modified acrylic sheet without GDPNR showed the rigid or brittle characteristics with low elongation and no yield point (Figure 4.5a). The brittle property of the modified acrylic sheet was gradually shifted to ductile property when the amount of graft copolymer was increased as shown in Figure 4.5b-d. The stress-strain curve of the modified acrylic sheet with 10 wt% of GDPNR clearly exhibited the yield point and the high percentage elongation. Similar behavior was also observed in the improving properties of modified acrylic sheet via addition of grafted NR [31].

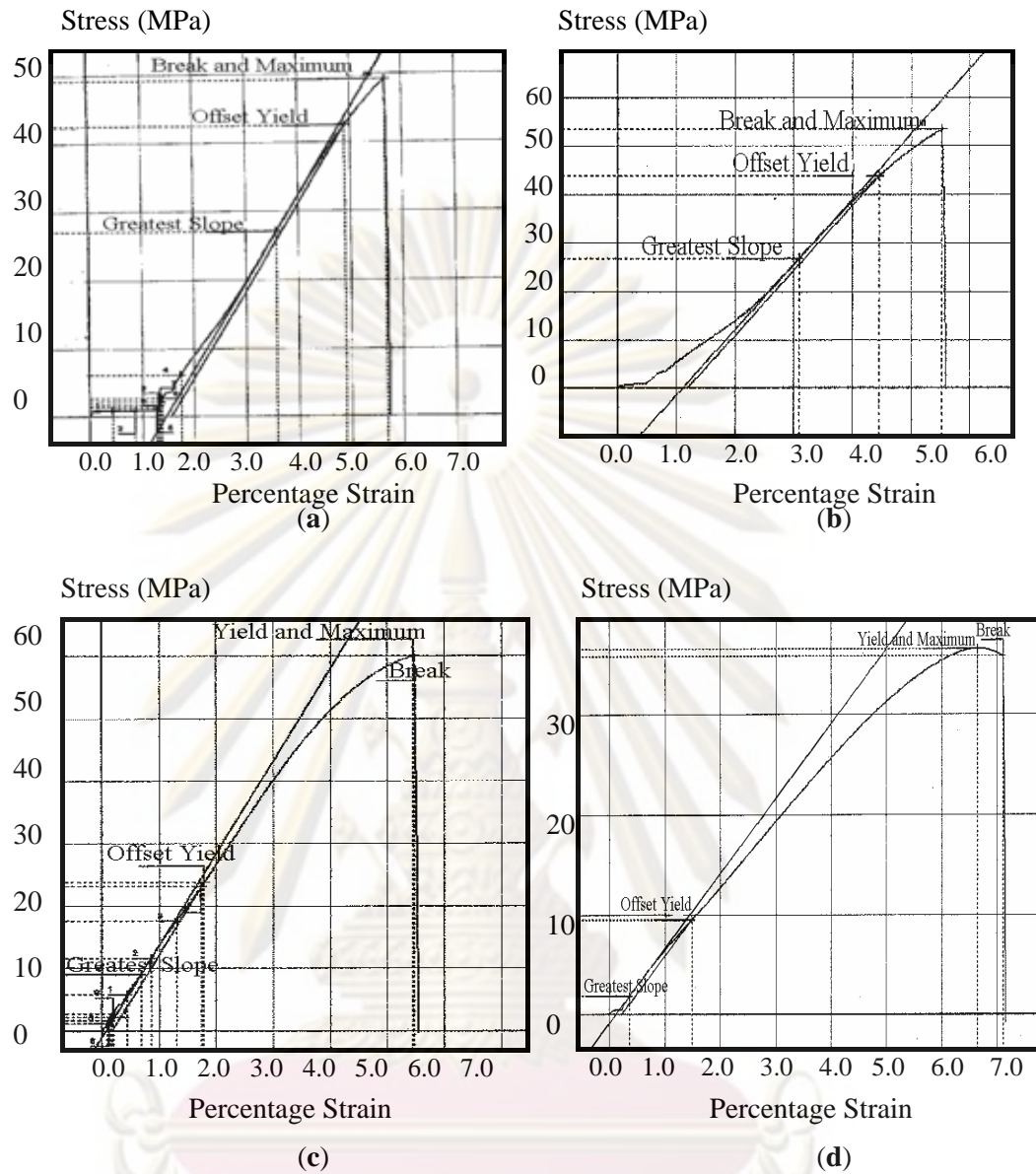


Figure 4.5 Stress-strain behavior of the modified acrylic sheets containing various GDPNR content: (a) 0, (b) 2, (c) 6 and (d) 10 wt%

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Figure 4.6 shows optical photograph of the fracture of the modified acrylic sheet after tensile test. The size and the intensity of the stress-whitening zone increased with increasing GDPNR content, whereas, it was not observed for the neat PMMA. During tensile test, the specimen became more whitening, showing a stable crack growth behavior. Therefore, the modified acrylic sheets with GDPNR showed a brittle-ductile transition behavior, whereas the neat PMMA was the brittle material. Similar behavior was also observed in the strain-rate effect of EVA/PMMA *in situ* polymerization blends [29].

From Table 4.4, the hardness of acrylic sheet without the addition of rubber was 78.8 shore D. The addition NR, DPNR, GNR and GDPNR, caused the hardness reduction of hardness of the modified acrylic sheets. The hardness of modified acrylic sheet containing rubber decreased from 78.8 shore D to ca. 76.9 and 76.1 shore D for 2.0 wt% DPNR and 1.5 wt% GNR, respectively. For the addition of GDPNR, the hardness of modified acrylic sheets decreased from 78.8 shore D to 70.1 shore D when %GDPNR in modified acrylic sheets was 10 wt%. This results may be explained that the rubber component of the graft rubber (GNR and GDPNR), NR and DPNR had more elastic properties. Consequently, the modified acrylic sheets with higher content of rubber phase easily deformed.

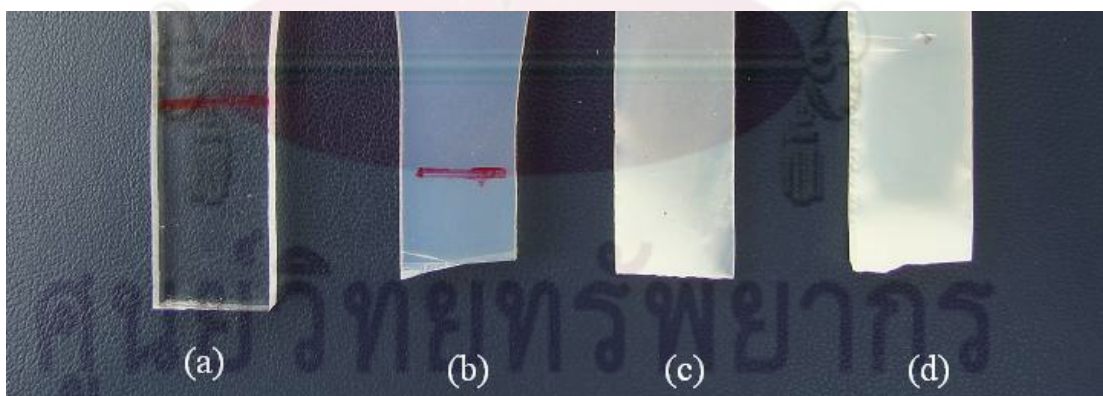


Figure 4.6 The stress-whitening zone of the modified acrylic sheets containing various GDPNR contents: (a) 0, (b) 2, (c) 6 and (d) 10 wt%

From Table 4.4, the rubber modifiers caused the reduction of transparency of the modified acrylic sheet. The opacity of pure acrylic sheet was 10.9%. This value increased to 11.2% when added 0.25 wt% NR was added in the modified acrylic sheet. The opacity of modified acrylic sheet increased to 57.9% and 33.8% when the modified acrylic sheets containing DPNR (2.0 wt%) and GNR (1.5 wt%), respectively. For addition of GDPNR, the opacity of modified acrylic sheets increased from 10.9 % to 84.7 % when GDPNR content in modified acrylic sheets increased to 10 wt%.

4.4 Stability of Modified Acrylic Sheet

In the previous section, it was found that the impact strength and tensile strength of the modified acrylic sheets could be improved by adding the small amount of rubbers. However, it is necessary to investigate the ageing resistance of these modified acrylic sheets for outdoor application. The thermal and ultraviolet (UV) resistances were examined the retention of the mechanical properties.

4.4.1 Thermal Stability of Modified Acrylic Sheet

The effect of the addition of rubber on the thermal stability of the modified acrylic sheet was investigated as a function of rubber content. This study was emphasized on the effect of the addition of DPNR and GDPNR on the thermal stability of the modified acrylic sheets as summarized in Table 4.5. The thermal stability of the modified acrylic sheets reported in the term of retention of mechanical properties such as tensile properties, impact strength and hardness.

From Table 4.5, the impact strength of the unmodified acrylic sheet was higher from 44.7 to 58.7 kJ/m² (%retention = 131.4) after thermal ageing due to the formation of self-crosslinking resulting from the remaining initiator in the acrylic sheet. When the DPNR or GDPNR was added into the acrylic sheets, the %retention for impact strength tended to decrease. It is possible that the rubber might inhibit the formation of crosslink during thermal ageing. Moreover, the rubber was possibly degraded after thermal ageing resulting to the reduction of the impact strength of the modified acrylic sheets.

The retention of TS of unmodified acrylic sheets was 96.3%. The addition DPNR and GDPNR into the acrylic sheet resulted to the retention of TS of modified acrylic sheets decreased with increasing rubber content. Moreover, the retention of EB of unmodified acrylic sheets also decreased when DPNR or GDPNR was added into the acrylic sheets. For comparison between DPNR and GDPNR at the same concentration, the %retention of tensile properties of modified acrylic sheets containing GDPNR was higher than ones containing DPNR due to the lower level of C=C bond of GDPNR compared to DPNR. This was possible that the modified acrylic sheet containing GDPNR had higher thermal resistance.

The retention of hardness of the modified acrylic sheets containing DPNR and GDPNR were approximately 100%. When the amount of these rubbers was not above 2.0 wt%. The higher loading of GDPNR caused the lower hardness retention due to

Table 4.5 Effect of grafted rubber content on thermal stability of modified acrylic sheet.

Rubber type	Rubber Content (wt%)	%Retention ¹			
		Impact strength	TS	EB	Hardness
-	-	131.4	96.3	146.6	99.2
DPNR	0.25	109.9	112.7	144.3	101.4
	0.5	109.4	113.2	133.2	100.7
	1.0	106.6	112.6	130.0	101.2
	1.5	105.6	91.5	126.8	100.8
	2.0	97.3	84.3	126.2	100.0
GDPNR	0.5	111.6	113.5	145.6	98.9
	1.0	109.0	113.0	114.6	100.6
	1.5	105.9	103.8	104.4	104.0
	2.0	105.5	107.4	97.1	100.2
	4.0	95.0	106.1	95.8	97.7
	6.0	93.1	105.8	85.1	96.6
	8.0	86.9	99.4	97.7	96.5
	10.0	68.0	91.9	94.8	85.6

¹%Retention = (Properties after aging / properties before aging) x 100

the thermal degradation of C=C bond in the main chain of rubber resulting to the decrease in the hardness of modified acrylic sheet. The similar behavior was also observed in the thermal decomposition of rubber [4].

4.4.2 Ultraviolet Stability of Modified Acrylic Sheet

Table 4.6 showed the UV stability of the modified acrylic sheet reported in the term of retention of mechanical properties such as tensile properties, impact strength and hardness. The retention of impact strength of acrylic sheets without the addition of rubber was 105.8% and that of ones containing DPNR increased to 103.1% when the amount of DPNR in modified acrylic sheets was 0.25 wt% and drastically decreased to 49.2% when the DPNR content increased to 2.0 wt%. For addition GDPNR, the retention of modified acrylic sheets decreased to 51.3% when GDPNR content in the modified acrylic sheets was 2.0 wt% due to the degradation of C=C bond in the main chain of rubber and chain scission of PMMA after UV ageing which caused the impact strength decreased [37]. Above 4 wt% of GDPNR in modified acrylic sheets, the retention of impact strength of modified acrylic sheets increased due to the opacity of modified acrylic sheet increasing, that can block out UV radiation was radiated to modified acrylic sheet.

The retention of TS and EB of unmodified acrylic sheets were 77.4 and 99.1%, respectively. The addition DPNR and GDPNR into the acrylic sheet resulted to the retention of TS of modified acrylic sheets decreased with increasing rubber content. Moreover, the retention of EB of unmodified acrylic sheets also decreased when DPNR or GDPNR was added into the acrylic sheets. For comparison between DPNR and GDPNR at the same concentration, the %retention of tensile properties of modified acrylic sheets containing GDPNR was higher than ones containing DPNR due to the lower level of C=C bond of GDPNR compared to DPNR. This was possible that the modified acrylic sheet containing GDPNR had higher UV resistance. When GDPNR modifier increasing from 4 to 10 wt%, the retention of that of the modified acrylic sheet increased due to the opacity of modified acrylic sheet increasing, that can block out UV radiation was radiated to modified acrylic sheet.

The retention of hardness of modified acrylic sheet with DPNR and GDPNR were approximately 100% when the amount of these rubbers not above 1.5 and 2.0

Table 4.6 Effect of rubber content on UV stability of modified acrylic sheet.

Rubber type	Rubber Content (%)	%Retention			
		Impact strength	TS	EB	Hardness
-	-	105.8	77.4	99.1	100
DPNR	0.25	103.1	80.4	101.8	100.5
	0.5	101.1	79.2	101.3	100.3
	1.0	61.4	88.0	100.5	100.5
	1.5	49.3	82.1	99.8	98.2
	2.0	49.2	90.2	99.2	97.8
GDPNR	0.5	102.6	103.1	103.4	100.5
	1.0	58.1	103.7	104.5	100.6
	1.5	54.4	99.1	103.3	101.0
	2.0	51.3	78.3	96.2	100.5
	4.0	72.1	89.4	96.9	96.1
	6.0	94.7	102.7	100.56	92.8
	8.0	96.1	105.9	101.56	93.8
	10.0	96.7	102.9	101.12	92.1

wt% of DPNR and GDPNR content, respectively. The higher loading of DPNR and GDPNR caused the lower hardness retention due to the UV degradation of C=C bond in the main chain of rubber and chain scission of PMMA after UV ageing.

4.5 Morphological Study

The scanning electron microscope (SEM) was employed to investigate the effect of the addition of GDPNR at various concentrations on the fracture surface of the modified acrylic sheets obtained from tensile properties test as shown in Figure 4.7.

For the graft copolymer of PMMA onto DPNR, DPNR contributed to the toughness of material, whereas the PMMA exhibited the good compatibility with thermoplastics. The increase in the impact strength of the modified acrylic sheet containing GDPNR was visualized using SEM technique. The result presented in

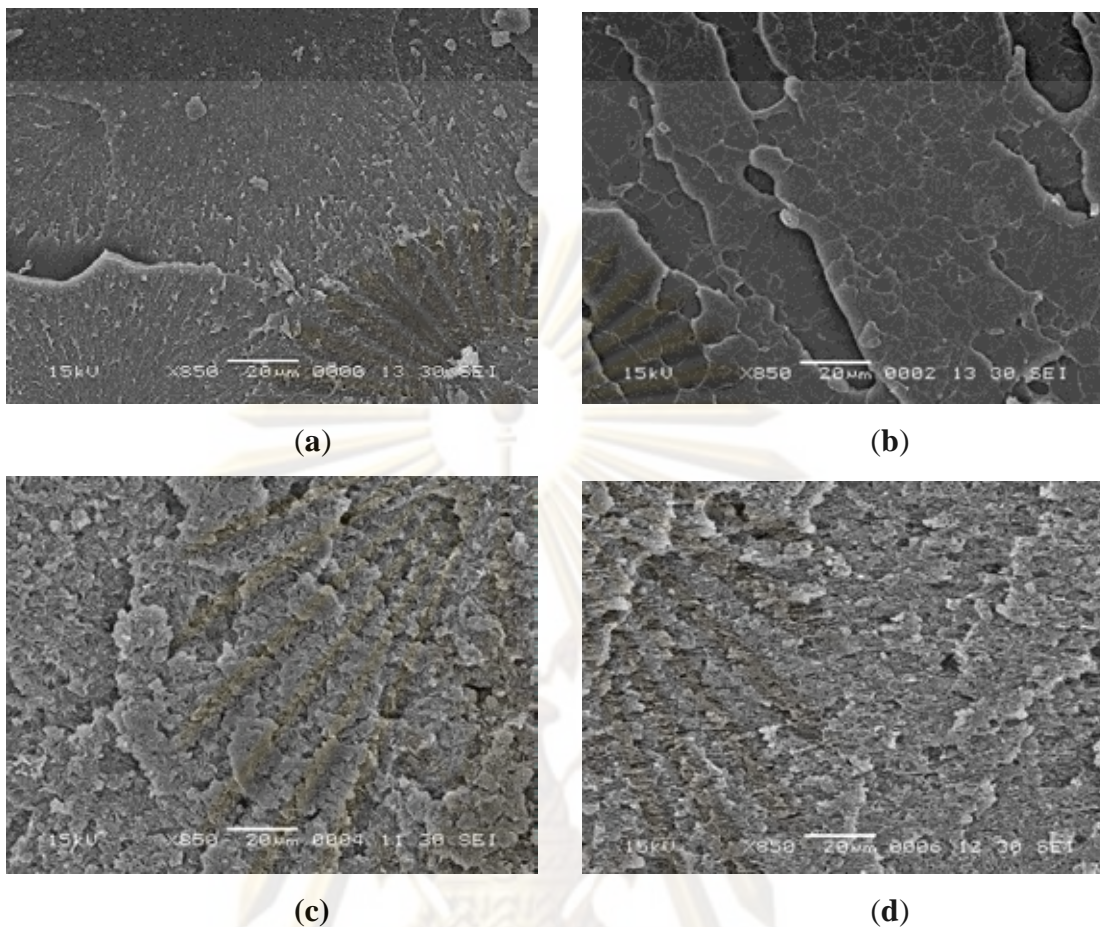


Figure 4.7 SEM photographs of modified acrylic sheet containing various GDPNR content: (a) 0 (b) 2 (c) 6 and (d) 10 wt%

Figure 4.7a indicated that the large cracking appeared on the fracture surface of the incompatible specimen. For the specimens containing 2, 6 and 10 wt% GDPNR content, the fracture surfaces of the modified acrylic sheets became smoother with increasing the GDPNR contents as shown in Figures 4.7b, 4.7c and 4.7d. It indicates that the GDPNR acted as the interfacial agent to give the compatibility with PMMA and the impact modifier to improve the impact strength of the modified acrylic sheet. The high Izod impact strength values of the compatible blends are in agreement with this anticipation.

4.6 Mechanical Properties and Stability of Modified Acrylic Sheet with GDPNR Containing Silica

The modified acrylic sheets containing GDPNR at 2 wt% and silica at 0.25 – 1.25 wt% were prepared by bulk polymerization. The effects of the silica content on the modified acrylic sheets were presented in Table 4.7 and Figure 4.8. The acrylic sheet was transparent when the silica content was 0.25 wt% (Figure 4.8b). Above 0.75 wt% of silica content, the acrylic sheet was opaque (Figure 4.8c). It was possible that the higher amount of silica particle was barked transparency of the modified acrylic sheet. From Table 4.7 and Figure 4.8, the modified acrylic sheet with 2 wt% of GDPNR content was little opaque when the modified acrylic sheets containing 0.25 wt% of silica content (Figure 4.8f). When the silica content was above 0.75 wt%, the modified acrylic sheet with 2 wt% GDPNR was opaque (Figure 4.8g). The appropriate silica content for the casting of acrylic sheet and the modified acrylic sheet was less than 0.5 and 1.25 wt%, respectively.

Table 4.7 Effect of silica content on preparation of the modified acrylic sheet

Rubber content (wt%)	Silica content (wt%)	Sheet appearance
-	-	transparent
-	0.25	transparent
-	0.75	little opaque
-	1.25	opaque
2	-	little opaque
2	0.25	little opaque
2	0.75	quite opaque
2	1.25	opaque

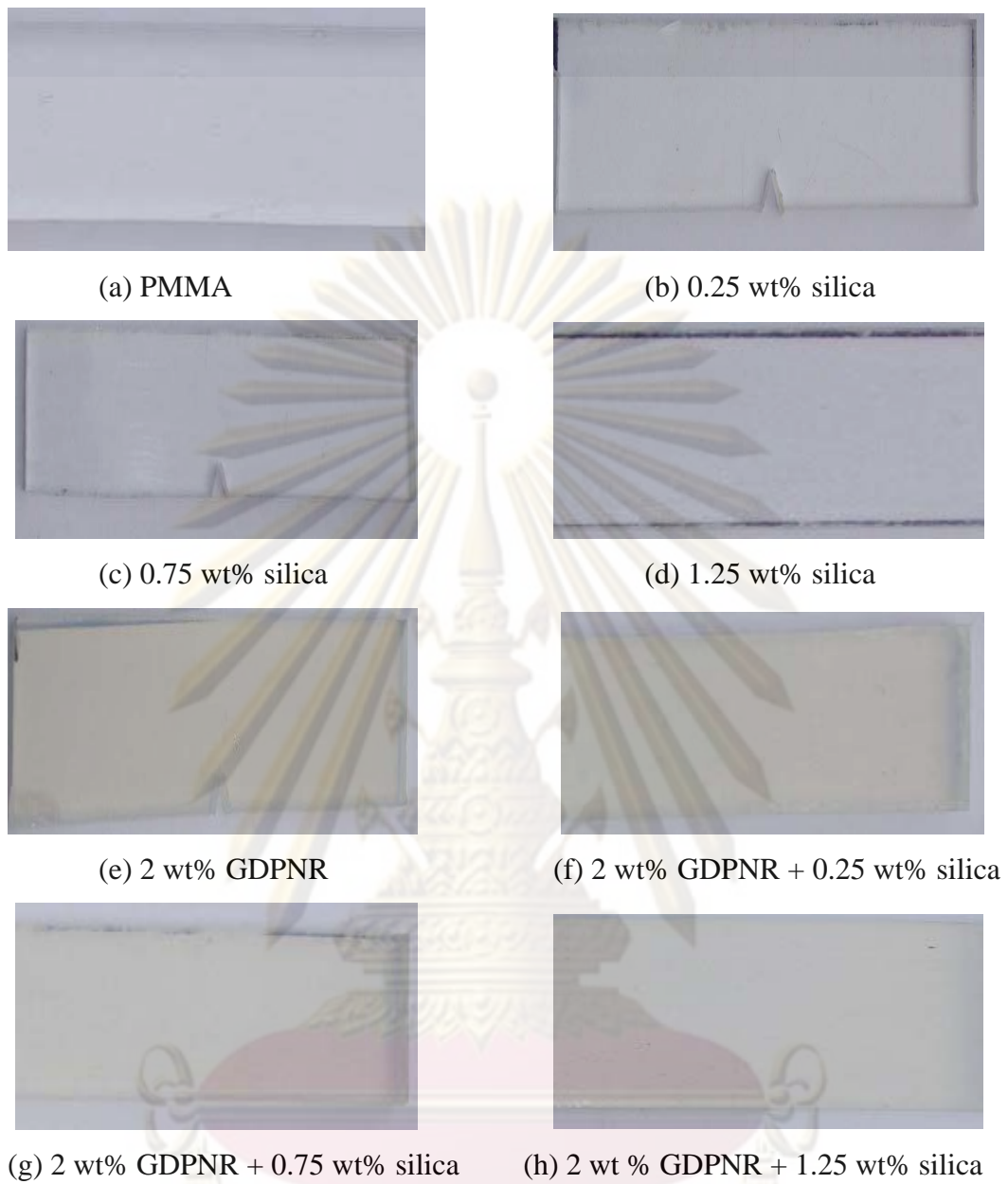


Figure 4.8 Sheet appearance of the modified acrylic sheet with GDPNR and silica.

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4.6.1 Mechanical and Physical Properties of the Modified Acrylic Sheet with GDPNR Containing Silica

The mechanical properties such as impact strength, tensile properties, and hardness of the modified acrylic sheets containing silica at various contents were investigated as presented in Table 4.8.

From Table 4.8, the impact strength of GDPNR modified acrylic sheet containing 0.25 wt% of silica (73 kJ/m^2) was higher than that of the pure acrylic sheet containing silica at the same content (68.3 kJ/m^2). The impact strength of the acrylic sheet decreased from 68.3 kJ/m^2 to 45.4 kJ/m^2 when silica content in acrylic sheets was in the range 0.25-1.25 wt%. For addition of GDPNR, the impact strength of modified acrylic sheet decreased from 73 kJ/m^2 to 52.2 kJ/m^2 when silica content in

Table 4.8 Effect of silica content on the mechanical properties and opacity of modified acrylic sheets

Silica content (wt%)	Grafted rubber (wt%)	Impact Strength (kJ/m^2)	TS (MPa)	EB (%)	Hardness (Shore D)	Opacity (%)
-	-	44.7 (2.81)	48.9 (1.9)	4.4 (0.15)	79.8 (0.78)	10.9 (0.01)
0.25	-	68.3 (4.82)	48.6 (3.17)	2.8 (0.35)	81.3 (0.82)	12.9 (0.71)
0.75	-	56.8 (2.82)	49.7 (1.92)	2.4 (0.28)	83.4 (0.84)	24.4 (1.01)
1.25	-	45.4 (6.28)	44.1 (2.65)	2.2 (0.09)	83.4 (0.84)	28.7 (0.57)
-	2	90.5 (3.0)	58.9 (1.90)	6.1 (0.44)	76.5 (0.70)	41.4 (0.01)
0.25	2	73.0 (4.95)	41.2 (3.42)	3.9 (0.65)	80.2 (0.63)	45.2 (0.85)
0.75	2	72.2 (4.60)	40.7 (3.66)	3.2 (0.07)	81.1 (0.78)	65.3 (1.40)
1.25	2	52.2 (2.51)	35.2 (5.19)	3.2 (0.49)	81.6 (0.51)	69.2 (0.91)

modified acrylic sheets was in the range 0.5-0.25 wt% due to the aggregation of the silica particles leads to poor properties of the modified acrylic sheet.. Similar behavior was also observed in the viscoelastic properties and thermal degradation kinetics of silica/PMMA nanocomposites [38].

The TS and EB of GDPNR modified acrylic sheet and the pure acrylic sheet containing silica decreased with increasing silica content. The TS of the pure acrylic sheets and GDPNR-modified acrylic sheet without silica were 48.9 MPa and 58.9 MPa, respectively and the EB of those acrylic sheets were 4.4% and 6.1%, respectively. When silica content was 1.25 wt%, the TS and EB of pure acrylic sheet s decreased to 44.1 MPa and 2.2 %, respectively, while those of GDPNR-modified acrylic sheets decreased to 35.2 MPa and 3.2 %.. The poor mechanical properties of silica/polymer composites are due to the poor interfacial bonding between organic polymer and inorganic silica and the aggregation of silica in the polymer matrix. Similar behavior was also observed in the effect of core-shell PMMA-SiO₂ nanoparticles on mechanical properties of PVC composites [39].

The silica caused the increase in the hardness of the modified acrylic sheet. The hardness of acrylic sheet increased from 81.3 shore D to 83.4 shore D when silica content in the pure acrylic sheets was in the range 0.25-1.25 wt%. For GDPNR-modified acrylic sheets, the hardness of specimens increased form 80.2 shore D to 81.6 shore D at the same level of silica content. This could explained that silica particle solid inorganic phase, effectively increased hardness of polymer. However, silica caused the reduction of transparency of both the GDPNR-modified acrylic sheet and acrylic sheet. The opacity of the GDPNR-modified acrylic sheet containing silica was higher than that of acrylic sheet containing only silica due to the aggregation of silica in PMMA matrix.

4.6.2 Thermal and UV Stability of Modified Acrylic Sheet Containing Silica

The modified acrylic sheet containing silica was improved stability by addition of small amount of silica. The retention of the mechanical properties such as impact strength, tensile properties and hardness and physical properties such as transparent properties, thermal resistance and UV resistance were investigated. The

mechanical of modified acrylic sheet containing silica after thermal and UV ageing as shown in Table 4.9 and 4.10, respectively

From Table 4.9, it showed that the retention of TS, EB, impact strength and hardness after ageing of the GDPNR-modified acrylic sheet containing silica was lower than that of the pure acrylic sheet containing silica due to the degradation of rubber part in the GDPNR. The retention of TS, EB, impact strength and hardness of the GDPNR modified acrylic sheet increased with increasing silica content possibly due to the accumula silica particles can accumulated thermal during ageing which caused easy degradable of rubber molecule in the modified acrylic sheet with GDPNR. The thermal resistance of the GDPNR modified acrylic sheet containing silica was lower than that of acrylic sheet containing silica. The thermal resistance of the modified acrylic sheet containing silica and the pure acrylic sheet containing silica increased with increasing silica content. It indicates that the silica can effectively improve the thermal stability of the pure acrylic sheets and GDPNR modified acrylic sheets.

The UV stability of the pure acrylic sheet and GDPNR modified acrylic sheet containing silica showed in Table 4.10, the retention of impact strength, TS, EB and hardness of the GDPNR modified acrylic sheet containing silica after UV ageing had the result same that of the pure acrylic sheet containing silica due to the opacity of GDPNR modified acrylic sheet increased with increasing silica content, that can block out UV radiation was radiated to modified acrylic sheets. The UV resistance of the GDPNR modified acrylic sheet silica was lower than that of the pure acrylic sheet containing silica. The UV resistance of the modified acrylic sheet containing silica and acrylic sheet containing silica slightly increased with increasing silica content due to the opacity of acrylic sheet and the GDPNR modified acrylic sheet increased can effectively block out UV radiation was radiated to modified acrylic sheet.

Table 4.9 The retention of mechanical properties of modified acrylic sheet containing silica after thermal aging.

Silica content (wt%)	Rubber content (wt%)	% Retention			
		Impact strength	TS	EB	Hardness
-	-	161.0	96.3	146.6	99.2
0.25	-	133.5	101.4	131.2	100.9
0.75	-	158.4	125.3	142.1	100.6
1.25	-	186.4	137.3	144.2	101.2
-	2	105.5	107.4	97.1	99.7
0.25	2	118.0	110.6	105.3	100.0
0.75	2	144.0	112.8	107.2	99.8
1.25	2	145.3	115.5	107.8	98.2

Table 4.10 The retention of mechanical properties of modified acrylic sheet containing silica after UV ageing.

Silica content (wt%)	Rubber content (wt%)	% Retention			
		Impact strength	TS	EB	Hardness
-	-	105.8	77.4	67.6	100.8
0.25	-	131.4	93.8	88.1	101.3
0.75	-	150.8	118.7	90.7	101.8
1.25	-	171.7	131.4	91.8	101.1
-	2	51.3	78.3	99.1	103.5
0.25	2	116.5	92.2	90.0	101.1
0.75	2	140.2	103.8	93.6	102.2
1.25	2	168.4	105.2	93.8	103.5

CHAPTER V

CONCLUSION AND RECOMMENDATION

In this research, an attempt was made to prepare graft copolymers of PMMA onto DPNR by emulsion polymerization using potassium persulfate as an initiator. The effect of DPNR latex on the conversion, grafting efficiency, percentage of free rubber, percentage of homopolymer and percentage of graft copolymer was recorded as a function of time. The graft DPNR (GDPNR) and silica were also used as an impact modifier and stabilizer for acrylic sheets, respectively. The mechanical and physical properties including the morphology of the modified acrylic sheet before and after thermal and ultraviolet ageing were also investigated.

5.1 GDPNR Preparation

The graft copolymerization of PMMA onto DPNR was carried out by emulsion polymerization initiated by potassium sulfate. The appropriate condition of graft copolymerization was the use of 1 phr of initiator and 90:10 wt ratio ratio of rubber to MMA monomer at 70°C for 3 h to achieve the GDPNR product consisting of 65.9% monomer conversion, 49.2% GE, 65.8% graft rubber, 28.0% free rubber and 6.1% free homopolymer.

For GNR preparation the graft copolymerization of PMMA onto NR gave the lower %GE and %graft copolymer than GDPNR at the same condition due to the inhibition effect of proteins in NR.

5.2 Utilization of GDPNR as Impact Modifier for Acrylic Sheet

The addition of GDPNR in acrylic sheets at appropriate content could improve the mechanical properties of modified acrylic sheets such as tensile strength, % elongation, and hardness. However, the opacity of the modified acrylic sheets slightly lower than that of opacity of modified acrylic sheets containing GNR at the same content. The impact strength of modified acrylic sheets increased from 44.7 to 152.8 kJ/m² with the addition of 10.0 wt% of GDPNR. The tensile strength and % elongation at break of modified acrylic sheet containing GDPNR increased with

increasing the rubber content and reached to a maximum tensile strength (63.3 MPa) at 4 wt% and elongation at break (7.2%) at 8 wt%.

From SEM micrographs, the addition of GDPNR in acrylic sheets decreased the fracture on the surfaces when graft rubber content increased. Thus, the GDPNR could act as the interfacial agent and the impact modifier to improve the impact strength of the modified acrylic sheet.

It was also found that the thermal and UV resistance of the modified acrylic sheet with GDPNR was higher than that of the modified acrylic sheet with DPNR.

5.3 Utilization of Silica as Stabilizer for Modified Acrylic Sheet

The thermal resistance of the modified acrylic sheet containing silica increased with increasing silica content. It indicates that the silica could effectively improve the thermal stability of acrylic sheet. The UV resistance of the modified acrylic sheets containing silica and ones containing silica and GDPNR slightly increased with increasing silica content due to the opacity of acrylic sheet.

5.4 Suggestion for the future work

A future investigation for the use of graft copolymer and silica as the impact modifier and stability for acrylic sheets should be concerned with the following aspects:

1. By applying a different rubber type for graft copolymerization, the white and pale crepe rubber should be further studied to use as impact modifier for acrylic sheet due to they are lightness when compared to NR.
2. To improve the miscibility between silica and polymer, the treatment and grafting polymer onto silica surface should be further studied.

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APPINDICES

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Appendix A

The Overall Composition of Rubber Latex

Table A-1 Typical properties of high ammonia deproteinized natural rubber latex.

Properties	Value
Total Solids Content, %	61.12
Dry Rubber Content, %	60.17
Non Rubber Content, %	0.96
Ammonia Content (on Total Weight), %	0.62
Ammonia Content (on Total Phase), %	1.60
pH Value	10.68
KOH Number	0.62
Volatile Fatty Acid Number (V.F.A)	0.020
Mechanical Stability Time @ 55% TS (secs)	1,030
Specific Gravity (on Solids), ppm	0.943
Magnesium Content (on Solids), ppm	22
Average water soluble protein content, ($\mu\text{g/g}$)	40

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Table A-2 Typical properties of high ammonia concentrated natural rubber latex

Properties	Value
Total Solids Content, %	62.0
Dry Rubber Content, %	60.65
Non Rubber Content, %	1.35
Ammonia Content (on Total Weight), %	0.70
Ammonia Content (on Total Phase), %	1.83
pH Value	10.4
KOH Number	0.566
Volatile Fatty Acid Number (V.F.A)	0.0165
Mechanical Stability Time @ 55% TS (sec)	720
Specific Gravity (on Solids), ppm	0.942
Magnesium Content (on Solids), ppm	33
Average water soluble protein content, ($\mu\text{g/g}$)	98

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APPENDIX B
Data of Graft Copolymerization

Table B-1 Determination of graft deproteinized natural rubber

Reaction properties	Reaction time for 2		Reaction time for 3		Reaction time for 4		Reaction time for 5		Reaction time for 6	
	1	2	1	2	1	2	1	2	1	2
DPNR Latex	150.53	150.44	150.07	150.5	151.31	150.09	150.23	150.55	150.7	150.22
DRC (% wt)	60.17	60.17	60.17	60.17	60.17	60.17	60.17	60.17	60.17	60.17
DPNR content(g	90.57	90.52	90.29	90.55	91.04	90.31	90.39	90.58	90.67	90.38
Graft Product (g)	94.22	95.11	98.19	98.11	98.95	97.02	97.32	98.36	98.66	98.26
Total Conversion	45.01	44.45	65.94	65.89	65.99	65.69	67.26	68.05	67.8	68.12
Sample for soxhlet	3.17	3.09	2.13	3.11	2	2.44	2.43	2.11	2.18	2.33
Sample after extraction by	1.40	1.33	1.53	2.23	1.43	1.75	1.74	1.49	1.56	1.66
Sample after extraction by	1.24	1.14	1.4	2.04	1.29	1.61	1.56	1.36	1.4	1.49
Free natural rubber (g)	1.77	1.75	0.59	0.87	0.56	0.68	0.68	0.61	0.61	0.66
Free homopolymer (g)	0.16	0.19	0.13	0.19	0.13	0.14	0.17	0.13	0.16	0.16
%Free natural rubber	55.77	56.77	27.92	28.12	28.47	27.87	28.32	29.16	28.17	28.43
%Free homopolymer	5.02	6.31	6.16	6.12	6.7	6.0	7.23	6.34	7.37	7.21
%Graft natural rubber	39.21	36.92	65.91	65.75	64.82	66.12	64.45	64.9	64.46	64.36
Total monomer (g)	8.12	10.32	11.97	11.47	11.99	10.23	10.36	11.29	11.79	11.57
Total free monomer (g)	4.73	6.00	6.05	6.00	6.63	5.82	7.03	6.23	7.20	7.08
Total Grafted monomer	3.38	4.31	5.92	5.46	5.35	4.40	3.32	5.05	4.51	4.48
Grafting Efficiency (% wt)	41.74	41.82	49.46	47.64	44.70	43.09	32.05	44.81	38.32	38.76

Table B-2 Determination of graft concentrated natural rubber

Reaction properties	Reaction time for 3 hrs	
	1	2
Concentrated natural rubber latex (g)	150.33	150.89
Dry rubber content (% wt)	60.65	60.65
Natural rubber content (g)	90.45	90.79
Graft product (g)	97.13	97.09
Total conversion (%)	60.12	61.06
Sample for soxhlet extraction (g)	3.0	2.09
Sample after extraction by LPE (g)	1.31	0.86
Sample after extraction by acetone (g)	1.05	0.70
Free natural rubber (g)	1.68	1.22
Free homopolymer (g)	0.26	0.16
%Free natural rubber (% wt)	56.05	58.77
%Free homopolymer (% wt)	8.87	7.67
%Grafted natural rubber (% wt)	35.08	33.56
Total monomer (g)	11.12	10.32
Total free monomer (g)	8.61	7.44
Total Grafted monomer (g)	2.50	2.87
Grafting efficiency (%)	22.51	27.83

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Appendix C

Data of Mechanical Properties of Modified Acrylic Sheet

Table C-1 Data of tensile properties of modified acrylic sheet

Rubber type	Rubber Content (wt%)	No. of Experiment of Tensile strength			Mean	S.D	No. of Experiment of elongation at break			Mean	S.D.
		1	2	3			1	2	3		
		-	-	50.37			46.75	49.57	48.90		
NR	0.25	61.29	60.28	59.34	60.30	0.97	4.49	4.97	4.28	4.58	0.35
	0.25	49.17	50.02	51.02	50.07	0.92	3.24	5.96	4.25	4.48	1.37
DPNR	0.5	52.34	43.69	58.27	51.43	7.33	4.83	4.19	4.60	4.78	0.16
	1.0	55.93	49.85	51.62	52.47	3.12	5.33	4.19	4.85	4.79	0.57
	1.5	63.36	65.61	62.39	63.79	1.65	5.47	5.59	4.92	5.32	0.35
	2.0	54.79	57.58	56.90	56.42	1.45	5.09	5.32	6.24	5.55	0.61
GNR	0.25	54.48	53.13	50.46	52.69	2.04	4.62	4.70	4.25	4.52	0.23
	0.5	64.33	63.26	61.92	63.17	1.20	4.82	4.58	4.88	4.76	0.15
	1.0	62.94	58.10	64.86	61.96	3.48	6.10	6.73	6.58	6.47	0.32
	1.5	56.28	57.41	55.86	56.52	0.79	5.12	5.77	5.06	5.32	0.39
GDPNR	0.5	49.20	45.18	52.81	45.73	3.23	4.53	4.75	4.62	4.63	0.11
	1.0	50.88	55.06	46.27	50.74	4.39	4.24	5.34	4.50	4.69	0.57
	1.5	54.74	57.96	53.06	55.25	2.49	6.13	6.08	5.82	6.01	0.16
	2.0	52.75	58.55	56.57	55.96	2.94	5.71	6.05	6.59	6.11	0.44
	4.0	65.67	62.97	61.44	63.36	2.14	6.83	5.96	6.84	6.55	0.50
	6.0	34.20	33.82	31.77	33.27	1.30	7.33	6.75	7.37	7.15	0.34
	8.0	29.54	28.05	30.78	29.46	1.36	7.34	7.11	7.12	7.19	0.12
	10.0	26.59	26.10	22.72	25.14	2.10	7.48	6.70	7.10	7.09	0.39

Table C-2 Data of impact strength of modified acrylic sheet

Rubber type	Rubber Content (wt%)	No. of Experiment					Mean	S.D.
		1	2	3	4	5		
-	-	44.58	45.69	45.64	40.06	47.49	44.71	2.81
NR	0.25	50.77	49.39	50.76	50.10	50.22	50.24	0.56
	0.25	48.58	46.03	45.66	50.48	45.08	47.16	2.28
DPNR	0.5	56.63	57.02	54.05	56.63	54.18	55.70	1.45
	1.0	73.66	68.58	65.76	70.04	74.05	70.41	3.49
	1.5	86.00	85.76	83.94	87.37	87.82	86.17	1.52
	2.0	81.77	84.58	80.54	80.22	82.23	81.86	1.73
GNR	0.25	48.61	49.43	48.02	48.18	48.86	48.62	0.56
	0.5	70.88	69.34	67.59	71.98	70.55	70.06	1.67
	1.0	84.46	84.07	84.99	85.88	86.19	85.11	0.90
	1.5	97.00	95.12	94.78	94.76	93.23	94.97	1.34
GDPNR	0.5	56.99	55.32	56.98	57.88	57.45	56.92	0.97
	1.0	79.77	81.69	76.45	76.83	77.00	78.34	2.28
	1.5	89.42	87.15	85.87	88.65	86.99	87.61	1.41
	2.0	95.34	89.25	91.56	87.70	88.99	90.56	3.00
	4.0	98.56	105.89	95.12	107.5	100.67	101.54	5.13
	6.0	130.72	122.88	120.67	125.1	123.15	124.50	3.81
	8.0	124.9	135.11	118.32	121.76	127.23	125.46	6.34
	10.0	146.84	163.73	149.15	153.84	150.83	125.87	6.58

Table C-3 Data of hardness of modified acrylic sheet

Rubber type	Rubber Content (wt%)	No. of Experiment										Mean	S.D.
		1	2	3	4	5	6	7	8	9	10		
-	-	80	81	79	80	80	81	79	80	79	79	78.8	0.78
NR	0.25	79	80	78	78	79	79	78	78	78	79	78.6	0.69
DPNR	0.25	80	78	80	78	79	78	79	79	80	79	79.0	0.81
	0.5	80	78	79	79	80	78	78	80	79	78	78.9	0.87
	1.0	78	80	80	78	79	78	79	80	79	79	79.0	0.81
	1.5	76	77	77	77	77	78	77	77	79	77	77.2	0.78
	2.0	78	77	78	78	77	77	76	77	75	76	76.9	0.99
GNR	0.25	78	79	79	80	79	78	79	78	80	78	78.8	0.78
	0.5	78	78	78	78	79	80	78	79	78	78	78.4	0.69
	1.0	77	77	78	77	76	77	76	75	76	77	76.6	0.84
	1.5	77	76	77	77	77	76	76	74	6	75	76.1	0.99
GDPNR	0.5	80	79	78	79	80	79	78	79	80	80	79.2	0.78
	1.0	79	78	79	79	79	79	79	80	78	79	80.9	0.56
	1.5	77	77	78	76	77	78	77	77	78	79	77.4	0.84
	2.0	76	77	77	75	76	76	77	77	77	77	76.5	0.70
	4.0	76	77	76	77	7	77	77	75	73	74	75.7	1.41
	6.0	72	73	71	72	74	75	75	73	72	71	72.8	1.47
	8.0	74	72	72	72	73	70	71	71	72	72	71.9	1.10
	10.0	70	70	71	71	69	70	69	70	70	71	70.1	0.73

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Table C-4 Data of opacity of modified acrylic sheet

Rubber type	Rubber Content (wt%)	No. of Experiment			Mean	S.D.
		1	2	3		
-	-	10.9	10.9	10.8	10.9	0.01
NR	0.25	11.2	11.3	11.1	11.2	0.01
	0.25	13.5	13.6	13.3	13.4	0.02
DPNR	0.5	16.9	17.0	17.0	17.0	0.01
	1.0	22.4	22.7	22.6	22.6	0.01
	1.5	26.6	26.6	26.5	26.6	0.01
	2.0	57.8	57.8	57.9	57.9	0.03
GNR	0.25	13.3	13.4	13.4	13.3	0.03
	0.5	15.9	16.2	16.0	16.0	0.11
	1.0	21.1	21.1	21.0	21.1	0.01
	1.5	33.7	33.9	33.7	33.8	0.03
GDPNR	0.5	14.8	14.8	14.7	14.8	0.01
	1.0	19.1	19.2	19.2	19.2	0.01
	1.5	30.2	30.3	30.3	30.3	0.02
	2.0	41.4	41.3	41.4	41.4	0.01
	4.0	60.8	60.6	60.8	60.8	0.05
	6.0	63.3	63.2	63.3	63.4	0.02
	8.0	83.6	83.5	83.7	83.6	0.07
	10.0	84.6	84.7	84.7	84.7	0.01

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Table C-5 Data of mechanical properties of modified acrylic sheet after thermal ageing

Rubber type	Rubber content (wt%)	Tensile strength			Mean	S.D	elongation at break			Mean	S.D	Impact strength					Mean	S.D
		1	2	3			1	2	3			1	2	3	4	5		
-	-	53.3	60.5	56.2	56.7	3.6	6.4	7.9	6.5	6.9	0.80	74.0	71.8	77.0	69.6	67.4	71.9	3.7
DPNR	0.25	59.8	57.2	56.9	58.0	1.5	6.8	6.0	5.7	6.2	0.54	48.0	52.0	53.6	50.4	55.0	51.8	2.7
	0.5	56.2	56.7	57.0	56.6	0.3	6.0	5.5	5.4	5.6	0.34	62.1	61.0	62.6	60.4	58.5	60.9	1.5
	1.0	58.0	60.5	58.7	59.1	1.3	7.0	7.5	6.2	6.9	0.64	75.4	72.6	77.6	76.4	73.4	75.1	2.0
	1.5	58.0	58.2	59.0	58.4	0.5	6.6	7.5	7.1	7.1	0.43	88.1	88.0	95.7	95.8	87.5	91.0	4.2
	2.0	43.8	44.9	53.9	47.6	5.5	6.9	6.8	7.3	7.0	0.26	77.8	81.8	82.5	79.1	76.9	79.6	2.4
GDPNR	0.5	57.6	58.4	55.8	57.3	1.2	5.4	5.6	4.9	5.3	0.38	70.9	76.6	79.9	72.1	74.4	74.8	3.5
	1.0	57.7	56.9	57.3	57.3	0.3	7.1	7.1	6.4	6.9	0.39	85.7	83.9	88.3	82.3	86.6	85.4	2.3
	1.5	58.8	55.0	58.3	57.3	2.0	6.4	6.1	6.2	6.2	0.16	93.8	97.8	98.5	94.0	104.5	97.7	4.3
	2.0	59.0	60.0	61.3	60.1	1.1	5.4	6.2	6.1	5.9	0.45	98.3	98.3	95.4	94.4	91.4	95.6	2.9
	4.0	57.6	56.0	55.7	56.4	1.0	8.5	9.0	8.4	8.6	0.31	92.1	90.8	94.4	92.1	92.4	92.4	1.2
	6.0	36.7	34.5	34.3	35.2	1.3	5.2	5.5	7.5	6.0	1.24	117.8	112.1	105.2	113.8	130.5	115.9	9.3
	8.0	29.1	30.1	28.6	29.3	0.7	6.3	7.4	7.2	7.0	0.56	106.4	107.7	107.0	119.3	105.0	109.1	5.8
	10.0	22.5	22.7	24.0	23.1	0.7	7.0	6.9	6.1	6.7	0.50	102.4	106.6	106.0	105.9	98.9	103.9	3.2

Table C-5 Continues

Rubber type	Rubber content (wt%)	Hardness										Mean	S.D	ΔE			Mean	S.D
		1	2	3	4	5	6	7	8	9	10			1	2	3		
-	-	81	80	80	78	79	79	79	80	78	80	79.2	0.7	1.2	1.2	1.2	1.2	0.01
DPNR	0.25	77	80	80	80	79	80	79	80	80	78	79.6	0.6	2.5	2.6	2.5	2.5	0.01
	0.5	80	78	79	79	80	80	80	80	79	80	79.2	0.7	4.21	4.2	4.2	4.2	0.01
	1.0	80	79	80	80	80	80	80	80	80	80	79.7	0.6	9.5	9.5	9.5	9.5	0.01
	1.5	80	79	80	80	79	78	80	80	79	79	79.3	0.6	8.0	8.0	8.0	8.0	0.005
	2.0	80	80	79	79	78	79	78	78	78	80	78.6	0.9	14.4	14.	14.	14.3	0.15
GDPNR	0.5	79	79	79	78	78	77	77	77	79	78	78	0.8	1.2	1.3	1.3	1.2	0.01
	1.0	80	79	79	78	79	78	80	79	79	79	78.9	0.5	9.2	9.2	9.2	9.2	0.01
	1.5	80	76	77	77	78	78	78	78	79	77	77.5	0.8	11.1	11.2	11.1	11.1	0.01
	2.0	80	79	78	75	74	75	77	78	76	73	76.3	2.0	13.2	13.2	13.2	13.2	0.01
	4.0	80	76	77	76	74	78	76	77	77	75	76.1	1.1	15.1	15.1	15.1	15.1	0.01
	6.0	75	76	75	74	74	78	76	78	75	77	75.8	1.4	16.6	16.6	16.6	16.6	0.005
	8.0	74	72	76	77	77	74	74	75	73		74.9	1.7	18.8	18.9	18.8	18.8	0.012
10.0	71	66	68	58	67	63	65	68	67	65	65.2	2.9	22.1	22.1	22.1	22.1	0.005	

Table C-6 Data of mechanical properties of modified acrylic sheet after UV ageing

Rubber type	Rubber content (wt%)	Tensile strength			Mean	S.D.	elongation at break			Mean	S.D.	Impact strength					Mean	S.D.
		1	2	3			1	2	3			1	2	3	4	5		
-	-	46.4	46.2	44.2	45.6	1.2	4.9	4.	4.	4.72	0.27	48.8	47.9	49.7	45.3	44.7	47.3	2.1
DPNR	0.25	55.0	56.5	54.1	55.2	1.2	4.6	5.	5.	5.26	0.52	45.1	50.7	47.7	46.7	50.2	48.3	2.8
	0.5	52.7	53.0	54.1	53.2	0.7	5.1	5.	5.	5.45	0.27	47.9	48.4	50.8	45.6	47.3	48.0	1.8
	1.0	55.1	53.8	52.4	53.7	1.3	5.4	5.	5.	5.45	0.06	44.1	45.4	44.5	42.0	40.1	43.2	2.1
	1.5	54.2	54.1	55.6	54.7	0.8	5.1	6.	6.	5.91	0.61	41.4	43.8	42.9	39.1	45.2	42.5	2.3
	2.0	56.8	58.5	57.1	57.5	0.8	7.4	6.	7.	7.12	0.27	39.1	40.4	39.5	42.0	40.1	40.2	1.11
GDPNR	0.5	53.3	52.5	49.4	51.7	2.0	5.0	4.	4.	4.80	0.22	47.7	48.5	459.8	47.0	48.8	48.4	1.0
	1.0	53.6	52.5	51.7	52.6	0.9	5.3	4.	5.	5.15	0.17	45.8	46.1	46.1	44.0	45.3	45.5	0.8
	1.5	53.4	54.5	56.3	54.7	1.4	6.3	6.	5.	5.21	0.24	38.5	39.6	37.9	40.1	38.5	38.9	0.9
	2.0	45.7	39.7	45.9	43.8	3.5	6.2	5.	5.	5.88	0.42	47.0	46.2	47.1	46.0	45.8	46.4	0.5
	4.0	56.2	55.1	58.6	56.6	1.7	6.1	5.	6.	6.35	0.54	72.0	72.5	74.5	73.5	73.1	73.1	0.9
	6.0	36.5	38.0	37.9	37.5	0.8	8.2	7.	7.	7.92	0.29	118.	117.	119.6	118.2	117.5	118.4	0.8
	8.0	32.6	35.7	34.0	34.1	1.5	8.1	6.	7.	7.58	0.83	120.	122.	119.2	121.1	119.9	120.5	1.1
	10.0	26.8	22.1	21.0	23.3	3.0	4.3	4.	4.	4.27	0.09	125.	126.	123.7	124.3	127.5	125.4	1.4

Table C-6 Continues

Rubber type	Rubber content (wt%)	Hardness										Mea n	S.D	ΔE			Mea n	S.D
		1	2	3	4	5	6	7	8	9	10			1	2	3		
-	-	81	81	81	80	80	81	80	81	80	80	80.5	0.52	3.2	3.3	3.2	3.2	0.01
DPNR	0.25	77	80	80	79	80	79	80	80	80	80	79.5	0.97	3.5	3.5	3.5	3.5	0.01
	0.5	80	78	80	79	79	79	80	80	81	80	79.6	0.84	3.2	3.2	3.1	3.2	0.01
	1.0	80	80	80	80	80	80	80	79	80	80	79.9	0.31	4.3	4.4	4.4	4.4	0.01
	1.5	80	79	79	80	79	79	79	78	79	87	79.2	0.63	4.4	4.4	4.4	4.4	0.01
	2.0	80	80	81	81	81	80	81	80	81	80	80.5	0.52	5.3	5.2	5.3	5.2	0.005
GDPNR	0.5	79	78	78	78	79	79	80	80	80	80	78.9	0.87	4.7	4.6	4.6	4.6	0.01
	1.0	80	79	80	80	78	80	79	80	80	81	79.7	0.82	6.5	6.4	6.5	6.5	0.01
	1.5	80	79	79	80	79	79	79	78	79	80	79.2	0.63	6.5	6.5	6.5	6.5	0.02
	2.0	80	78	79	78	78	82	79	79	80	80	79.2	1.22	7.8	6.9	7.8	7.5	0.50
	4.0	80	81	82	82	80	80	80	80	79	80	80.3	1.05	6.8	6.8	6.8	6.8	0.01
	6.0	75	76	75	74	75	74	74	75	75	74	74.7	0.67	6.9	6.9	6.9	6.9	0.02
	8.0	74	76	74	76	74	77	74	75	77	75	75.2	1.22	2.8	2.8	2.8	2.8	0.02
10.0	71	73	73	73	74	74	74	75	73	73	73.3	1.05	5.5	5.5	4.9	5.3	0.37	

Appendix D

Data of Mechanical Properties of Modified Acrylic Sheet Containing Silica

Table D-1 Data of tensile strength of acrylic sheet containing silica before and after heat and UV ageing

	Silica content (wt%)	No. of Experiment			Mean	S.D.
		1	2	3		
Before ageing	-	50.37	46.75	49.57	48.90	1.90
	0.25	50.45	44.52	47.2	48.6	3.66
	0.75	47.32	50.72	52.60	49.7	3.42
	1.25	40.64	48.60	42.19	44.1	4.22
After heat ageing	-	43.40	50.60	46.20	47.09	3.64
	0.25	52.69	47.40	45.94	49.28	3.54
	0.75	58.82	65.54	60.57	62.27	3.48
	1.25	64.12	58.73	60.18	60.54	7.99
After UV ageing	-	36.42	36.22	44.24	37.84	1.20
	0.25	48.00	43.47	43.23	45.58	4.88
	0.75	53.96	57.67	63.01	58.99	5.49
	1.25	52.51	57.83	59.01	57.9	2.43

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Table D-2 Data of tensile strength of 2 % wt GDPNR-modified acrylic sheet containing silica before and after heat and UV ageing

	Silica content (wt%)	No. of Experiment			Mean	S.D.
		1	2	3		
Before ageing	-	52.75	58.55	56.57	58.96	2.94
	0.25	40.36	40.03	45.68	41.2	3.17
	0.75	41.92	38.21	39.20	40.7	1.92
	1.25	38.58	30.42	35.02	35.2	7.31
After heat ageing	-	59.00	65.10	61.30	63.10	1.15
	0.25	41.34	50.13	51.60	45.69	5.54
	0.75	54.13	33.95	44.21	45.9	11.57
	1.25	40.11	40.40	42.79	41.00	1.44
After UV ageing	-	45.79	39.75	45.99	46.16	3.54
	0.25	38.81	34.82	40.40	37.98	2.87
	0.75	42.83	42.12	42.41	42.24	3.21
	1.25	38.42	29.59	40.62	37.03	9.46

Table D-3 Data of elongation at break of acrylic sheet containing silica before and after heat and UV ageing

	Silica content (wt%)	No. of Experiment			Mean	S.D.
		1	2	3		
Before ageing	-	4.38	4.63	4.45	4.45	0.15
	0.25 % silica	2.97	3.14	2.46	2.85	0.35
	0.75 % silica	2.22	2.43	2.79	2.48	0.28
	1.25 % silica	2.76	3.92	3.03	2.23	0.60
After heat ageing	-	6.44	7.91	6.59	6.98	0.80
	0.25 % silica	4.65	3.33	3.70	3.73	0.68
	0.75 % silica	3.45	3.47	3.63	3.52	0.10
	1.25 % silica	3.57	2.56	4.12	3.42	0.79
After UV ageing	-	4.91	4.40	4.85	4.72	0.27
	0.25 % silica	3.65	2.96	3.67	3.43	0.40
	0.75 % silica	3.40	2.94	3.24	3.19	0.23
	1.25 % silica	2.84	2.72	3.04	2.87	0.16

Table D-4 Data of elongation at break of 2 wt% of GDPNR-modified acrylic sheet containing silica before and after heat and UV ageing

	Silica content (wt%)	No. of Experiment			Mean	S.D.
		1	2	3		
Before ageing	-	5.71	6.05	6.59	6.1	0.44
	0.25 % silica	3.91	3.36	4.66	3.9	0.65
	0.75 % silica	3.75	3.61	3.65	3.2	0.07
	1.25 % silica	3.73	3.53	3.83	3.2	0.15
After heat ageing	-	5.42	6.29	6.10	5.94	0.45
	0.25 % silica	3.52	3.93	4.29	3.91	0.38
	0.75 % silica	3.77	3.74	3.31	3.61	0.25
	1.25 % silica	3.25	3.29	3.52	3.36	0.14
After UV ageing	-	6.25	5.42	5.98	5.88	0.42
	0.25 % silica	3.73	2.93	3.91	3.52	0.51
	0.75 % silica	3.30	3.42	3.42	3.38	0.07
	1.25 % silica	3.49	3.07	3.44	3.33	0.22

Table D-5 Data of impact strength of acrylic sheet containing silica before and after heat and UV ageing

	Silica content (wt%)	No. of Experiment					Mean	S.D.
		1	2	3	4	5		
Before ageing	-	44.58	45.69	45.64	40.06	47.57	44.71	2.81
	0.25 % silica	70.10	60.87	70.71	65.88	64.32	68.37	5.54
	0.75 % silica	55.78	57.97	61.33	54.92	54.44	56.88	2.82
	1.25 % silica	43.10	47.71	44.18	39.80	46.71	45.40	5.13
After heat ageing	-	74.01	71.88	77.02	69.60	67.44	71.99	3.73
	0.25 % silica	105.57	95.13	92.64	96.29	93.03	91.53	5.27
	0.75 % silica	90.32	89.08	88.31	92.25	90.58	90.10	1.51
	1.25 % silica	78.60	82.10	82.19	80.25	76.10	79.84	2.56
After UV ageing	-	48.84	47.97	49.79	45.33	44.77	47.34	2.19
	0.25 % silica	108.16	107.28	109.54	109.79	106.85	108.32	1.31
	0.75 % silica	98.66	98.44	99.37	96.45	95.55	97.69	1.61
	1.25 % silica	99.81	95.19	97.62	94.95	98.82	97.27	2.16

Table D-6 Data of impact strength of 2 wt% GDPNR-modified acrylic sheet containing silica before and after heat and UV ageing

	Silica content (wt%)	No. of Experiment					.Mean	S.D.
		1	2	3	4	5		
Before ageing	-	95.34	89.25	91.56	87.70	88.99	90.56	3.00
	0.25 % silica	96.48	93.87	98.59	100.59	96.44	73.0	2.53
	0.75 % silica	71.55	66.66	69.52	75.26	78.31	72.2	4.60
	1.25 % silica	52.19	52.20	56.72	54.31	49.31	52.2	3.93
After heat ageing	-	98.37	98.37	95.45	94.43	91.43	95.61	2.92
	0.25 % silica	90.95	89.56	89.41	90.54	92.88	86.14	1.39
	0.75 % silica	98.61	94.64	106.77	107.61	109.03	103.96	3.09
	1.25 % silica	67.47	65.62	63.07	57.32	60.60	75.9	4.02
After UV ageing	-	47.07	46.29	47.16	46.05	45.85	46.48	0.59
	0.25 % silica	80.72	78.30	85.80	88.15	83.13	85.04	3.91
	0.75 % silica	95.50	107.72	99.14	105.17	92.49	101.22	3.50
	1.25 % silica	85.24	85.97	87.82	81.84	81.11	87.39	5.09

Table D-7 Data of hardness properties of acrylic sheet containing silica before and after heat and UV ageing

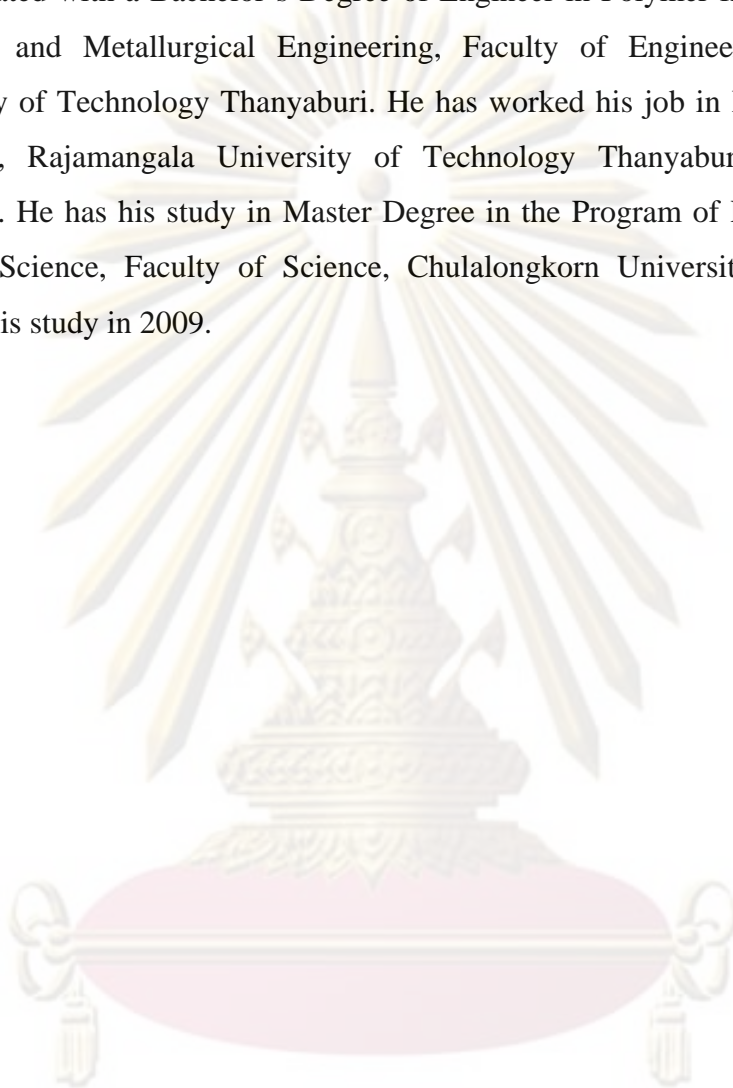
	Silica content (wt%)	No. of Experiment										Mean.	S.D.
		1	2	3	4	5	6	7	8	9	10		
Before ageing	-	80	81	79	80	80	81	79	80	79	79	79.8	0.78
	0.25 % silica	82	81	81	82	80	82	81	82	82	80	81.3	0.82
	0.75 % silica	82	84	83	83	84	84	82	84	84	84	83.4	0.84
	1.25 % silica	85	82	84	85	82	83	84	83	84	85	83.7	1.15
After heat ageing	-	79	80	80	78	79	79	79	80	78	80	79.2	0.78
	0.25 % silica	80	82	82	83	83	82	83	82	83	83	82.3	0.94
	0.75 % silica	84	84	85	84	84	83	84	83	84	84	83.9	0.56
	1.25 % silica	84	85	83	85	84	84	85	84	85	85	84.4	0.69
After UV ageing	-	81	81	81	80	80	81	80	81	80	80	80.5	0.52
	0.25 % silica	83	83	82	83	82	83	82	82	82	82	82.4	0.51
	0.75 % silica	84	84	84	85	85	85	84	84	84	84	84.3	0.48
	1.25 % silica	85	83	83	85	83	83	84	85	85	85	83.9	0.99

Table D-8 Data of Harness properties of 2 % wt GDPNR-modified acrylic sheet containing silica before and after heat and UV ageing

	Silica content (wt%)	No. of Experiment										Mean.	S.D.	
		1	2	3	4	5	6	7	8	9	10			
Before ageing	-	76	77	77	75	76	76	77	77	77	77	76.5	0.70	
	0.25 % silica	81	81	80	79	80	80	81	80	8	80	80.2	0.63	
	0.75 % silica	80	81	81	81	80	82	82	82	82	81	82	81.2	0.78
	1.25 % silica	82	82	81	82	81	81	82	81	82	82	81.6	0.51	
After heat ageing	-	78	79	78	75	74	75	77	78	76	73	76.3	2.00	
	0.25 % silica	83	84	83	83	83	84	83	83	82	82	83	0.66	
	0.75 % silica	80	82	82	80	80	83	82	80	82	80	81.1	1.19	
	1.25 % silica	80	80	82	80	81	79	77	75	76	80	79	2.26	
After UV ageing	-	80	78	79	78	78	82	79	79	79	80	79.2	1.22	
	0.25 % silica	82	81	82	80	80	82	83	80	80	81	81.1	1.10	
	0.75 % silica	85	85	85	85	85	83	83	83	83	85	84.1	0.99	
	1.25 % silica	82	83	82	83	82	83	83	82	82	82	82.4	0.51	

VITA

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