สารเคลือบผิวเชิงประกอบอินทรีย์/อนินทรีย์ระบบพอลิออล-ไอโซไซยาเนต/โซล-เจล

นาย ราชโรจน์ เจริญศักดิ์

ORGANIC/INORGANIC COATING COMPOSITES BASED ON

POLYOL-ISOCYANATE/SOL-GEL SYSTEM

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A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science in Applied Polymer Science and Textile Technology

Department of Materials Science

Faculty of Science

Chulalongkorn University

Academic Year 2000

Thesis Title   ORGANIC/INORGANIC COATING COMPOSITES BASED ON

         POLYOL-ISOCYANATE/SOL-GEL

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นายราชโรจน์ เจริญศักดิ์ : สารเคลือบผิวเชิงประกอบอินทรีย์/อนินทรีย์ระบบพอลิออล-ไอโซไซยาเนต/โซล-เจล. (ORGANIC/INORGANIC COATING COMPOSITES BASED ON POLYOL-ISOCYANATE/SOL-GEL) อ. ที่ปรึกษา : ผศ.ดร. กาวี ศรีกูลกิจ, 56 หน้า. ISBN 974-346-572-3.

ได้เตรียมสารเชิงประกอบอินทรีย์/อนินทรีย์ระบบพอลิออลที่ได้ปรับเปลี่ยนด้วยหมู่ฟังก์ชันไซเลนและโซล-เจล พอลิออลถูกปรับเปลี่ยนหมู่ฟังก์ชันที่ 30%, 50% และ 70% ด้วยปฏิกิริยาของ poly(2-hydroxyethyl methacrylate) กับ 3-isocyanatopropyl(trietyoxysilane) สูตรการเตรียมสารเคลือบผิวเตรียมได้โดยผสม PHEMA ที่ถูกปรับเปลี่ยนฟังก์ชันกับ 4,4'-diphenylmethane diisocyanate โดยมี กรด ρ-toluenesulfonic เป็นตัวเร่งปฏิกิริยา

สารเคลือบผิวจะถูกเคลือบบนแผ่นพอลิคาร์บอเนตและแผ่นอะคริลิกที่ความหนาของฟิล์ม 30 ไมครอนและอบที่ 120 องศาเซลเซียสเป็นเวลา 3 ชั่วโมง ฟิล์มที่ได้จะมีความเรียบและใสแสดงให้เห็นว่าไม่มีการแยกตัวของสารในระบบการเคลือบ FT-IR และ solid state ^{29}Si-NMR ใช้ทำการวิเคราะห์ฟิล์มที่ได้พบว่าหมู่ไฮดรอกซิลของ PHEMA กับ MDI สามารถเกิดปฏิกิริยาการเชื่อมโยงของสารอินทรีย์ได้ในขณะเดียวกันปฏิกิริยาโซล-เจลของหมู่ไซลอกซิลนำไปสู่การเชื่อมโยงส่วนอนินทรีย์ ประสิทธิภาพของฟิล์มบนพื้นผิวดีขึ้นและจากผลการทดสอบแสดงให้เห็นว่าปริมาณสารประกอบอนินทรีย์เป็นส่วนสำคัญในการพัฒนาสมบัติความคงทนต่อการขีดขูดและการขัดถูของสารเคลือบผิวเชิงประกอบอินทรีย์/อนินทรีย์

ภาควิชา วัสดุศาสตร์	ลายมือชื่อนิสิต ....
สาขาวิชา วิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ	ลายมือชื่ออาจารย์ที่ปรึกษา ....
ปีการศึกษา 2543	

4172411323   : MAJOR   APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY

KEY WORD: Poly(2-hydroxyethyl methacrylate) / Coating / Composite / Sol-gel

RATCHAROJ CHAREONSAK : ORGANIC/INORGANIC COATING COMPOSITES BASED ON POLYOL-ISOCYANATE/SOL-GEL.   (สารเคลือบผิวเชิงประกอบอินทรีย์/อนินทรีย์ระบบพอลิออล-ไอโซไซยาเนต/โซล-เจล) THESIS ADVISOR: ASSISTANT PROFESSOR KAWEE SRIKULKIT Ph.D., 56 pp. ISBN 974-346-572-3.

Organic/inorganic composites based on silane group functionalized polyol/sol-gel system were undertaken. The functionalized polyols of 30%, 50% and 70% degree functionalization was successfully prepared by reacting poly(2-hydroxyethyl methacrylate) (PHEMA) with 3-isocyanatopropyl(triethoxysilane). Coating formulation was prepared by thoroughly mixing functionalized PHEMA(s) with 4,4'-diphynylmethane diisocyanate(MDI) in the present of ρ-toluenesulfonic acid as a catalyst.

The coating solutions were applied onto polycarbonate sheet and acrylic sheet to achieve film thickness of 30 micron, then followed by curing at temperature of $120^{\circ}C$ for 3 hours. Smooth and transparent film obtained indicated no phase separation between organic and inorganic compounds. FT-IR and solid state ^{29}Si-NMR analysis of coating showed that the reaction of HEMA hydroxyl group with MDI produced organic network while sol-gel reaction among siloxyl pendant groups led to the formation of inorganic siloxane network. Surface performance of coated PC was markedly improved. The finding results also revealed that inorganic component content played an important role in improving the abrasion resistance of coated substrate.

Department of **Materials Science**   Student's signature…………………………………..

Field of study Applied polymer science and textile technology   Advisor's signature…………………………………..

Academic year 2000

ACKNOWLEDGEMENTS

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CHAPTER I
INTRODUCTION

Polymeric materials are based on the molecules of high molecular weights. The properties of polymer vary greatly, for example, thermoplastic or thermosetting because of the nature of their chemical and physical structures. By understanding the characteristics of polymeric materials a variety of inventions could be made in order to improve living standard of mankind. For example, optical polymers have been realized to play a role as substitutes for inorganic glasses because of their advantageous properties in terms of lightweight, durability processing simplicity and low cost. Typical applications include safety shields, lens, glazing, electrical relay covers, headlights and transparent part of furniture. Acrylic and polycarbonate are the well known for making film or sheet of excellent optical properties[1, 2, 3]. However, plastics always have poor abrasion and scratching resistance which limits their applications.

The application of surface hardening coating onto plastics is aimed at improving surface hardness and scratch/abrasion resistance. Surface coating for transparent plastics should be clear and has refractive index near these plastics. Among these coating materials, organic compounds such as melamine, polyurethane, and acrylic-based polymer are often used. The hardening effect is a result of chemical reactions which convert molecules of coating layer into a highly crosslinked network structure. Inorganic materials can also be used for surface coating on plastic substrates. The sol-gel reaction of inorganic coating material is wholly responsible for the improvement in scratch/abrasion resistance of coated substrates.

Recently, there is an increasing interest in searching for organic/inorganic hybrid materials. Various approaches have been adopted to prepare organic/inorganic composite materials.

In this work, new organic/inorganic materials were proposed for transparent coating. Poly(2-hydroxyethyl methacrylate) will be partially functionalized with an inorganic group(silane group). Transparent film would be prepared by mixing functionalized PHEMA with 4,4'-diphenylmethane diisocyanate as a crosslinking agent. Two types of different networks are expected to be produced; organic network formed by reaction of polymer hydroxyl group with isocyanate group of crosslinking agent and inorganic network formed by sol-gel reaction of silane pendant group. Scratch/abrasion resistance as well as optical properties are evaluated. It is expected that this coating system will give superior performance with low volume shrinkage.

CHAPTER II
LITERATURE SURVEY

2.1 Coating Materials

Surface coating is a technology which could improve the standard of living for human beings. A wide variety of raw materials may be combined to produce three basic classes of coating [4, 5]: 1. Paint is a mixture of hiding pigment, binder or vehicle, solvents and additives, 2. Varnish is single-element coating. Their mission was protection of surfaces without hiding natural beauty, 3. Lacquer is a solution consisting of resins in an organic solvent. The hardening of film on the surface depends on the evaporation of the solvent. However, an understanding of the chemistry and molecular structure of the polymers on which coatings are based is extremely important in determining the properties and predicting the behavior of surface coating.

Acrylic polymer constitutes one of the most important types of coating materials. The general chemistry and properties of the acrylic considered to be most widely used and specifically applicable as coating [2]. Acrylic resin can be produced in many forms such as solid, solution and emulsion, after drying, film was thermoplastic generally, and crosslinking reaction of thermoset can occur when polymer contains suitable functional groups. Advantageous properties of acrylic film were ultraviolet resistance, chemical resistance, gloss, good surface adhesive etc. Surface of metal, wood, leather, ceramic and plastic can be applied by acrylic film.

Poly(2-hydroxyethyl methacrylate) (PHEMA) was a raw material from renewable sources has claimed the attention of a great number of scientific

research groups during the last three decades. The hydroxyl functional polymer system offer numerous advantages and versatility in various industrial applications. Linear and crossliked homo- and copolymers based on PHEMA are one of the most studied hydroxyl systems such as biomaterials, surface coatings, pharmaceutical industry etc [6, 7].

2.2 Research Cited

There is an increasing interest in novel organic/inorganic materials. The main objective is to conceive new materials which improve physical or mechanical properties of coated substrates. The combination of different materials such as organic and inorganic compounds in the order of nanoscale synthesis usually produce nanocomposite materials. The hybrid materials with different ratios of organic/inorganic content display interesting structure- properties behavior [8, 9]. For example, a higher inorganic content shows higher refractive index and higher modulus while at higher organic content, material shows higher flexibility. An inorganic component is usually based on metal alkoxide and exhibits transparency. In general, silicon, aluminium, titanium or metal alkoxides have been used as the starting inorganic materials and processed by sol-gel method to obtain the inorganic network reaction [10, 11]. The silicon alkoxy compounds were mostly investigated. For example, (3-isocyanatopropyl)triethoxysilane is one type of silicon alkoxy compound containing isocyanate functional group . Hence, it is possible to introduce an inorganic component into the organic polymer chain in order to prepare the precursor of hybrid materials [12, 13, 14].

Tamami et al [15] have synthesized a newly optical abrasion resistance coating materials. Organic/inorganic hybrid materials have been developed from melamine and triphenylphosphine oxide (TAPO). Triethoxysilane was used to cap melamine and TAPO. The reaction schemes of those hybrid materials are given in Figure 2.1 and Figure 2.2.
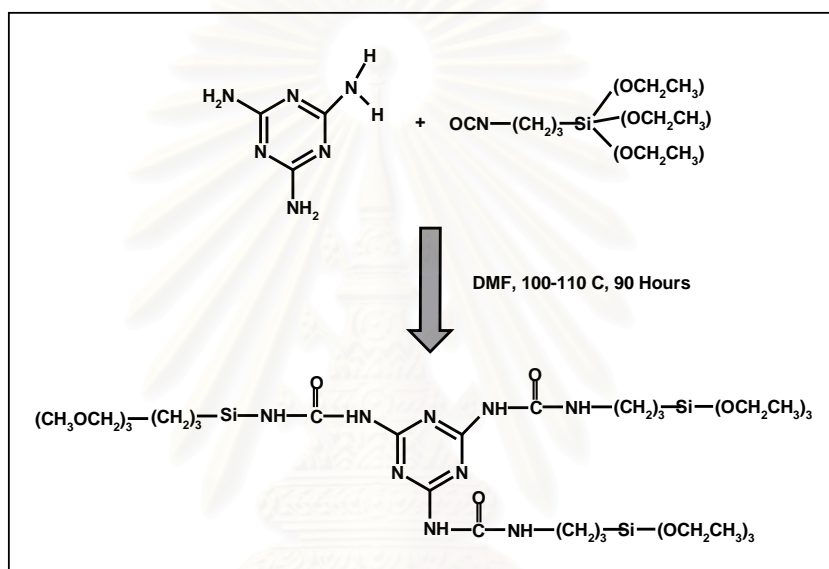
Figure 2.1 the reaction scheme of melamine and IPSE
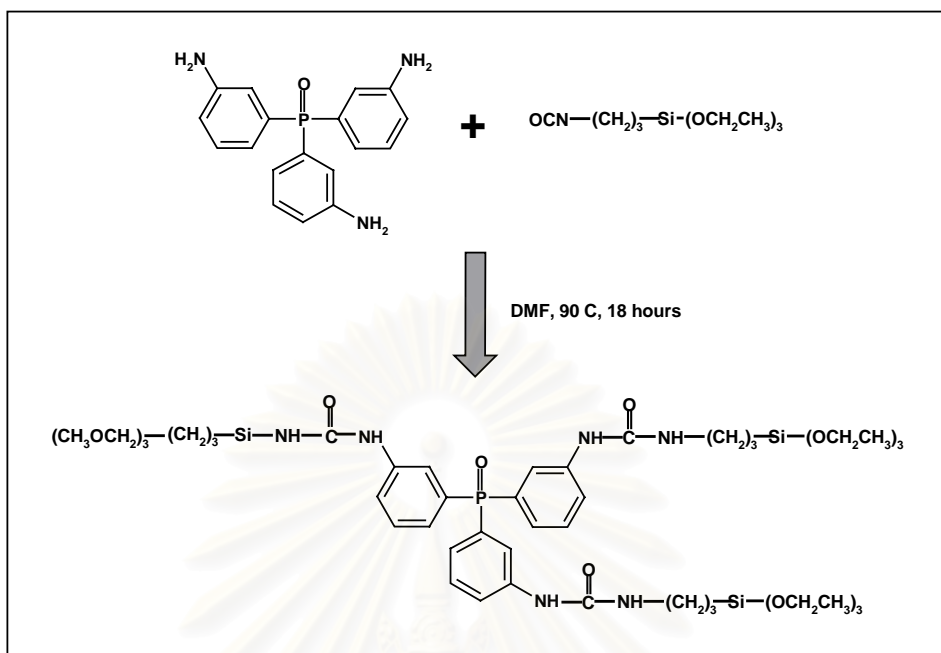
Figure 2.2 the reaction of TAPO and IPSE

These compounds were applied onto PC substrate and followed by curing. Films exhibited good transparency and good adhesion to the substrate. The crosslinked hybrid coating was formed through an inorganic or sol-gel reaction. The result showed that the abrasion resistance of coated sample was better than uncoated sample.

J.I. Chen et al [16] developed coating materials based on functionalized acrylic polymer and hexamethoxymethylmelamine. Poly(2-hydroxyethyl methacrylate) was selected as the acrylic polymer based. Partial functionalization of hydroxy group with 3-isocyanatopropyl(triethoxysilane) were successfully prepared. The prepared compound was mixed with HMMM and then applied onto PC substrate followed by curing at high temperature. Coating films showed highly

crosslinked network. It was found that both organic and inorganic crosslinking reactions occurred and were responsible for the excellent optical quality film. The coating material were tested both their scratch and abrasion resistance. The results showed that the higher percent of inorganic segment in PHEMA dominated the higher scratch and abrasion resistance than virgin polycarbonate.

2.3 Crosslinking Agent

The selection of crosslinking agents for the coating applications is important. Each type of crossslinking agents must be suitable for specific application and governs the performance properties of coating film. High solids coating currently used in the automotive industry as top coats are typically thermoset systems which derive most of their physical properties from the formation of highly crosslinked network. The two systems generally used are based on the methoxymetyl melamine/polyol system and isocyanate/polyol system [17, 18]. The properties of film mostly depend on structure of polyol.
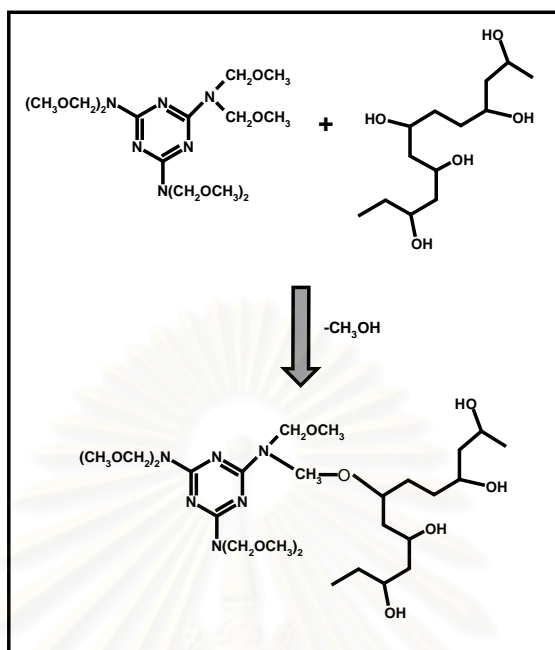
Figure 2.3 the reaction scheme of methoxymethyl melamine/polyol
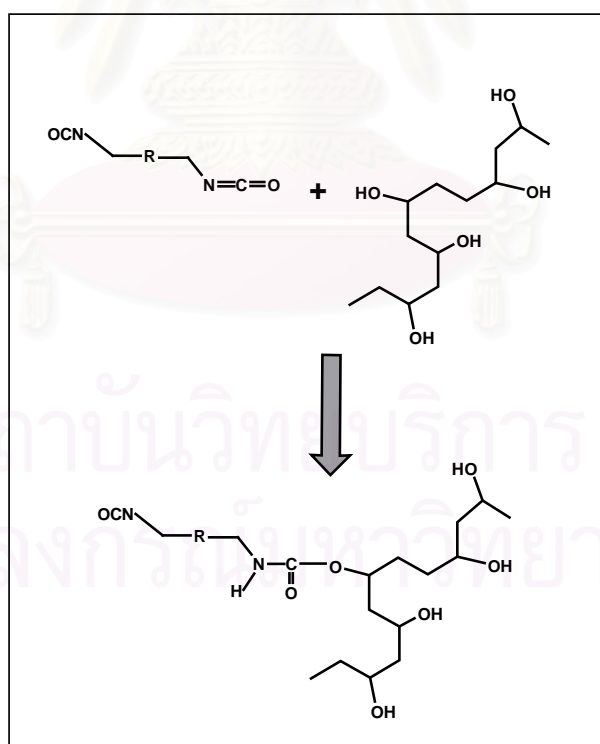
Figure 2.4 the reaction scheme of isocyanate and polyol

The research of E.S. Ntsihlele et al [19] , studies about the reaction of methoxymethyl melamine and isocyanate in the system of crosslinking agent. This work was divided into two parts as two-component system based on methoxymethyl melamine/polyol and three component system based on methoxymethyl melamine/ isocyanate/polyol. Both two- and three-component systems were capable of producing high solids, the overall result showed that highly crosslinked networks were achieved at high curing temperatures. The two-components showed that reaction between methoxymethyl melamine and isocyanate occured. The three components showed that all the crosslinking reactions namely melamine-acrylic and melamine-isocyanate can occur. But no reaction of acrylic-isocyanate. The isocyanate will react with any free methanol that has been released from methoxymethyl melamine/acrylic reaction. This work showed that isocyanate did not suitable use with methoxymetyl melamine as a crosslinking of acrylic.

Isocyanate/polyol systems forming crosslinked urethane coatings are also extensively used and have been extensively studied. Typically, acrylic polymer in term of homo- and copolymer were used . Because isocayanate reacted very fast, it is suitable for the application which needs short time of film forming. MDI (4,4'-diphenylmethane diisocyante) as a crosslinking reaction has been widely employed commercially. The application of this system is found in the fields of adhesives and films.

2.4 Sol-Gel Process

The sol-gel process has attracted an attention from researchers more than four decades [2, 10, 20, 21]. Basically the sol-gel process means the synthesis of an inorganic network by a chemical reaction in solution at low temperature. The formation of the inorganic backbone is based on a condensation step including the formation of metal/oxygen/metal bonds. The condensation step can take place at low temperatures, e.g. at the boiling temperature of organic solvents like ethanol. For the formation of densified glasses or sintered ceramics. High temperature are required (e.g. T_g of glasses) and at these temperatures, organic groupings are generally oxidized or pyrolyzed. However, the presence of non volatile organic groupings, especially if they are linked to the inorganic backbone, leads to an interesting type of materials (inorganic-organic composite ormocers, organically modified ceramic, polycerams or ceramers). An organic group can be used to improve the structure effects of the materials as follows:

1. They can be used for the modification of the inorganic backbone, reducing the network connectivity and leading to processing temperatures low enough to fabricate dense materials without distroying the organics.
2. They can additionally be used for building up a second type of network by polymerizing or polycondensing appropriate organic groupings.
3. They can be used for achieving special functions (acids, bases, electron donating or accepting functions).

Sol-Gel reactions can be characterized by several reaction steps. At first, soluble precursors in form of monomers, oligomers or clusters, react with active species mostly by addition of water and the subsequent formation of reactive $\equiv$MeOH (Me$\equiv$ metal ion) groups.

Hydrolysis

$\equiv$Me(OR) + H_2O $\Longrightarrow$ $\equiv$MeOH + ROH

Condensation

$\equiv$MeOH + (RO)Me$\equiv$ $\Longrightarrow$ $\equiv$Me-O-Me$\equiv$ + ROH

$\equiv$MeOH + HOMe$\equiv$ $\Longrightarrow$ $\equiv$Me-O-Me$\equiv$ + H_2O
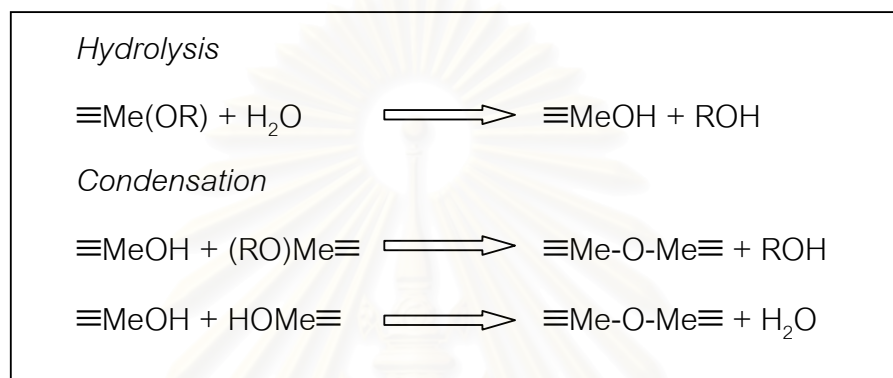
Figure 2.5 the reaction mechanism for sol-gel process and formation of

inorganic network

In the case of silicon based compounds, e.g. organoalkoxysilanes the link between the inorganic and organic phase can be obtained by the SiC bond which is a very stable one. This principle, however, can not be used for other elements since metal carbon bonds in general are not stable under hydrolytic conditions. As shown elsewhere, the use of double bond containing organoalkoxysilanes (methacryloxy or vinyl) leads to inorganic-organic composites on a molecular level, and coatings for various applications have been synthesized.

Among sol-gel processed materials, thin films are the true leader, and some examples are given as follows:

- Abrasion-resistant Coating
- Corrosion-resistant Coating

- Optical Thin Film

- Electronic and Magnetic Film

- Etc.

2.5 Test of film hardness

This method is used for test dry film. Hardness shows the efficiency of film that must touch something. We can study the hardness of film from line's appearance. Scratch and abrasion tests are the process that can display hardness of film.

Scratch test [17]: this way is commonly used for rating film hardness by observing the line. Scratch test can be classified into three methods as follows:

1. Pencil hardness test: this test utilizes pencil with leads of varying hardness. The hardest pencil, usually 6H, is pushed into the film. Successively softer pencils are pushed in. the first pencil whose point breaks determines the pencil hardness of the film. In effect, this system rates a hardness of coating material by which pencil's point is crumbled when it tries to penetrate the coating's surface. If the coating is hard enough to break the pint of a hardest (6H) pencil point, then it rates 6H, and is a hard surface indeed. If it can be penetrated by all the pencil harder than the softest (6B), which it causes to disintegrate, then it is a soft coating.

2. Sward rocker hardness test: this test is more scientific. The sward rocker has two 4-inch metal wheels attached to each other in parallel. A weight is placed on one side of the arrangement; and starting at a fixed standard position, the rocker teeters back and forth until it comes to equilibrium with the weighted portion on the bottom. The softer the coating the more the rocker will be damped and the less it

will oscillate. Conversely, the harder the coating the greater the oscillations of the rocker. The tester counts the number of oscillations of the rocker on the coating under test. Regular plate glass is used as a standard, it has a Sward Hardness of 50.

3. Mechanized scratch test apparatus: the sample substrate is placed on the stand that can be remove by motor. The substrate must be parallel with scratch way. The standard needle was fixed in the arm. The needle arm was loaded with weight. Weights totaling 2000 g and providing increments of 100 g are supplied. The needle arm will scratch film when the substrate moved. The hardness of film is the minimum weights that can penetrated the film.
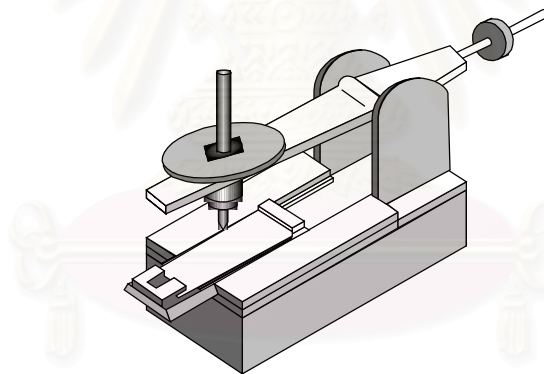
Figure 2.6 Mechanical Scratch Test

Abrasion Test: The ability of a coating to withstand the effects of scraping and scratching action is measured by its resistance to the wearing effect of sand, one of the hardest materials to which a coating is likely to be exposed.

1. Taber Abraser: Two carborundum wheels on the machine rubs from the center toward the outside, and the other from the outside toward the center of the

test specimen. Applied to the carborundum wheels are loads that can be varied from 250 to 500 to 1,000 grams. Results of the test can be stated in terms of weight loss per given number of cycles of the wheels at a stated load, or it may be the number of cycles required to wear through the film.

2. Wet Abrasion Scrub Tester: This machine composes which two brushes that move on the sample. The method relate properties that affect the wear resistance of surface. The abrasion of film show in term of number of brush cycles.
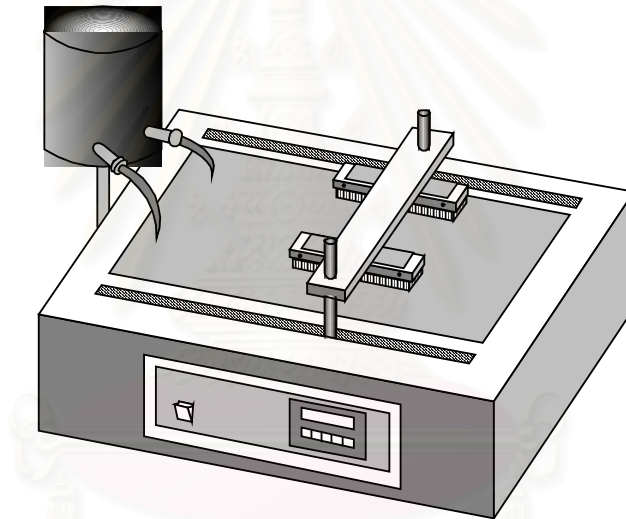
Figure 2.7 Wet Abrasion Scrub Tester

3. Other Abrasion Tests: Other tests available are *the Falling Sand Method, Air Blast Abrasion Method and the Armstrong Sandpaper Abrasion Machine.* These methods used standard sand to abase the coating's surface by compared zinc or acrylic sheet.

2.6 The concept of this research

The development of hybrid materials based on organic/inorganic composite is particularly interesting for coating technologist. This invented materials have distinct advantages which are derived from excellent properties of both organic and inorganic materials. Most importantly, to obtain the best performance such as optical and mechanical properties both organic and inorganic components must be evenly distributed in each other without phase separation.

In this work, new transparent coating materials based on functionalized poly(2-hydroxyethyl methacrylate) and 4,4'-diphenylmethane diisocyanate(MDI) was designed. The material produced was expected to exhibit both organic and inorganic properties in the same material. Two types of crosslinked networks, organic and inorganic network were responsible for excellent performance of the material. The organic network was formed by the reaction between polymer hydroxyl group and MDI. While the sol-gel reaction among siloxyl pendant group produced siloxane network. The coating film obtained was expected to exhibit good abrasion/scratch resistance thanks to high density of crosslinks produced.
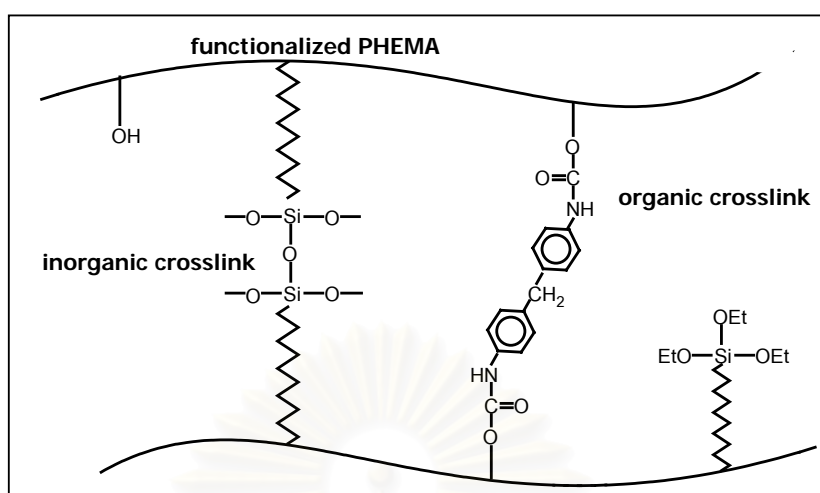
Figure 2.8 the reaction scheme of organic and inorganic crosslinking reaction in a coating material.

The scopes of this research are as follows:

1. Preparation of the coating material based on organic/inorganic composites.

2. Test the properties of film including scratch resistance, abrasion resistance, chemical resistance and thermal analysis.

CHAPTER III

EXPERIMENTAL

3.1 Materials and Equipment

3.1.1 2-Hydroxyethyl Methacrylate (HEMA)
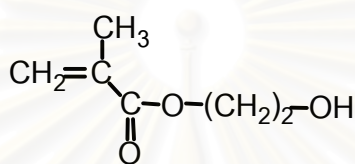
Typical properties

Attribute	Units	limits
Appearance	Clear and free from suspended matter	
Inorganic/content(color)	Pt/Co	10 max
Water Content	% mass	0.1 max
Inhibitor (MEHQ)	ppm mass	200-240
Molecular Weight (AV)		130

3.1.2 4,4'-Diphenylmethane diisocyanate (MDI)

The 4,4'-diphenylmethane diisocyante (MDI) used in this experiment is a modified MDI. It is also known as polycarbodiimide and sold under the commercial name of isonate 143L liquid at room temperature. This product has low viscosity

and good storage stability down to 24°C. The polycarbodiimide adduct offers extra flexibility because adduct formation is reversible(dissociation generates an additional isocyanate function). The carbodiimide linkage aids the stabilization of the polymer against hydrolytic degradation.
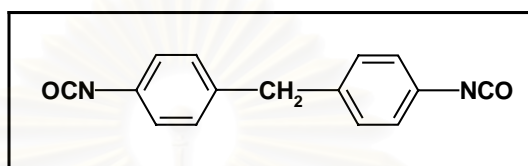
Typical Properties

Properties	Unit	Typical value
Isocyanate equivalent weight		144.5
NCO content by weight	%	29.2
Viscosity	cps at 25°C	33
Density	g/ml at 25°C	1.214
Extrapolate boiling point	$^{\circ}$C	314
Appx. Decomposition point	$^{\circ}$C	230
Specific heat	gm.cal/gm. $^{\circ}$C	0.43

3.1.3 3-Isocyanatopropyl(triethoxysilane) (IPSE)

3-Isocyanatopropyl(triethoxysilane) (IPSE, Fluka) is an alkoxide based compound which contains two types of functional groups; ethoxy silane and isocyanate group. The ethoxy silane groups can undergo sol-gel reaction to produce siloxane inorganic network, aiming at imparting inorganic properties into

inorganic/organic composites. Highly reactive isocyanate group was desired in order to incorporate IPSE into polymer chain of polyols. The chemical structure of IPSE is shown below:
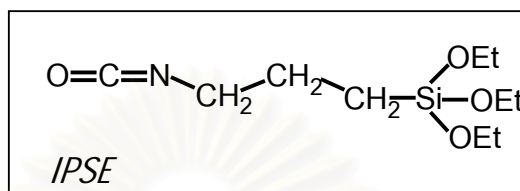
3.1.4 Dimethyl formamide(Caro Erba) and *Ethanol*(Commercial grade) was used as the solvent without further purifications.

3.1.5 Four Side Applicator(Sheen Instrument Co. Ltd.) was used for preparing film. The applicator have four sides which each can control the thickness of film at 30, 60,90 and 120 μm.
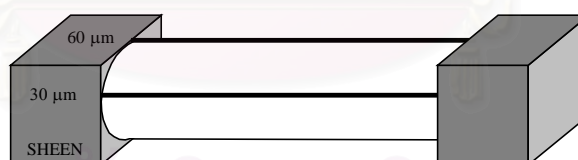
Figure 3.1 Four Side Applicator

3.2 Synthetic Procedures

3.2.1 Preparation of Poly(2-hydroxyethyl methacrylate)

Poly(2-hydroxyethyl methacrylate) was prepared by free radical polylmerization of 2-hydroxyethyl methacrylate in ethanol using AIBN as an initiator. Lauryl mercaptan was used as chain transfer agent. The mixture was added into three necked round flask purged with nitrogen gas. Then reaction was heated to 76°C under stirring. Polymerization was allowed at this temperature for 6 hours.

The PHEMA were isolated by a precipitation technique in benzene:hexane (1:1 by volume) mixture. Precipitated polymer was white in color and dried in an oven at 60°C for 24 h.

3.2.2 Functionalization of Poly(2-hydroxyethyl methacrylate) with IPSE

Functionalized PHEMA containing two functional groups, hydroxyethyl group and siloxyl group was prepared. The functionalization was carried out by the partial reaction of the HEMA hydroxy groups with isocyanate group of 3-isocyanatopropyl(triethoxysilane). The reaction involved may be schematically represented as shown in Figure 3.2. The PHEMA(s) with various degrees of IPSE contents were prepared by reacting the PHEMA with appropriate amounts of IPSE (calculated based on mole % of hydroxyl group).
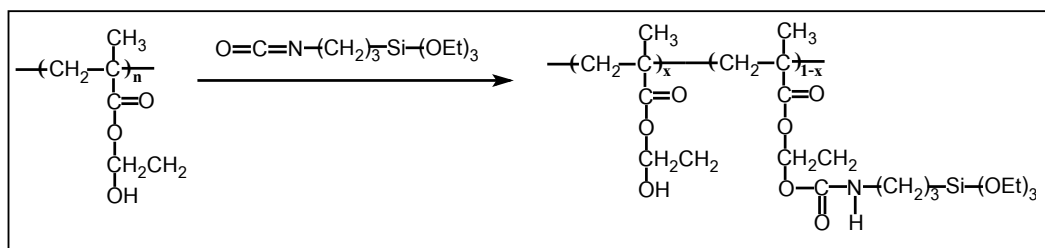
Figure 3.2 the reaction between PHEMA hydroxyl group with IPSE

In this experiment, the IPSE functionalized PHEMA with degrees of functionalization of 30%, 50% and 70% were prepared and designated as F-30, F-50 and F-70, respectively.

<u>Method</u>

The synthesis of F-30 was taken as an example of PHEMA (1.217 g, .0936 mole) was dissolved in dried dimethyl formamide to obtain the PHEMA solution of 20 wt%. A 25 ml round bottom flask containing the prepared solution was sealed with rubber stopper. The PHEMA solution was heated to 80°C until the stable temperature was observed. Then, 0.69 ml. of IPSE was injected through syringe into the flask. The reaction was allowed to continue for 3 hrs to ensure the complete reaction. Then the complete reaction was confirmed using FT-IR spectroscopy.

Table 3.1 The amounts of PHEMA, DMF and IPSE used to prepare
functionalized PHEMA at different degrees of functionalization.

Sample Code	PHEMA/g	DMF/g	IPSE/g
F-30	1.217	6.030	0.69
F-50	1.280	6.720	1.20
F-70	1.289	6.619	1.70

3.2.3 Preparation and application of organic/inorganic coating on plastic substrate

A typical coating formulation was prepared by mixing functionalized PHEMA with 4,4'-diphenylmethane diisocyanate(MDI) in DMF medium. MDI, a crosslinking agent, could undergo a crosslinking reaction with PHEMA hydroxyl groups to form organic crosslink network. While the pendant siloxyl groups could be hydrolyzed and followed by condensation to produce inorganic crosslink network; this type of reaction is called sol-gel reaction. A catalyst was necessary for sol-gel reaction to promote the extent of crosslinking reaction. In this experiment, ρ-toluenesulfonic acid(1 wt%) of total solid content was employed. Various samples of coating formulations were prepared and detailed coating formulations were given in Table 3.2.

Table 3.2 Coating composition of inorganic/organic coating.

Sample	Functionalized PHEMA, g	MDI, g**	DMF, g
F-0	0.978*	0.302	4.930
F-30	0.873	0.183	2.807
F-50	0.832	0.141	2.235
F-70	1.111	0.148	2.460

* unfunctionalized PHEMA

** Calculated based on the functionalized PHEMA hydroxyl groups available.

The coating mixture was stirred well in a small beaker. The resulting homogenous solution was immediately applied onto PC substrate and acrylic sheet using a four-sided applicator (Sheen Instruments). The coated sample was then cured at 120°C for 3 hours.

3.3 Analytical Procedures

3.3.1 Infrared spectroscopic Analysis

Infrared (IR) spectra were recorded using Nicolet Fourier Transform IR Spectrometer (Model 400D Impact). The recording parameters were used as follows: scan number of 32 and a resolution of 4 cm^{-1}.

Potassium Bromide (KBr) window was used as a sampling technique. The sample solution was dropped on KBr and covered it with another KBr disc. In the case of cured film, the sample was coated directly onto KBr window. It was required that the cured film should be as thin as possible to obtain high-resolution spectrum.

3.3.2 Differential Scanning Calorimetric Analysis (DSC)

The glass transition temperature of film was measured on a Perkin-Elmer Differential Scanning Calorimeter(DSC-7) using heating rate of 20°C/min and nitrogen flow rate of 20 mL/min.

3.3.3 Thermal Gravimetric Analysis

The decomposition behavior of coating composites was determined by Thermogravimetric analyzer (Perkin-Elmer, TGA-7) under a nitrogen flow, with

heating rate of 20 $^{\circ}$C/min. Operation temperature between 25°C to 850°C was studied.

3.3.4 ^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR)

The ^{1}H-Nuclear Magnetic Resonance spectra were obtained using a JNM-A500 spectrometer at 26.7°C, operating at 500 MHz. Test samples were prepared in deuterated acetone.

3.3.5 Solid State ^{29}Si-Nuclear Magnetic Resonance (Solid State ^{29}Si-NMR)

Solid State Nuclear Magnetic Resonance spectra were acquired using Advance 300 MHz Digital Nuclear Magnetic Resonance Spectrometer (Bruker, DPX-300) operating at a frequency of 70 MHz for ^{29}Si. A standard double air bearing CP/MAS probe was used.

3.3.6 Gel Permeation Chromatography (GPC)

Molecular weight of PHEMA was important for coating application. Suitable molecular weight leads to an ease of coating preparation and high quality of coating film. Gel Permeation Chromatography (CHROMATOPAC CR4A) was used to measure molecular weight of poly(2-hydroxyethyl methacrylate). Molecular weight was determined against polystyrene standard. Tetrahydrofuran (THF) was a common mobile phase for GPC analysis. However in this experiment, ethanol/THF mixture was used due to the fact that PHEMA is insoluble in THF medium.

3.3.7 Light Transmittance Measurement

Spectrophotometer (Macbeth[®], Color-eye 7000) was used to measure light transmission of abraded coated substrate. Measurement was carried out in wavelengths between 400 and 700 cm^{-1} in correlated haze mode.

3.4 Testing Procedures

3.4.1 Abrasion Test

Wet Abrasion Tester (Sheen Instrument Co. Ltd.) has been developed for test paints, wall finishes, polishes etc. Abrasion resistance test was carried out in dry condition. The abrasion resistance was performed by means of abrasion scrub tester (Sheen Instruments). The stoke length is easily adjustable to suit a sample length of 100 to 300 mm. A five digit resettable counter is fitted to record abrasion cycles of brushes and 1000 cycles were selected. The abraded specimen was subjected to light transmittance using spectrophotometer.

3.4.2 Scratch Test

This automatic machine has been called Scratch Test Apparatus (Sheen Instrument Co. Ltd.). Performance is related to many factors including the hardness of the coating and other physical properties such as adhesion, lubrication, resilience etc. The principle test method is to use the standard needle moved on the surface of coated samples. The needle was loaded by weights of 100, 200, 300 to 1000 g, respectively. The scratch lines could be observed by naked eyes.

3.4.3 Solubility Test

Ethanol, Dimethyformamide (DMF) and Tetrahydrofuran (THF) were selected to test for solvent resistance of coating film. Solvents were added into the small cup, then covered with coated sample before turning upside down. Surface of film was observed against times.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of Poly(2-hydroxyethyl methacrylate) (PHEMA)

The radical polymerization of 2-hydroxyethyl methacrylate in ethanol solution was observed by [1]H-Nuclear Magnetic Resonance (^{1}H-NMR). Gel Permeation Chromatrography (GPC) was employed to measure molecular weight of the polymer. The obtained PHEMA was white solid. The ^{1}H-NMR spectrum of the structure of PHEMA is shown in Figure 4.1
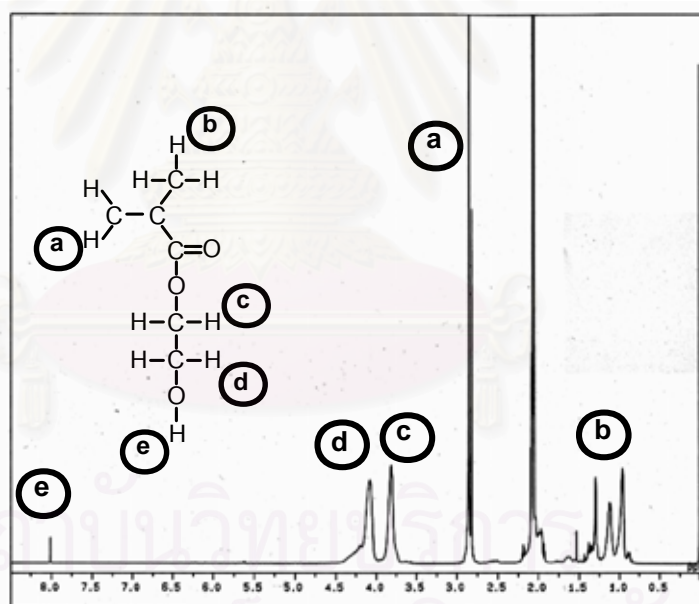
Figure 4.1 the ^{1}H-NMR spectra of PHEMA

The ^{1}H-NMR of HEMA monomer is shown in Figure 4.2. From Figure 4.2, the characteristic absorption of vinylene protons are observed at about 5.6 and 6.3 ppm. which correspond to cis- and trans- configurations, respectively.

Figure 4.2 ^{1}H-NMR of HEMA monomer

Thus, the spectrum shown in Figure 4.1 confirms that HEMA could be completely converted to poly(2-hydroxyethyl methacrylate) as well as highly purified product obtained, proven by total disappearance of vinylene protons signals.

4.2 Determination of the molecular weight by GPC

It should be pointed out that the inappropriate molecular weight of the polymer could give rise to the application problems and undesired properties. In the case of polymer of too low molecular weight, flaw film due to cracking may be commonly observed. On the other hand, the polymer of too high Mw could produce highly viscous coating solution, causing the difficulty in application. Hence, it is

important to prepare polymer having suitable Mw in order to control the desirable results.

The molecular weight of PHEMA was characterized by GPC. THF/ethanol mixture was employed as mobile phase due to poor solubility of PHEMA in pure THF. Little amount of ethanol was used as possible in order not to cause change in volume fraction of THF standard mobile phase. Hence, it is believed that THF/ethanol mixture behaved like pure THF mobile phase. The result is shown in Figure 4.3 . Preferably, polymers having low molecular weight are suitable for coating applications in terms of an easy control of the viscosity of coating formulation and obtaining better mixing when multicomponents are involved. The average molecular weight of prepared PHEMA determined by Gel Permeation Chromatography are follows: Mn = 2324, Mw = 3540 and Mw/Mn = 1.523 .
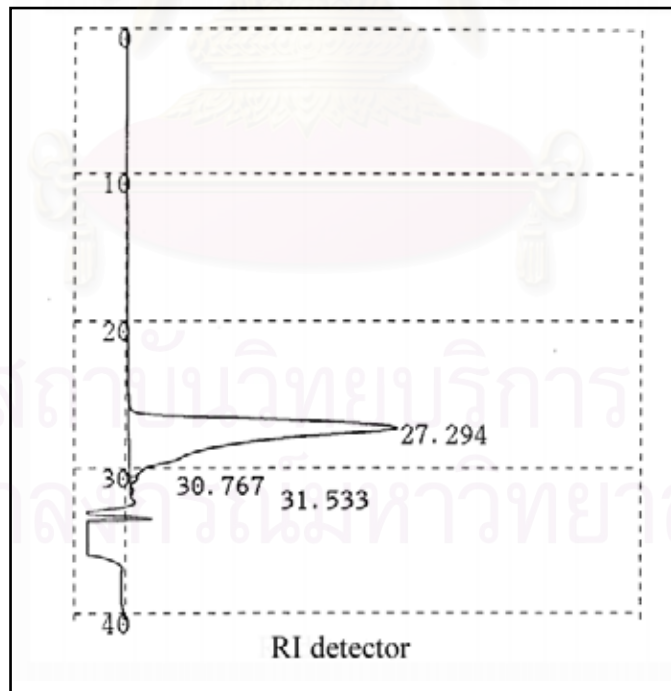

Figure 4.3 GPC chromatogram of PHEMA using RI Detector

4.3 Functionalization of PHEMA with IPSE

This was the important part of this research. The introduction of inorganic component into organic polymeric chain was carried out. Functionalized PHEMA(s) with various degrees of funcitonalization, namely 30%, 50% and 70% were prepared.

Three components were well mixed. Small amount of the mixture was taken and immediately subjected to FT-IR analysis. Presumably, at this stage no reaction took place, hence the resulting FT-IR spectra (Figure 4.4,4.5 and 4.6 start) represented the absorption peaks of virgin PHEMA and IPSE as well as DMF. The reaction mixture was heated to 76°C and continued at the constant temperature for 3 hrs. The FT-IR spectra of the reaction mixture taken at various times are shown in Figure 4.4, 4.5 and 4.6 stop. From Figure 4.4, 4.5 and 4.6 start, the strong absorption band of PHEMA hydroxyl group at 3,300 cm^{-1} and isocyanate group of IPSE at 2,270 cm^{-1} are dominant, indicating that both starting compounds still individually presented in the mixture. The reaction of two compounds proceeded quantitatively as the reaction times increased, evidenced by the gradual decrease in the intensity of isocyanate bands (from Figure 4.4,4.5 and 4.6 start to Figure 4.4, 4.5 and 4.6 stop). Complete reaction could be observed by the total disappearance of isocyanate group (Figure 4.4, 4.5 and 4.6 stop). The reaction between PHEMA hydroxyl group and isocyanate group of IPSE yielded the urethane linkage which appeared around 1,700 cm^{-1}. However, the identification of this peak is quite difficult due to the interference of DMF peak.
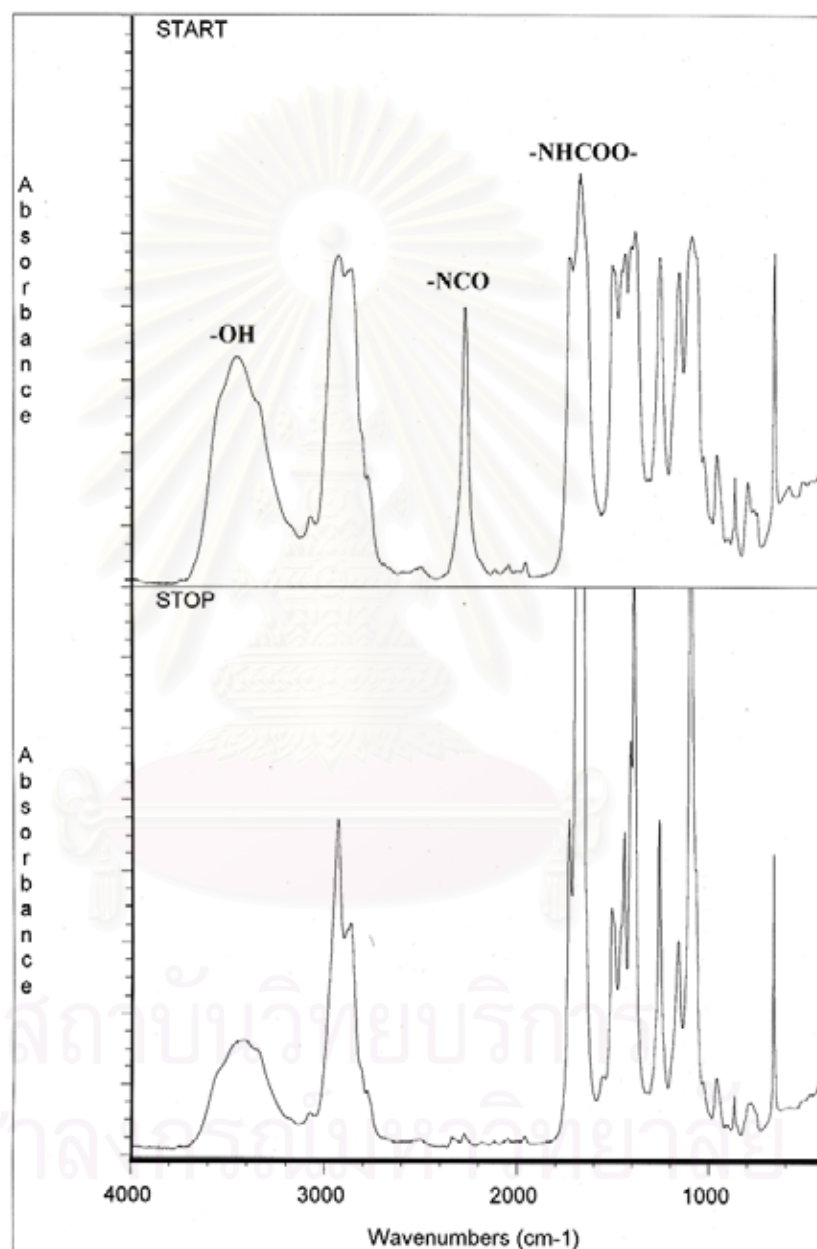
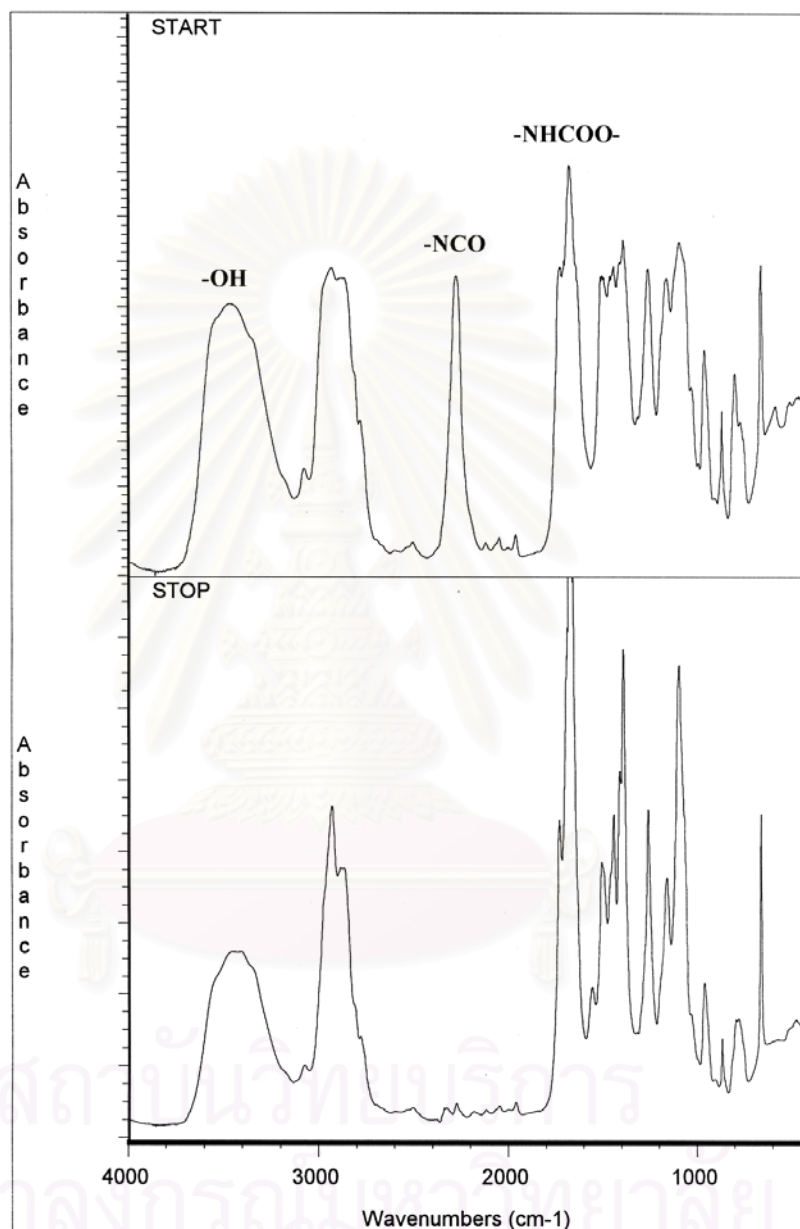Figure 4.4 IR spectra of functionalization PHEMA at 30% of IPSE(F-30).

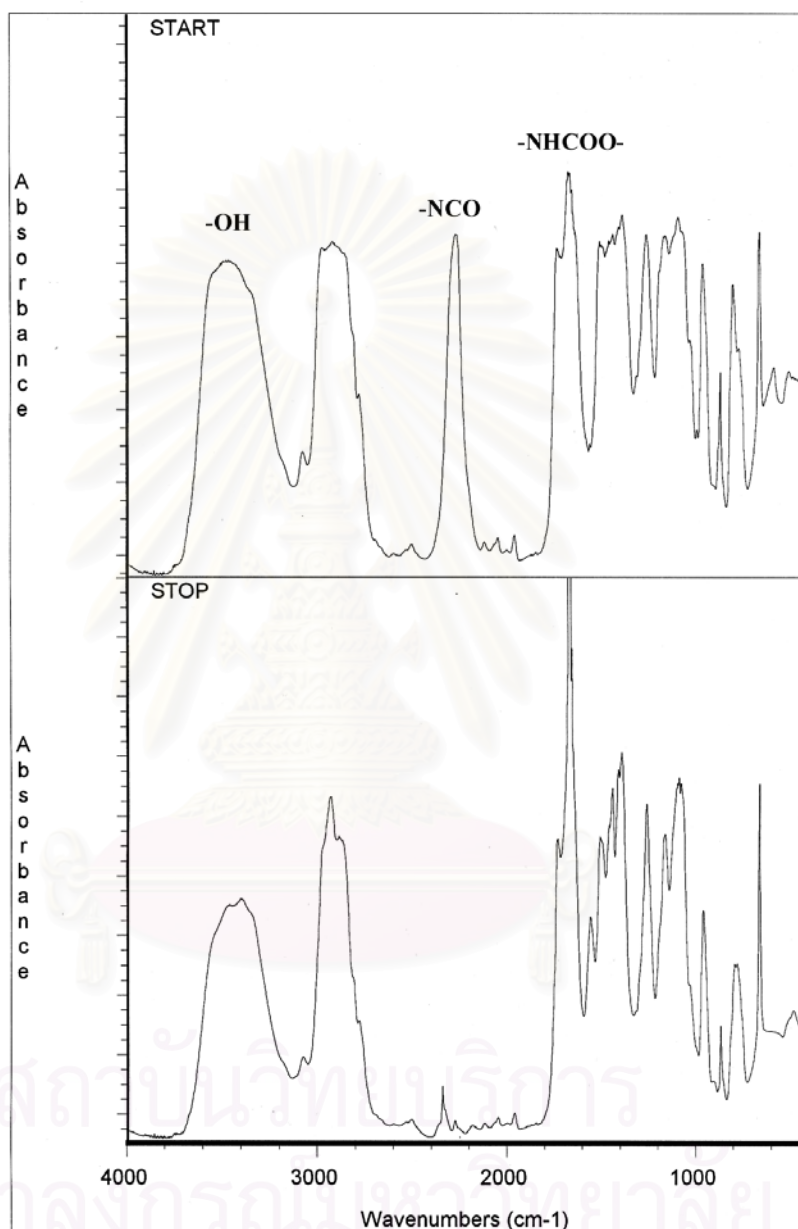Figure 4.5 IR spectra of functionalization PHEMA at 50% of IPSE(F-50).

Figure 4.6 IR spectra of functionalization PHEMA at 70% of IPSE(F-70).

4.4 Application of coating formulation

Coating formulation was prepared by mixing the functionalized PHEMA solution with MDI (a crosslinking agent). An amount of ρ-toluenesulfonic acid was added as a catalyst for sol-gel reaction. The prepared solution was applied onto PC and acrylic sheets using a four-sided coating applicator (Sheen Instrument). The coatings films achieved on both PC sheet and acrylic sheet were transparent and smooth. Moreover, coating film on acrylic sheet was easily obtained compared to those obtained from PC.

FT-IR technique was used to investigate the crosslinking reactions (sol-gel reaction and polyol/MDI system). Figure 4.7, 4.8 and 4.9 showed typical FT-IR spectra of a coating films, (start) before subjecting to curing and (stop) after curing. Characteristic band of –OH stretching at 3,335 cm^{-1} which remain from functionalization of PHEMA was decreased by isocyanate group of crosslinking agent. It is apparent that the isocyanate peak at 2,270 cm^{-1} almost disappeared in all of the spectra of cured films, suggesting that isocyanate groups undergoing chemical reaction. The transformation of isocyanate groups was found to be such a high rate, judged by curing times about 10-15 min that was taken to obtain the complete disappearance of isocyanate peak. The other crosslink was inorganic network which is based on the sol-gel process. It is well known that the bands in the region of 1,200-1,000 cm^{-1} are assigned to the Si-O-Si band. Ethoxy silane (Si-O-Et) was hydrolyzed to hydroxysilane and followed by condensation reaction to form siloxane network(Si-O-Si). However, identification of this band by FT-IR analysis is quite difficult due to peaks interference. It is also known that isocyanate groups to produce a urethane linkage. This peak could be easily observed at 1,670 cm^{-1} which shows up strongly.
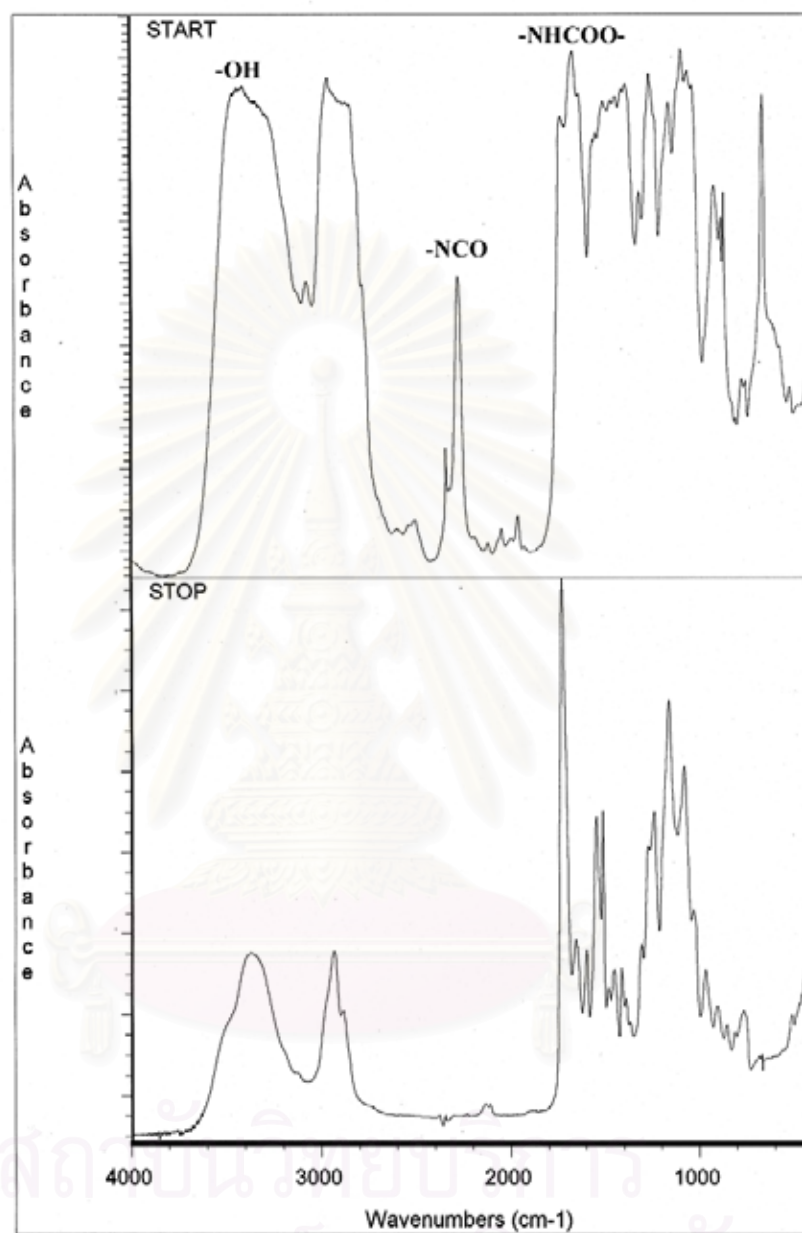
Figure 4.7 The FT-IR spectra of coating film (F-30) at beginning and the end
of reaction.
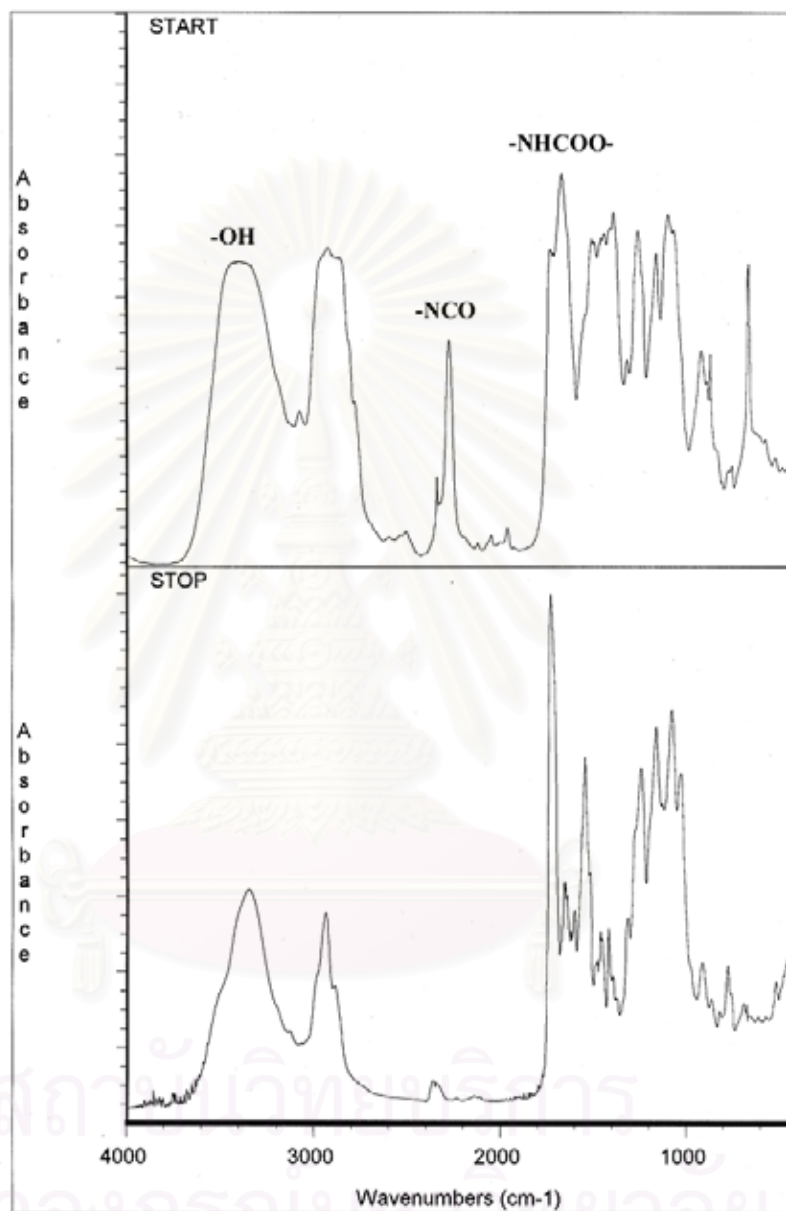
Figure 4.8 The FT-IR spectra of coating film (F-50) at beginning and the end
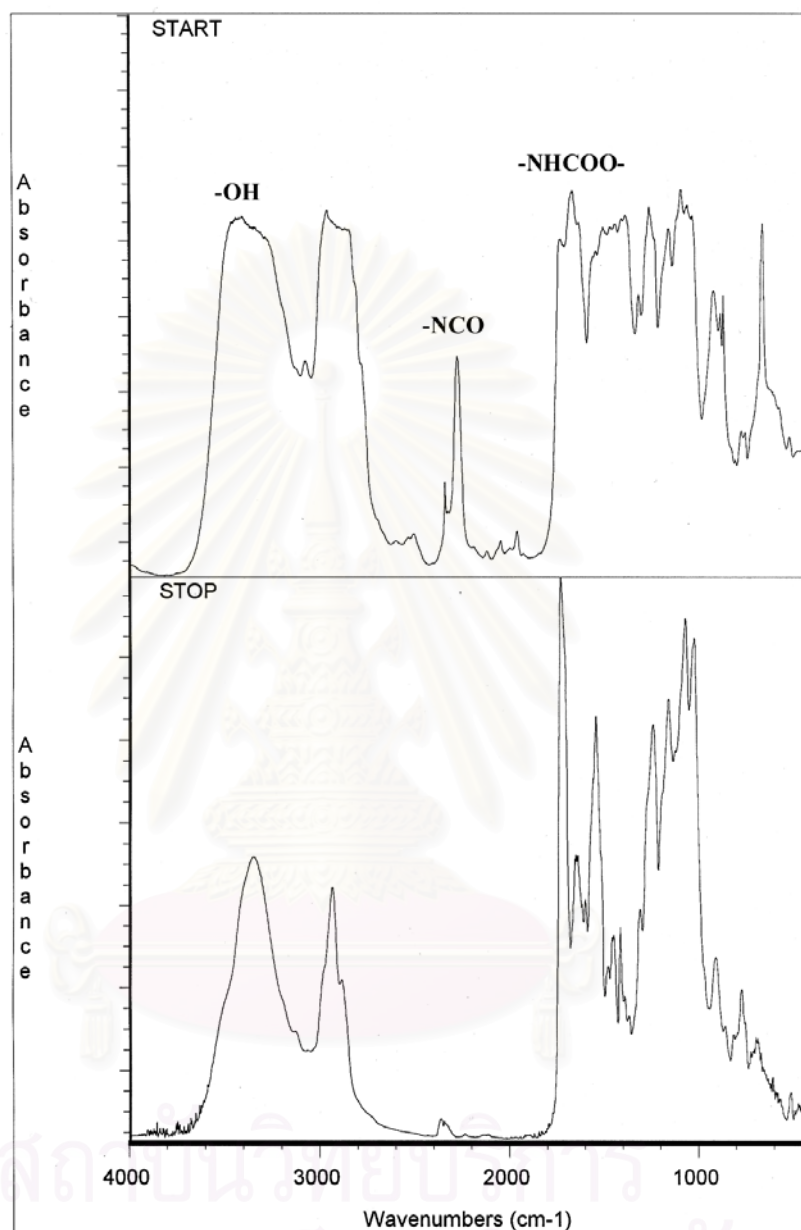
of reaction.

Figure 4.9 The FT-IR spectra of coating film (F-70) at beginning and the end
of reaction.

4.5 The [29]Si-Nuclear Magnetic Resonance Analysis.

The nuclear magnetic resonance method is useful for analysis of hydrolysis and condensation of the silane groups. This is due to an ease of assignment of the ^{29}Si-NMR peak of silane group in comparison with the IR spectrum method.
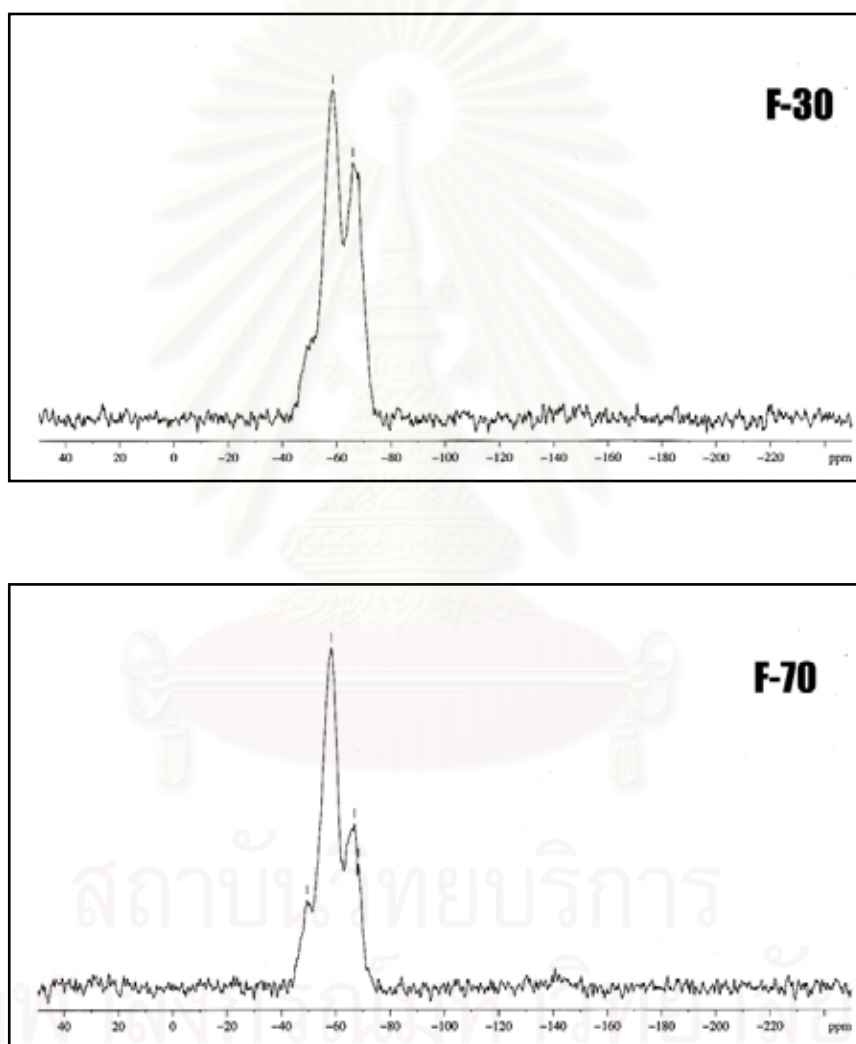
Figure 4.10 Solid state [29]silicon NMR of coating films from F-30 and F-70.

Coating films containing PHEMA samples with degree of functionalization of 30% and 70% were subjected to solid state ^{29}Si-NMR analysis. Based on the sol-gel process, firstly an acid catalyst produced hydroxysilane group due to hydrolysis. From literature[22], the signal at –42 ppm. was responsible for the presence of the hydroxysilane group. The hydrolysis reaction is represented as belows:
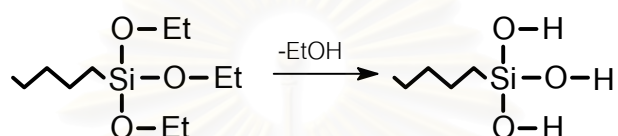
However, from the NMR spectra the hydroxysilane peak did not show up, indicating that the subsequent reaction of hydroxysilane groups proceeded immediately. The NMR results also reveal that hydroxysilane proceeded immediately to condensation step to produce siloxane linkage, albeit not complete condensation obtained. In the case of incomplete condensation, three types of condensation species could possibly be produced as shown in the following scheme:
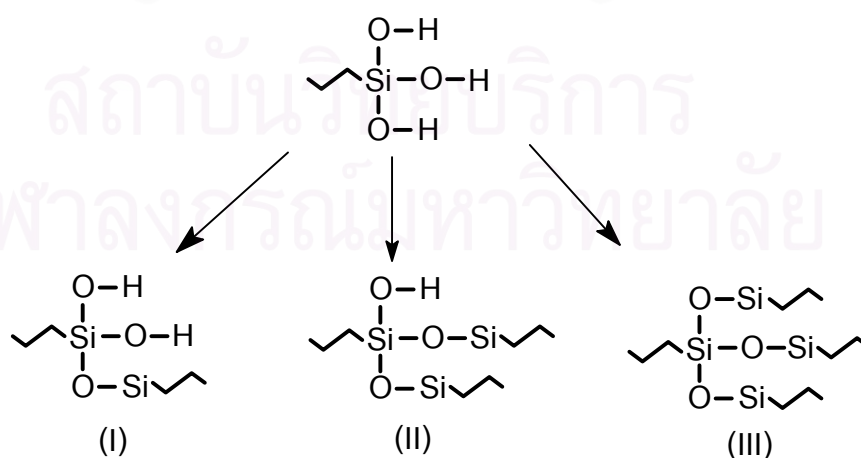
The signals at –58, -59 and –63 ppm were assigned to presence of species I, II and III respectively. The presence of species I and II indicated that the incomplete condensation with dominant specie II was obtained. Although all of hydroxy silane would not be converted to specie III via condensation reaction but the content of specie II probably were enough to produce the high degree of inorganically crosslinked network. Solid state ^{29}Si-NMR showed that sol-gel reaction did take place.

4.6 Evaluation of properties of coating film

4.6.1 Scratch Resistance Test.

This test utilized standard needle that was automatically moved on the surface of coated/cured substrate. The minimum weight was 100 gram and a series of additional weight of 100 gram was added until the scratch line was observed. Figure 4.10 shows the results of minimum weight required to produce scratch line on coated PC sheet.
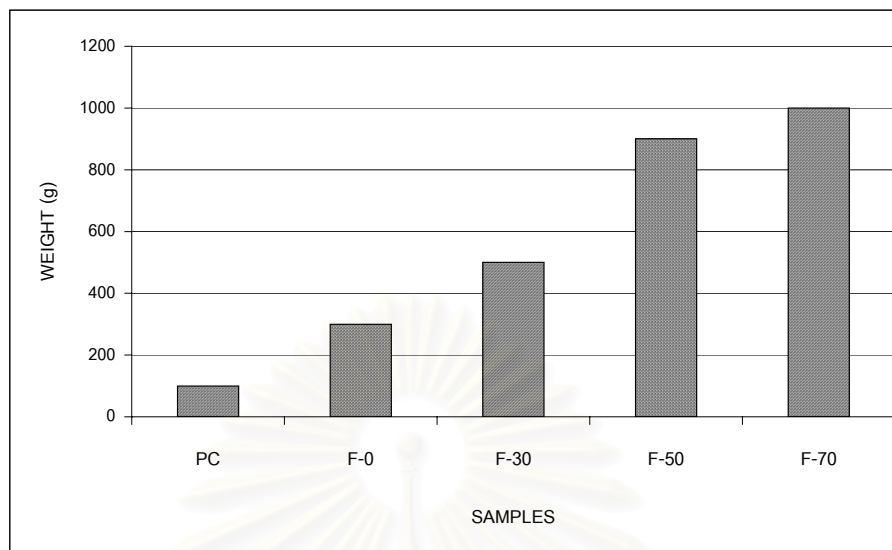
Figure 4.11 Minimum weight required to observe the scratching line on PC
substrate.

The results show that uncoated PC exhibited poor scratch resistance; scratch line was first observed when only the load of 100 gram was applied. Trend of scratch resistance of coating film increased with an increase in the degree of functionalization. The formulation containing the copolymer with 70% of functionalization(F-70) shows that highest resistance to scratch. This may suggest that the scratch resistance of coating film was closely related to the degree of inorganic content of a coating formulation.

For the coating on acrylic sheet, the results were not that impressive. The scratch lines appeared only when a load of 100 grams was applied. No different results are observed among different coatings formulations. Probably, the adhesion of coating films on acrylic sheet was poor when compared to PC substrate.
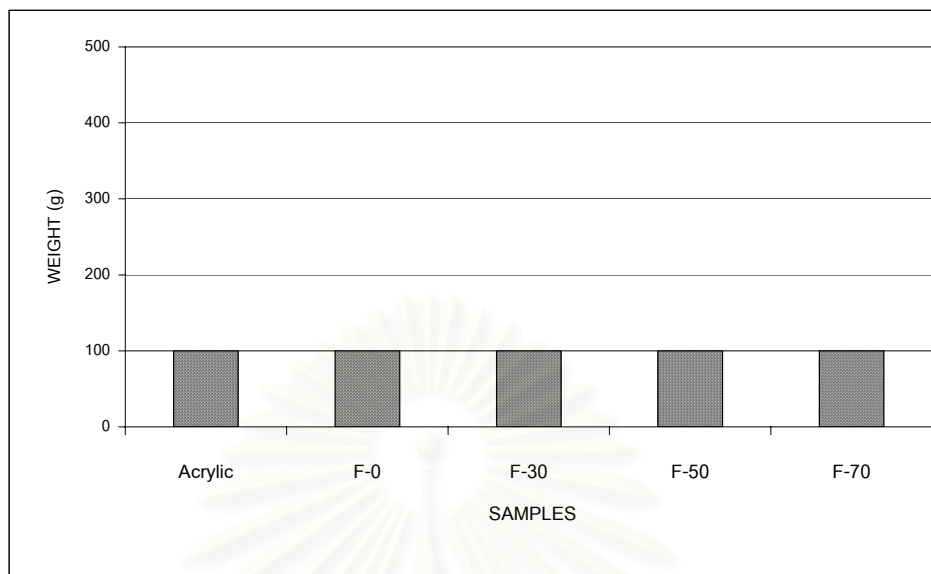
Figure 4.12 Weight load required to produce scratching line on acrylic sheet

4.6.2 Abrasion Resistance Test

The coated samples were abraded at 1000 cycles by Wet Abrasion Tester. A brush weight of 0.45 kg. was used for wearing the surface of the film. The coating was applied onto one-half of the substrate in order to easily compare the appearance as well as abrasion resistance between coated and uncoated areas.

After being applied of coating, coated substrate exhibited excellent clarity. This may imply that organic/inorganic coating composite obtained showed no phase separation between organic and inorganic components. After abrasion test, the coated samples showed better abrasion resistance than pristine substrate judged by naked eyes as shown in Figure 4.13. Therefore, it can be claimed that application of organic/inorganic coating offered an improvement an surface performance of coated plastic.

Figure 4.13 example of uncoated/coated film on the PC substrate.

UV/Vis spectrophotometer was used to measure light transmittance of abraded samples. Evaluation of abrasion resistance of abraded samples is reported as relative correlated haze value which is calculated using the following equation:

$$\text{Relative correlated haze} = \frac{\text{Correlated haze of coated substrate}}{\text{Correlated haze of uncoated substrate}} \times 100$$

The results are shown in Figure 4.14 and 4.15. The uncoated film was used as a control.

Figure 4.14 and Figure 4.15 show that at wavelength 420 nm., the relative correlated haze value decreases with an increase in the degree of functionalization. The F-0 sample exhibited the highest relative correlated haze value compared to other coated samples and no difference compared to pristine PC substrate. For other samples, abrasion resistance property of coating film was closely dependent on the degree of functionalization. In another word, the abrasion resistance property was closely related to inorganic network. From the results, F-70 sample which contained the highest inorganic content performed better resistance to a abrasion than F-50 and F30 according to its lowest relative correlated haze value obtained.
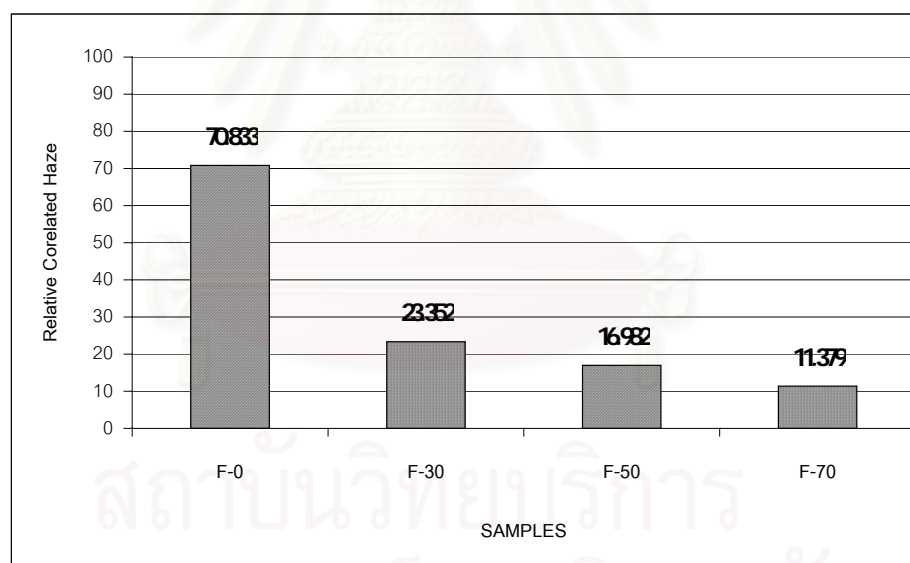
Figure 4.14 Relative correlated haze functionalized PHEMA 0%, 30%, 50% and 70% on Acrylic Sheet at wavelength 420 nm.
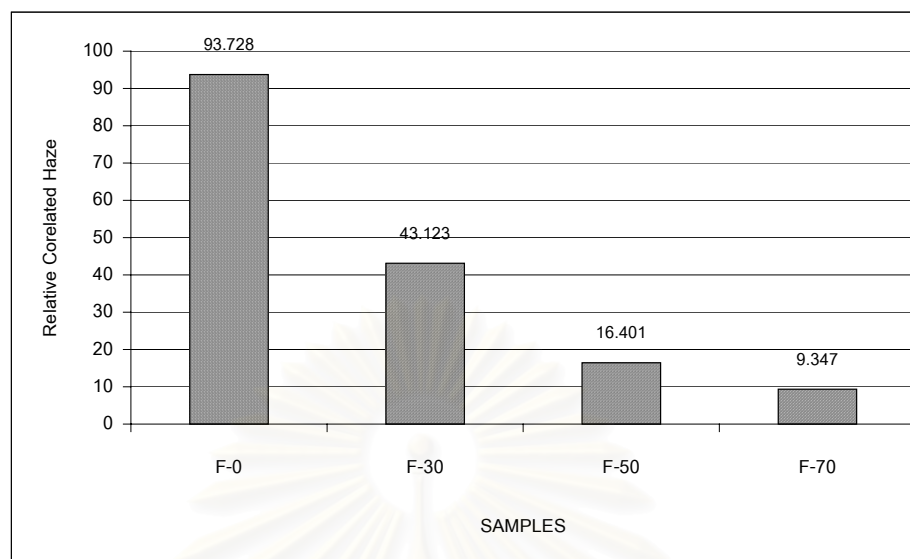
Figure 4.15 Relative correlated haze value obtained from coating samples,   F-0,

F-30, F-50 and F-70 on PC sheet taken at 420 nm.

4.6.3 Solubility Test with DMF, THF and Ethanol

Resistance property of coating films to chemicals was performed to evaluate crosslink density of network structure. The effect of three types of organic solvents, dimethyl formamide(DMF), ethanol, and tetrahydrofuran(THF) was studied. Ethanol is good solvent for PHEMA while DMF and THF are aprotic solvents which are considered as powerful solvent. The swollen films when treated with strong solvents(figure 4.16) indicated that film of coatings was highly crosslinked network.

Table 4.1 The swelling of film from chemical resistance test.

Substate	Solvent											
	Ethanol				DMF				THF			
Coated PC	At 18 hours				At 6 hours				At 3 hours			
	F-0	F-30	F-50	F-70	F-0	F-30	F-50	F-70	F-0	F-30	F-50	F-70
	S	X	X	X	S	S	S	S	S	S	S	S
Coated Acrylic	At 18 hours				At 6 hours				At 3 hours			
	F-0	F-30	F-50	F-70	F-0	F-30	F-50	F-70	F-0	F-30	F-50	F-70
	S	X	X	X	S	S	S	S	S	S	S	S

S = Swelling
X = No Swelling
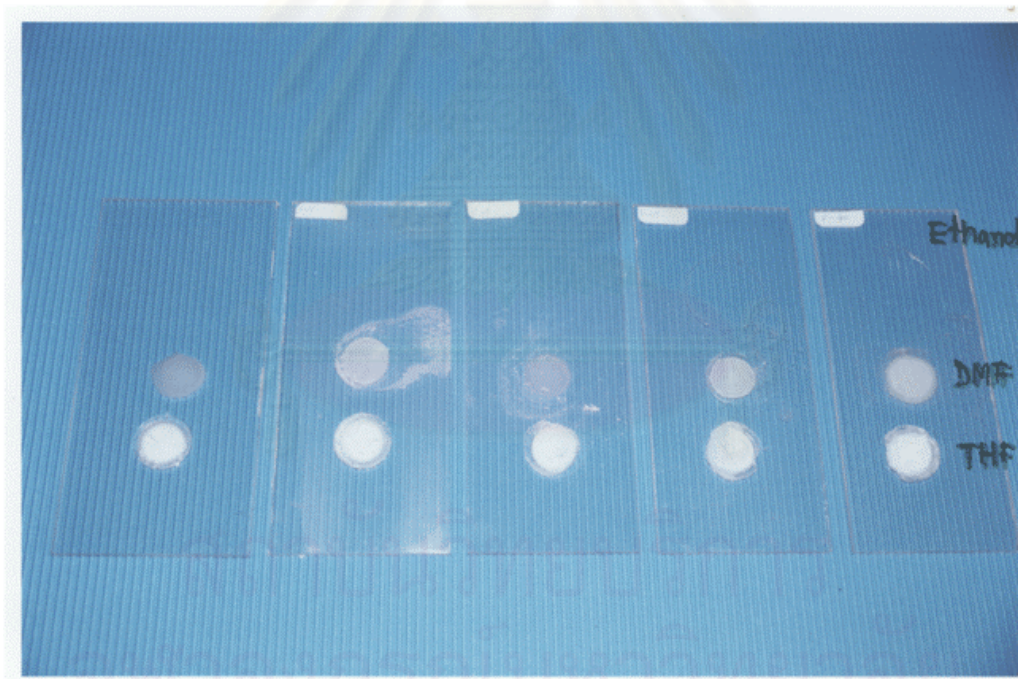
Figure 4.16 show the photograph of coated substrate after chemical test.

4.7 Thermal Analysis

4.7.1 Thermogravimetric Analysis (TGA)

TGA analysis was performed on TGA-7 (Perkin Elmer) to study the thermal stability of coating film. Temperature range between 50 to 850 $^{\circ}$C was investigated. The thermograms obtained are shown in Figure 4.17.
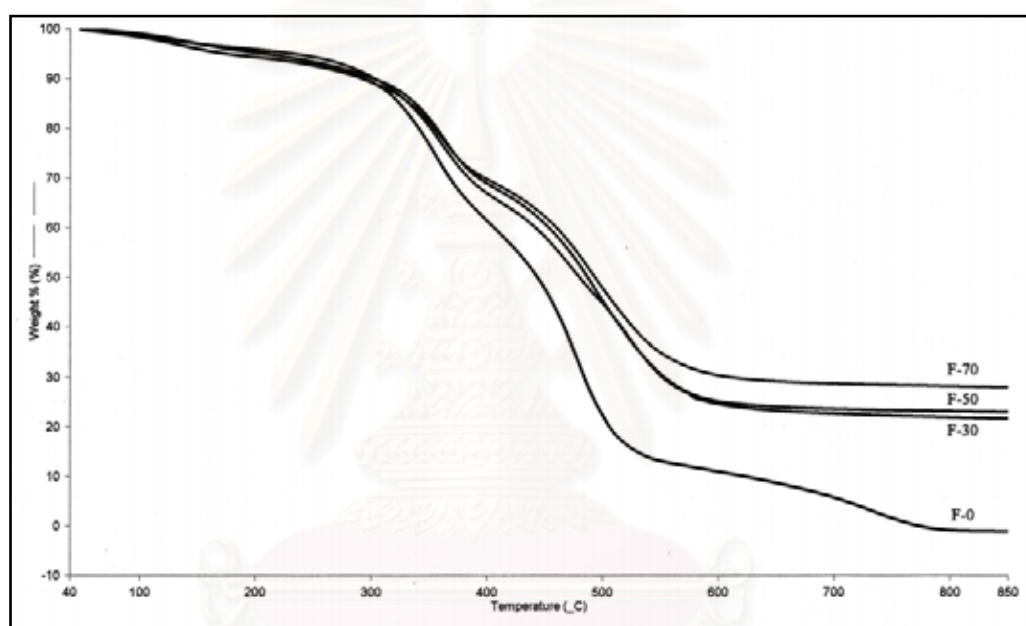
Figure 4.17 TGA thermogram for 0%, 30%, 50% and 70% functionalized PHEMA.

The decomposition process shows two steps of weight loss rates. The weight loss step observed at temperatures ranging form 400 $^{\circ}$C – 600 $^{\circ}$C was attributed to the decomposition of organic network which accounted to 30% in all cases. Upon further heating, little change in weight loss was observed, the residue of thermally stable ash which accounted for 0.88%, 21.92%, 23.06% and 28.19%

for F-0, F-30, F-50 and F-70, respectively. The calculated values of inorganic remaining are 0 wt%, 9.33 wt%, 12.75 wt% and 15.46 wt%, respectively. Siloxane (Si-O-Si) network is the part of coating material that was thermally stable up to 600°C. The results showed that the presence of inorganic residue increased with an increase in the degree of functionalization. The silica content obtained experimentally and from theoretical values are presented in Table 4.2.

Table 4.2 calculation of percent of inorganic in coating material.

Sample	%SiO$_2$ (theoritical value)	%SiO$_2$ (Actual value)
F-0	0	0.88
F-30	9.33	21.92
F-50	12.75	23.06
F-70	15.46	28.18

It is quite obvious that the actual values are higher than theoretical ones. It is possible that inorganic residue might contain the organic component as a result of incomplete degradation. However the remaining inorganic content tends to increase with an increase in the amount of inorganic component.

4.7.2 Differential Scanning Calorimetric Analysis (DSC)

The coating films (F-0, F-30, F-50 and F-70) were subjected to DSC analysis. The studying temperature ranges were between 50 and 150°C since the glass temperature of virgin PHEMA is about 85°C. the DSC thermograms are shown in Figure 4.18. The thermogram curves show that no onset temperature was observed

in all cases of coating samples, indicating that coating films did not have T_g. This was due to the fact that functionalized PHEMA components underwent crosslinking reaction to produce high density of crosslink net work which usually exhibits no T_g. DSC result confirmed that the coating films contained crosslink network which played a significant role in improving the surface performance of coated substrates.
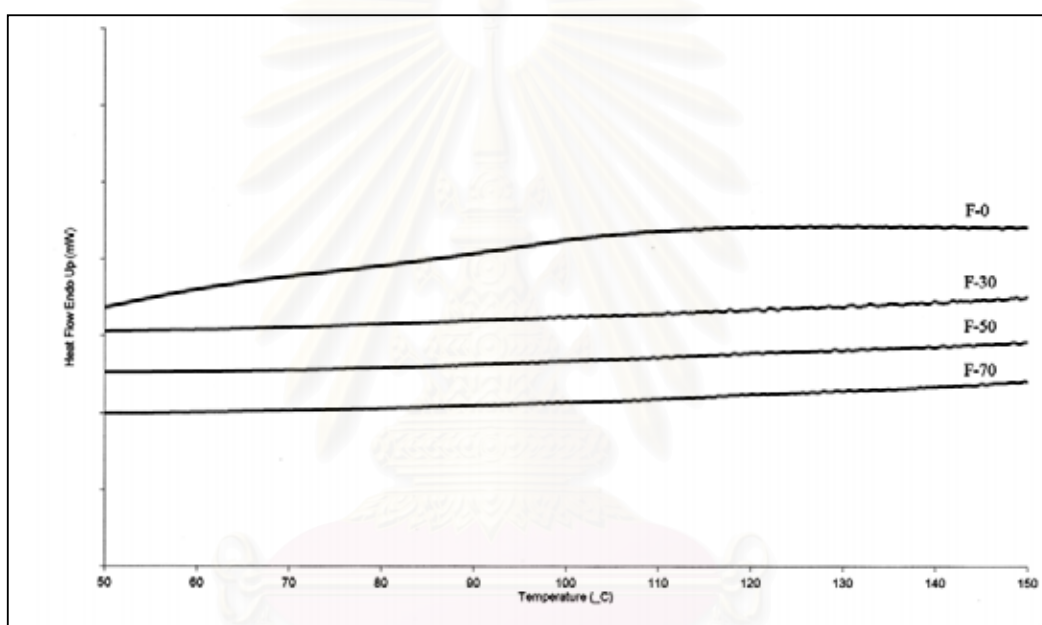

Figure 4.18 Differential scanning calorimetric curves of F-0, F-30, F-50 and F70
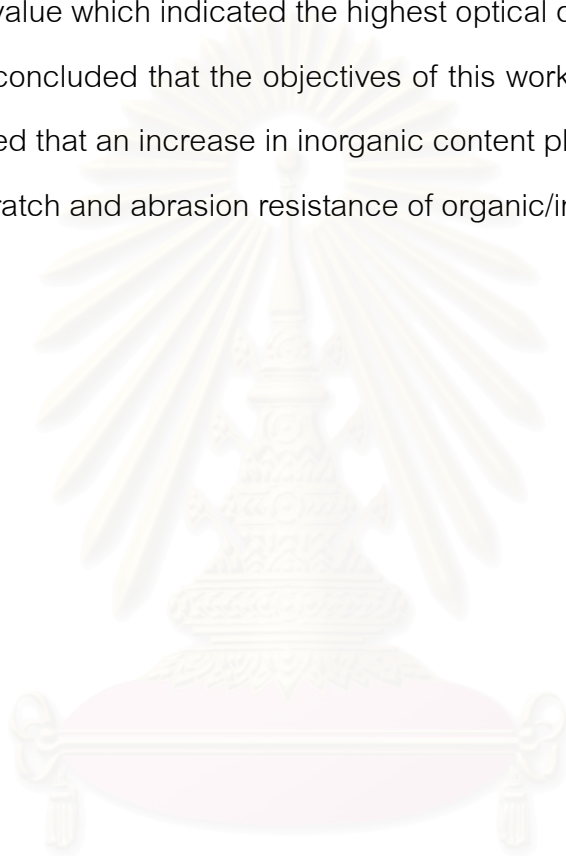
CHAPTER V
CONCLUSIONS

The PHEMA as organic component of organic/inorganic composite was prepared in ethanol. The GPC results showed that their molecular weight were in the range suitable for coating application. The functionalization of PHEMA with IPSE carried out at $76^{\circ}C$ gave the functionalized PHEMA(s) with the degree of inorganic content of 30%, 50%, and 70%. FT-IR was employed to confirm the successful functionalization.

Organic/inorganic coating based on functionalized PHEMA and MDI was investigated. Organic crosslink network produced by the reaction of PHEMA hydroxyl group and isocyanate group of MDI and inorganic network produced by sol-gel reaction of siloxyl pendant group of functionalized PHEMA were achieved by curing coating film at $120^{\circ}C$ for 3 hours. ^{29}Si-NMR was used to confirm to confirm the presence of siloxane network in hybrid coating. Coating film was applied on PC and acrylic sheet. The cured film exhibited excellent optical quality.

The coating films were tested for the scratch/abrasion resistance. Swelling test was used for evaluating chemical resistance. DSC results did not show T_g of PHEMA which is generally seen at $85^{\circ}C$ for virgin PHEMA. This indicated thermosetting property of coating film as a result of network formation. TGA results showed that ash content increased with an increase in inorganic content albeit higher than theoretical calculation. From the scratch resistance test, F-70 showed the highest resistance and followed by F-50, F-30, F-0 and pristine PC respectively. However, this trend was not observed on acrylic sheet. Probably, the adhesive between film and substrate was not good. The relative correlate haze value was

used to determine the optical properties of film after abrasion test. The relative correlated haze value was selected at 420 nm. The high value of relative correlated haze value indicative of poor optical property. The abrasion result showed that relative correlated haze value decreased when the inorganic content increased. So F-70 had lowest value which indicated the highest optical quality.

It can be concluded that the objectives of this work could be achieved. The findings suggested that an increase in inorganic content played an important role in improving the scratch and abrasion resistance of organic/inorganic coatings film.

CHAPTER VI
RECOMMENTDATION FOR FUTURE WORK

The use of alternative crosslinking agents which are lower reactive than MDI should be studied in order to control the early gellation of coating solution.

The curing temperature of 120°C could cause the warpens of plastic substrates. Therefore, the study of effect of temperatures at lower temperature may be interesting to avoid the deflective problem of the materials.

The extent of crosslink density should be undertaken to achieve the optimum surface performance of coated substrates.

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Academic Works and Received Awards

1999: - Received the award for outstanding academic presentation (poster) at the Annual Academic Meeting, Faculty of Science.

- Writer of the academic article "Organic/inorganic composite materials for coating applications" which received publication in Journal of Applied Polymer Science, Vol. 74, 1999.

- Received an invitation to present an academic work at the 1999 Asia/Australia Regional Meeting organized by the Polymer Processing Society (PPS).

- Teaching Assistant in Polymer Science Lab and Textile Dyeing Lab.

2000: - Received an invitation to present an academic work at 1st Academic Conference for Graduate Students, hosted by Chiangmai University.