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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ภาควิชาวัสดุศาสตร์

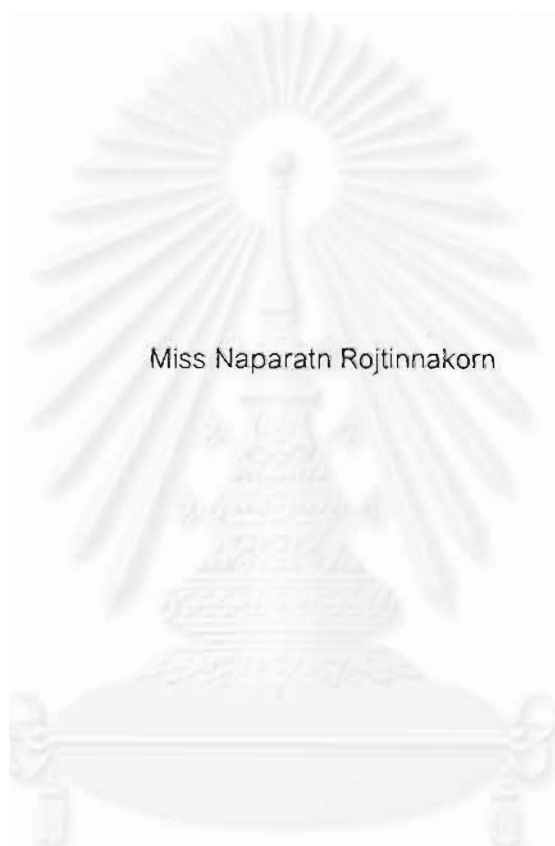
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SYNTHESIS OF ORGANIC/INORGANIC HYBRID MATERIALS FOR
COATING APPLICATIONS



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

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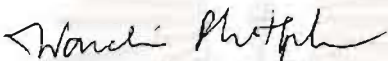
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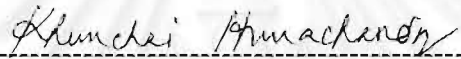
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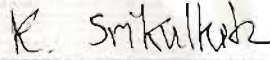
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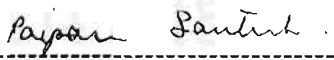

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ได้สังเคราะห์โคพอลิเมอร์น้ำหนักโมเลกุลต่ำที่มีหมู่ไฮดรอกซิลเพื่อวัตถุประสงค์นำไปเป็นสารเคลือบผิวไฮบริดระหว่างสารอินทรีย์/อนินทรีย์ สารเคลือบผิวที่เตรียมขึ้นแบ่งออกเป็นสองระบบคือ สารเคลือบผิวระบบสององค์ประกอบ (สารโคพอลิเมอร์ที่มีหมู่ฟังก์ชันไฮดรอกซิลและเอชเอ็มเอ็มเอ็ม) และสารเคลือบผิวระบบสามองค์ประกอบ (สารโคพอลิเมอร์ที่มีหมู่ฟังก์ชันไฮดรอกซิล เอชเอ็มเอ็มเอ็มและเตตระเอทิลออลโทซิลิเกต) สารเคลือบผิวทั้งสองระบบจะนำมาเปรียบเทียบสมบัติทางผิวของแผ่นพอลิคาร์บอนเนตที่ผ่านการเคลือบ ได้แก่ ความโปร่งแสง ความคงทนต่อการขีดถู และการขีดข่วน

ฟิล์มเคลือบจากทั้งสองระบบแสดงสมบัติความโปร่งแสงที่ดี ซึ่งเป็นผลจากปริมาณสารอนินทรีย์ ในกรณีของสารเคลือบผิวระบบสามองค์ประกอบส่วนของเตตระเอทิลออลโทซิลิเกตควรที่จะเชื่อมโยงติดเข้าไปเป็นส่วนหนึ่งขององค์ประกอบอินทรีย์โดยอาศัยตัวเชื่อมคือหมู่ไฮดรอกซิล เพื่อไม่ให้เกิดการแยกเฟสขึ้น หมู่ฟังก์ชันไฮดรอกซิลสูงจะแสดงความโปร่งแสงที่ดีกว่า สมบัติความทนต่อการขีดถูของแผ่นพอลิคาร์บอนเนตหลังการเคลือบดีกว่าก่อนเคลือบ ความแข็งแรงของฟิล์มสารเคลือบผิวนั้นมาจากการเกิดโครงสร้างตาข่ายสองชนิดคือ โครงสร้างตาข่ายสารอินทรีย์ได้จากหมู่ไฮดรอกซิลของโคพอลิเมอร์เกิดปฏิกิริยาทรานส์เทอริฟิเคชันกับหมู่เมทิลอลของไฮดรอกซิลเมทิลเมลามีน และโครงสร้างตาข่ายสารอนินทรีย์เกิดจากปฏิกิริยาซิล-เจล ผลการทดลองแสดงให้เห็นว่าโครงสร้างตาข่ายสารอนินทรีย์เป็นปัจจัยสำคัญในการเพิ่มสมบัติทางผิวให้กับพอลิคาร์บอนเนต

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AN ABSTRACT

4072487023 : MAJOR APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY

KEY WORD: ORGANIC/INORGANIC HYBRID COMPOSITE / COATING / OPTICAL TRANSPARENCY / ABRASION/SCRATCH RESISTANCE. /

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Siloxyl group functionalized copolymer of low molecular weight was synthesized, aiming at preparing transparent inorganic/organic coating composite. Two types of coating systems; two component system (based on functionalized copolymer-HMMM) and three component system (based on functionalized copolymer-HMMM-TEOS) were investigated. Their surface performance was compared.

Coating films obtained from both systems exhibited good optical clarity. The results indicated that the optical clarity of coating films was largely dependent on the amounts of the inorganic contents. In the case of three component system, it was necessary that the TEOS component should be effectively linked to the organic component through pendent siloxyl groups to prevent phase separation. Hence, the coating formula containing a functionalized copolymer of high degree of pendent siloxyl group showed better optical transparency. Abrasion/scratch resistance properties of coated/cured PC sheets were greatly improved when compared to uncoated one. Two crosslink networks; organic network resulting from transesterification between copolymer hydroxyl group and HMMM methylol group, and inorganic network resulting from sol-gel reaction were responsible for the hardening effect of coating films. Finding results also revealed that the inorganic network mainly contributed to improved surface performance of coated PC samples.

ภาควิชา **วัสดุศาสตร์** ลายมือชื่อนิสิต **ณพรัตน์ ไกรนันทกร**
สาขาวิชา **วิทยาศาสตร์และเทคโนโลยีแห่งมหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี** ลายมือชื่ออาจารย์ที่ปรึกษา **ดร. นพวิมล**
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CHAPTER 1

INTRODUCTION

Plastics are often used to replace glasses due to their light weight, good mechanical strength, high impact resistance, as well as easy processability for shaping into complicated structures. However, in order to enhance the overall performance of plastic parts, surface hardening coatings are applied on plastic substrates. Among these coating materials, organic compounds such as melamine, polyurethane, and acrylic-based polymers are often used. The hardening effect is a result of chemical reactions which convert molecules of the coating layer into a highly crosslinked network structure.

Melamine compounds are widely used as protective coating due to their transparency, good adhesion as well as heat and chemical resistance. Hexamethoxymethylmelamine (HMMM) is fully alkylated melamine¹. Since active hydroxyl groups are no longer present, it has a longer shelf life than other types of melamine. HMMM has been used with acrylic copolymers containing hydroxyl group on the side chains. Such a combination is often referred to as a melamine/polyol system². The crosslinking reaction of this system is based on the transesterification between melamine and the pendant hydroxyl groups of the copolymer under an acid catalyzed condition³. The reaction kinetics and mechanism of such a reaction were studied extensively. Upon baking at elevated temperature, a highly crosslinked polymer network is formed. Inorganic materials can be also used for surface coating on substrates. This is usually achieved by a sol-gel reaction since the traditional melting process for glasses at high temperature is not suitable when organic polymer substrates are used. Through the hydrolysis and condensation reaction, vitrification can occur leading to glassy inorganic materials⁴.

For example, Accuglass, a coating material marketed by Allied Signal, is based on oligomers with reactive side groups, Si-O-R, where R can be either alkyl or phenyl. After heating and vitrification at an elevated temperature, the resulting coating layer is virtually silica glass. However, in order to achieve a sufficient degree of reaction for obtaining good film properties, a high processing temperature is required.

In addition, the film thickness is only in the order of a few thousand angstroms. When thickness is increased, cracking can easily occur during vitrification due to film shrinkage⁵. Sol-gel reaction is also commonly observed when silane-coupling agents are used for surface property modifications as well as for coupling between glass fibers and polymers in fiber reinforced composite materials⁶.

There is an increasing interest in synthesizing hybrid of organic and inorganic materials. Various approaches have been adopted to prepare organic/inorganic composite materials. The in-situ polymerization of tetraethoxysilane groups. Through sol-gel reaction, organically modified sol-gel glasses were prepared. Nanocomposites were prepared by aging of a solution which allows radical polymerization of monomers and sol-gel reaction to occur concurrently. Other related works have also been reported, such as non-shrinking organic/inorganic composites for nonlinear optical application, etc⁷. These works were based on the sol-gel reaction of alkoxy silane functionalities in some organic polymer components, but no chemical reaction was involved in the organic polymers.

Tamami et al. have developed an abrasion resistant transparent coating material based on material functionalized with trialkoxysilane group. After processing and heating of this compound, a crosslinked organic/inorganic hybrid coating layer was formed through a sol-gel reaction. Although the melamine moiety does not involve in any chemical reaction in this work, it provides a good adhesion to the substrate as well as rigidity to the film. The abrasion resistance of coated polycarbonate samples was superior to that of uncoated ones. The thickness of these films was in the range of 1 to 3 μm only, which may still be too thin to provide a long service life. However, this work demonstrated that highly crosslinked materials based on sol-gel reaction of the alkoxy silane group exhibit optical transparency and good abrasion resistance⁴. Organic/inorganic composite materials based on HMMM/alkoxy silane functionalized acrylic polymers was investigated by Chen. Et al⁸. A transparent network film was obtained by curing the dried coating composition at high temperature. Two types of crosslinking reactions were expected, transesterification of acrylic polymers hydroxyl groups with HMMM and sol-gel

reaction. The Coated film exhibited good optical transparency. However, this was a limitation in terms of increasing the clarity property of the hybrid materials.

Therefore, this experiment extends the study of the previous research. Triethoxyorthosilicate (TEOS) as an external inorganic network precursor was introduced to alkoxy silane functionalized acrylic polymer/HMMM system. Surface performance, including abrasion and scratch resistance as well as optical properties, was investigated.



CHAPTER 2

FUNDAMENTAL AND LITERATURE REVIEW

2.1 Polycarbonate Plastics

2.1.1 Polycarbonate (PC)

Polycarbonate (PC) based on bisphenol A is an amorphous thermoplastic polymer with high molecular weight. Flow properties of PC molten state exhibit non-Newtonian characteristic due to a low proportion of chain branching which leads to a high melt viscosity with low shear rates. The chemical structure of polycarbonate can be indicated as follows;

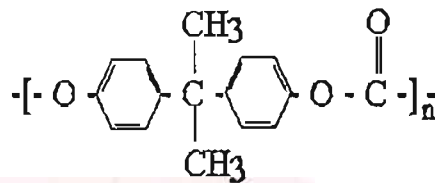


Figure 2.1 The chemical structure of polycarbonate plastics⁹

2.1.2 Processing

Drying :

The granules must be pre-dried for 2 to 3 hours at 120°C in a high-speed dryer or other suitable drying units. And the extruder machine as a vent zone in the barrel¹⁰.

Extrusion :

Polycarbonate plastic is processed exclusively on single - screw Extruder. The melt temperature at the end of the screw should be between 250 and 280° C. It is best to work with a barrel temperature profile that falls from 280 - 250°C between the feed opening (feed hopper) and the screw tip. The temperatures selected for the individual calibrator zones will depend primarily on the thickness of the twin-wall sheet or twin-wall profile and the take-off speed. As a rule, the front section of the calibrator will be operated at a lower temperature than the rear section. In the event of problems in achieving plane sheet, the top of the calibrator can be set at a higher temperature than the bottom. The temperatures will generally be between 60 and 100°C. With thin twin-wall sheet, in particular, it may be necessary for the sheet to be annealed in order to ensure that it is completely plane. Units heated with hot air or IR radiators should be used for this. The temperature of the sheet passing through them should be between 130 and 140°C. In the event of interruptions to production the extruder must be purged. It is recommended that the temperature of all the components in contact with the polycarbonate melt (extruder barrel, screen changer, melt pump, adapter, die, etc.) be kept at temperature of 160 to 170°C ¹⁰. The process of polycarbonate sheet can be illustrated in Figure 2.2

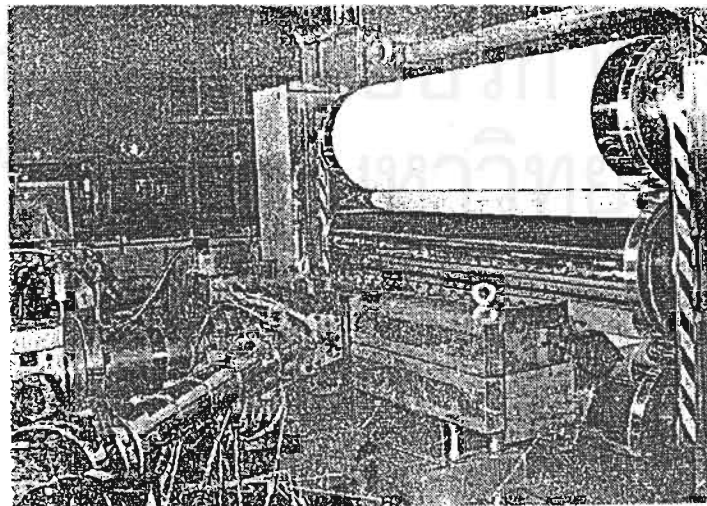


Figure 2.2 The production process of polycarbonate sheet by extrusion¹⁰

2.1.3 Properties

The properties of polycarbonate plastics can be summarized as follows;

- high light transmission in the visible spectrum range for colourless grades
- ability to produce complex profile cross sections
- favourable flame retardance classification
- excellent impact and break resistance
- high mechanical properties
- high cold bending properties
- high stiffness in conjunction with low weight per unit area
- high thermal stability and high heat deflection temperature
- a low melt viscosity in the high shear region inside the extruder, restriction the extent to which the melt is heated friction and ensuring a relatively low electricity consumption for the drive, together with a high output
- a high melt viscosity between the die orifice and the calibration unit, elimination virtually all drawdown

The mechanical properties of polycarbonate sheet and its relation between melt viscosity and shear rate are show in Table 2.1. The properties for polycarbonate sheet can illustrate at Table 2.2 and Figure 2.3, respectively⁹.

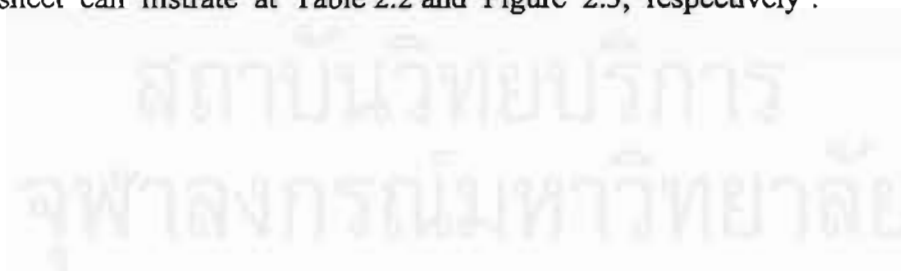


Table 2.1 The mechanical properties of polycarbonate resin⁹.

Properties	SI Units	ISO	DIN	ASTM
Density	1.19 g/cm ³	/R 1183	53479	D792
Tensile stress at yield	75 N/mm ²	/R 527	53455	D638
Tensile strain at yield	5%	/R 527	53455	D638
Elongation at break	80/100 %	/R 527	53455	D638
Ultimate tensile strength	60 N/mm ²	/R 527	53455	D638
Tensile modulus	2,600 N/mm ²	-	53457-t	D638
Impact strength (CHARPY) (specimen : 50 mm x 6 mm x 4 mm)	no Failure	179/2D	53453	-
Vicat softening temperature	130 °C	306	53460	-

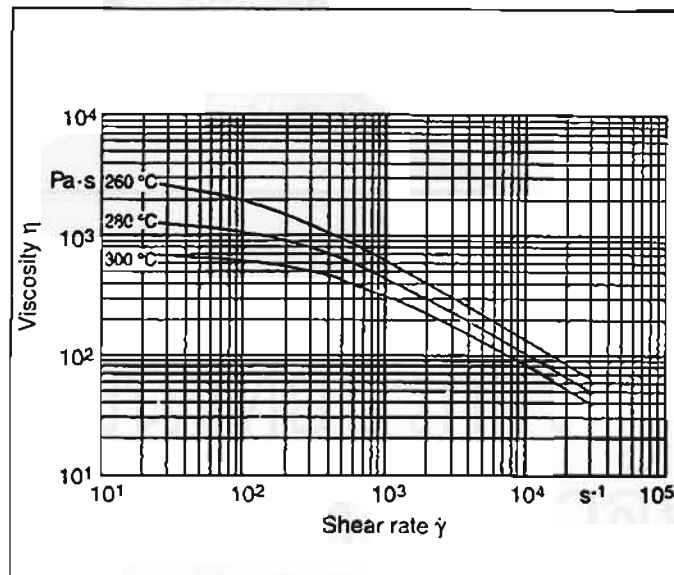
Figure 2.3 Melt viscosity as a function of shear rate⁹

Table 2.2 The properties of PC sheet⁹

Properties (Characteristic Property)	Units	Standards
Melt flow index (MFI) (300° c ; 1.2 kg)	6 g/10 min	ISO/R 1133, DIN 53735, ASTM D1238
Refractive index ND	1,586	ISO/R 489, DIN 53491, ASTM D542
Tensile stress at yield	63 N/mm ²	ISO/R 527, DIN 53455, ASTM D638
Elongation at break	125 %	ISO/R 527, DIN 53455, ASTM D638
Tensile modulus	2,400 N/mm ²	DIN 53457-t, ASTM D638
Notched impact strength (50 mm x 6 mm x 4 mm) 23°C	40 kJ/m ²	DIN 5345, ISO 179/2C (Radios 0.04mm)
Vicat softening temperature	149°C	Din 53460, ISO 306
Coefficient of linear thermal Expansion (23 – 80°C)	0 , 70 10 ⁻⁴ .k ⁻¹	ASTM D696, ISO 53752
Oxygen index	26 %	ASTM D2863
Water vapor permeability	ca.15 g/m ² .d	DIN 53122

2.1.4 Advantages

The polycarbonate offers unique characteristics which make this materials suitable to produce high value-added articles. The distinct properties of polycarbonate plastic include;

- high transparency
- good resistance to rough handling in transition and installation
- high thermal resistance
- good bonding to itself and to other substrates with a variety of adhesives
- good mechanical properties
- excellent toughness characteristic
- resistance to fading and weathering

2.1.5 Disadvantages

The disadvantages of PC sheet products can be summarized as follows;

- poor flexibility
- poor chemical resistance
- poor UV concentrate resistance
- poor scratch and abrasion resistance
- high cost

2.1.6 Application

PC is an **engineering plastic**. It can be used in products ranging from automotive parts to **sunglasses**. The product **samples** of polycarbonate are the following;

- **interior and exterior automotive** part (see figure 2.1)
- lighting
- sunglasses
- sheet glazing in buses, trains and buildings.
- **lenses**
- **roofing using plastic corrugated** sheet, need UV protection coated (see Figure 2.5)

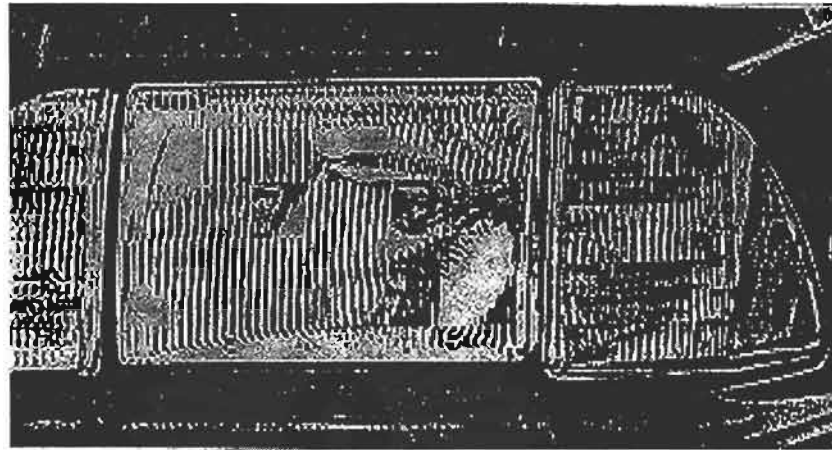


Figure 2.4 Automotive headlights made of PC⁹

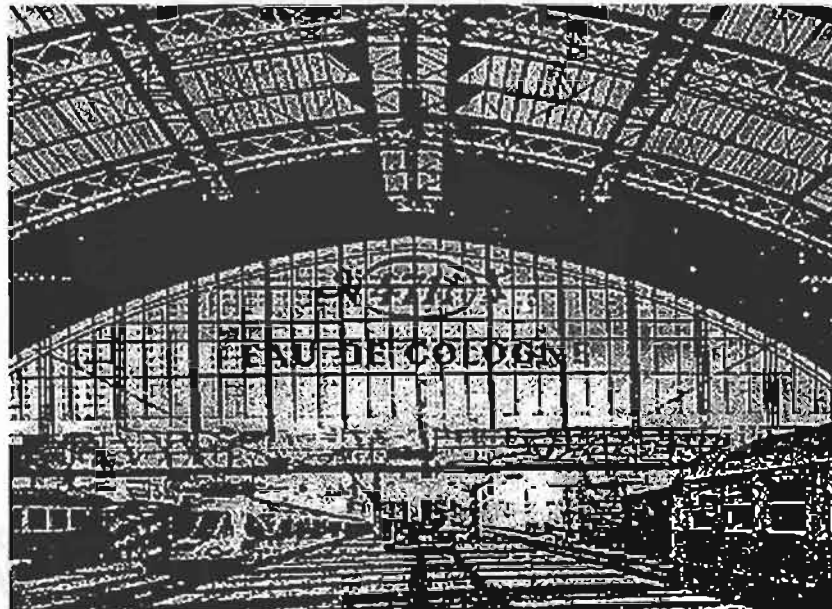


Figure 2.5 Cologne Train Station, The roof made of PC sheet⁹

2.2 Surface Coating

2.2.1 Organic Coating Materials

2.2.1.1 Acrylic - based polymers

Acrylic homopolymers and copolymers are amorphous polymer and copolymers. Thermoplastic acrylics are prepared by the homopolymerization or copolymerization starting from acrylic and methacrylic monomers¹¹. The general structure of polymethacrylate and polyacrylate can be given as shown in Figure 2.6

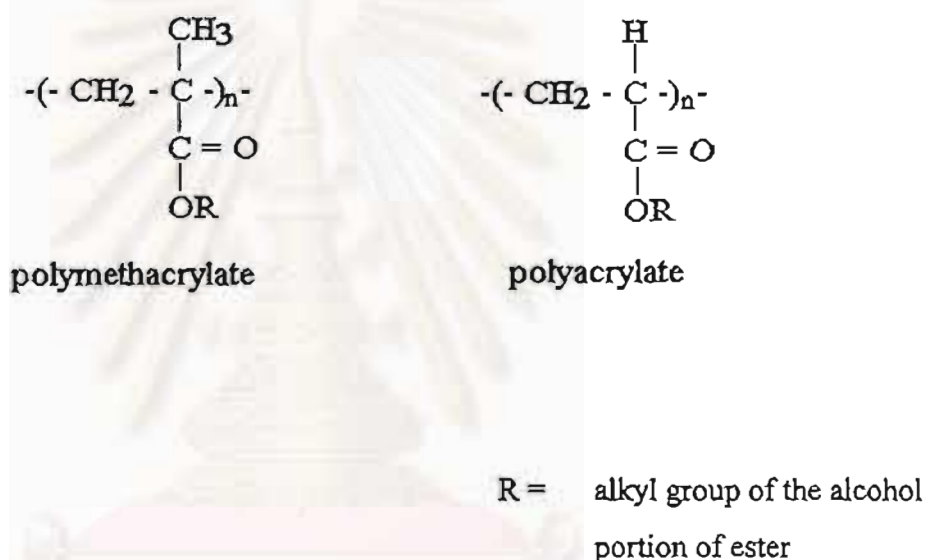


Figure 2.6 The chemical structure of polymethacrylate and polyacrylate¹²

The flexibility and hardness properties can be determined by the molecular weight, and the glass transition temperature (T_g) can be determined by molecular orientation. Acrylic polymers do not exhibit sharp melting points but have second - order transition temperatures at which a glass - like solid converts to a rubbery or semi - tacky state¹³.

The onset of polymer softening is usually identified as glass transition temperature (T_g), but the entire transition may occur over a wide temperature range. In addition, the change in the properties of acrylic polymers with the nature of the alcohol or side group R is affected¹⁴. The influence of the side - chain length on the polymer properties is summarized in Table 2.3. T_g has been shown to bear a direct relationship to very important properties such as softening point, brittle point, “tack temperature” and also “minimum film - forming temperature” in the case of dispersion. T_g of a random copolymer can be predicted by Fox equation (1956)¹⁴. The empirical equation for calculation of the T_g of a copolymer from the known T_g values of their parent polymers is displayed in Figure 2.7.

$$\frac{1}{T_g(\text{copolymer})} = \frac{T_{g1}}{W_1} + \frac{T_{g2}}{W_2}$$

Figure 2.7 The empirical equation for calculated T_g of copolymers¹⁴

Where W_1 and W_2 are the weight fractions of each acrylic monomer in a copolymer, and T_{g1} and T_{g2} are the glass transition temperatures of the homopolymers.

T_g values have been used as a valuable tool for the selection of a proper resin for the development of a particular coating formulation. For example, copolymers having T_g values of 35 -60°C show suitable reflow and hardness characteristics for thermosetting automotive, reflow finishes and thus exhibit excellent durability and resistance properties as finished enamel coatings¹².

Table 2.3 Effect of side - chain length on polyacrylic properties¹⁴

Polymer	Tensile strength (lb/m ²) ^a	Elongation at break (%)
Methyl methacrylate	10,000	1
Ethyl methacrylate	5,400	25
n-Butyl methacrylate	500	300
Methyl acrylate	1,005	750
Ethyl acrylate	33	1,800
n-Butyl acrylate	3	2,000

a = to convert (lb/m²) to Pa, divide by 0.145

2.2.1.1.1 Properties

The main properties imparted by the acrylics are outstanding outdoor durability, water - white colour, excellent clarity, resistance to chemical fumes, alkalis, acid and water, high gloss and excellent gloss retention. Table 2.4 shows some general properties of **acrylic** and methacrylic monomers¹⁵.

Table 2.4 General polymer properties imparted by acrylic and methacrylic monomers¹⁵

Properties	Methyl methacrylate	Methyl acrylate	Ethyl acrylate	Butyl acrylate
Tackiness	Tack - free	Almost tack - free	Tacky	Very tacky
Softness	Fairly hard	Fairly soft	Soft and plastic	Very soft and plastic
Tensile strength	High	Moderately high	Low	Very low
Elongation	Low	Moderately high	Very high	Extremely high
Water absorption	Slight	Fairly high	Slight	Very small
Brittle point	High	Moderately high	Low	Extremely low

Another important property to be considered in the selection of monomers is the polarity and its effects on the solubility of the resins. Polymers from acrylic and methacrylic esters of lower alcohols are usually soluble in aromatic hydrocarbons, esters, ketones, and various chlorinated solvents. Solubility in weak polar solvents such as mineral thinners and Naphtha can be achieved by selecting methacrylate and acrylate esters of long chain alcohols. In general, higher polar acrylic will have better petrol resistance, while the hydrophobic acrylic will give the best water resistance¹⁶.

2.2.1.1.2 Advantage

The advantage properties imparted by the acrylics are as follows ;

- transparent film appearance
- compatibility with other film formers
- good resistance to hydrolysis and ultraviolet degradation
- chemical and water resistance
- resistance to chemical fumes

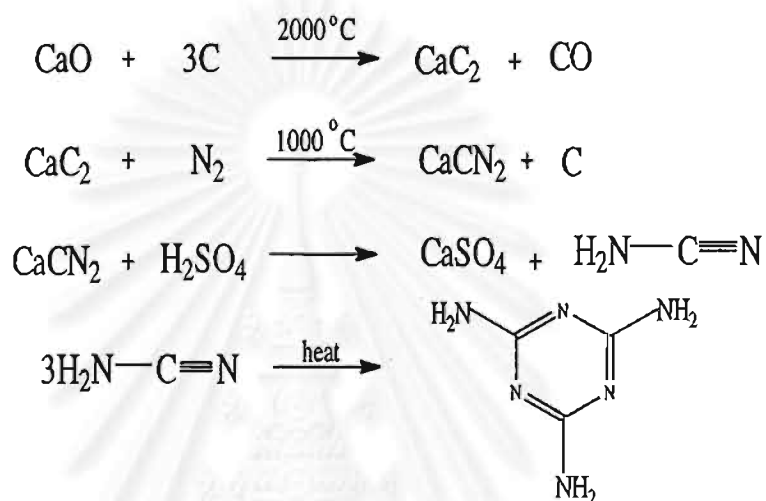
2.2.1.1.3 Applications

The acrylic polymers are used commercially in the field of protective coating, especially in high-solids coating for industrial applications. The important applications include automotive finishes, clear lacquers for polished metals, finishes for aluminium sidings, enamels for washing machines, exterior and interior water-thinned coatings for masonry, wood, plaster, cinder block and wallboard. The other main areas of applications for thermoplastic acrylics are still in the automotive industry, where they are used extensively for refinishing and have completely replaced nitrocellulose lacquers in new car manufacture where non-convertible coatings are still in use¹⁵.

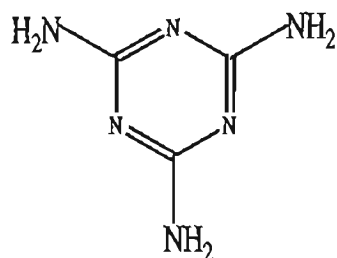


2.2.1.2 Melamine

Melamine, the material used together with acrylic resin, is an aromatic heterocyclic compound prepared from cyanamide. The overall process, including synthesis, is shown below; ¹².

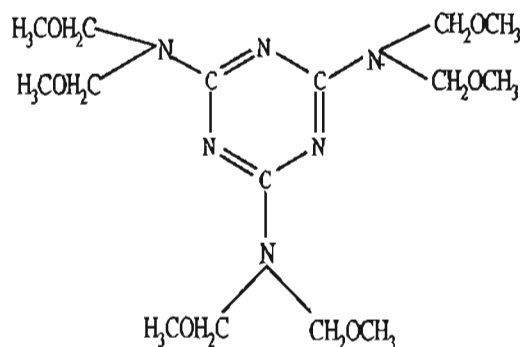


Melamine resins are widely used for the production of decorative laminates. These are usually assembled with a core of phenolic-impregnated paper and a melamine-impregnated overlay sheet. They are cured by heat processing and are used for counters, cabinets, and table tops¹⁶. Melamine resins are widely used for adhesives, largely for plywood and furniture. The chemical structure of melamine can be illustrated as follows¹²;



Melamine

The most important member of the series of methylated melamine resins is the fully substituted derivative, hexamethoxymethyl melamine (HMMM) which has the following chemical structure^{12,17}:



HMMM

The reaction of (HMMM) formed by melamine with formaldehyde (in 1 : 9 of melamine to formaldehyde ratio) in aqueous solution, followed by reaction with acidified methanol¹². The commercial products may be liquid and contain some condensed molecules and some unreacted amino hydrogens. It is useful to combine HMMM with polyol eg., in non-chlorine retentive cellulose textile finishes. HMMM can be also used as a crosslinking agent in alkyd, epoxy and other resins^{12,18}.

Yamamoto et al. (1988) investigated the curing reaction of hexamethoxymethyl melamine (HMMM) with acrylic polyol in the presence of weak acid catalyst such as acrylic acid which was incorporated into the acrylic polyol. It has been shown that primary hydroxyl groups exhibit higher reactivity than the secondary hydroxyl groups, and the former rendered the transesterification reaction at cure temperature of 140°C or below, but at 160°C or above the self-condensation competed. However, for secondary hydroxyl groups, both reactions occurred at all the curing temperatures investigated³.

The transesterification reaction can be represented schematically according the following reaction;

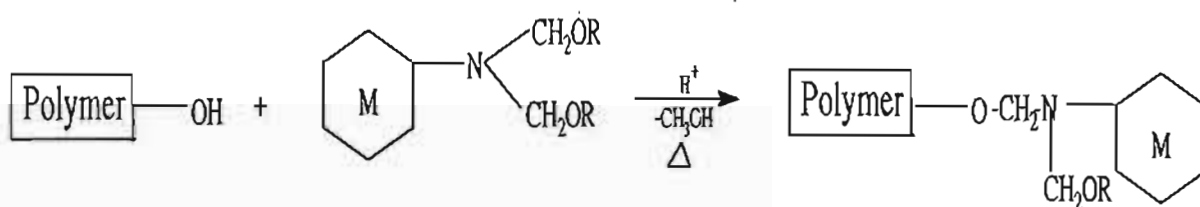


Figure 2.8 The transesterification reaction of HMMM with polyol³

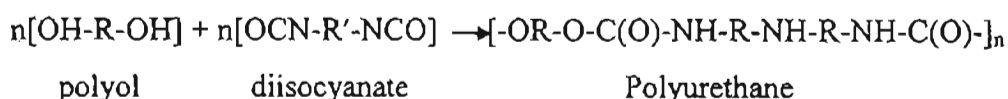
The systems crosslinked with HMMM require the addition of a strong acid catalyst. Sulfonic acids are preferred for their reactivity and solubility characteristics. The most reactive available acid is p-toluene sulfonic acid. The high crosslinking efficiency of HMMM enables cured films to be prepared having greatly improved flexibility, translucent, shown by the increased impact resistance, better compatibility and improved chemical resistance at equivalent film hardness³. HMMM is compatible with a wide range of polymers and resins, including saturated polyesters, alkyds, acrylics, epoxides, vinyl copolymers, nitrocellulose and cellulose acetate butyrate¹⁶.

Furthermore, the optimum coating properties of the film after cure have been correlated with controlling the composition of volatile products formed during curing. The curing product can be characterized by ¹H NMR³

2.2.1.3 Polyurethanes (PU)

Polyurethane is a polymer which contains urethane (-NHCOO-) groups in the polymer chain. They contain the urethane groups as a part of every repeating unit. Polyurethanes were discovered by Otto Bayer and his co-workers in 1937. They range in their structural types from regular polyurethanes, consisting of regularly repeating urethane groups. Although urethane extended prepolymers contain relatively few irregularly spaced urethane groups linking, the copolymer of PU can be generated^{9,17}.

In the commercial polyurethanes, the urethane groups are nearly always formed by reaction of a diisocyanate with a diol (or polyol) the reaction of diisocyanate with polyol is shown below¹¹;



The rate of polymerization reaction depends on the structure of both the isocyanate and the polyol. This is a step-growth polymerization, but unlike many other polymerizations, no small molecule is eliminated, so that it cannot be described as a condensation polymerization¹¹.

Sometimes this type of polymerization is called a polyaddition or rearrangement polymerization. If a polyol containing more than two hydroxyl groups is used, then a branched or crosslinked polymer is formed. The crosslinking reaction may also be done by reacting a NCO- containing polymer with a polyol such as some polyacrylics. The resultant pendent hydroxyl groups along the backbone can react with diisocyanate to give urethane crosslinks. The very important area of coating technology is based on a reaction in Figure 2.9¹⁹.

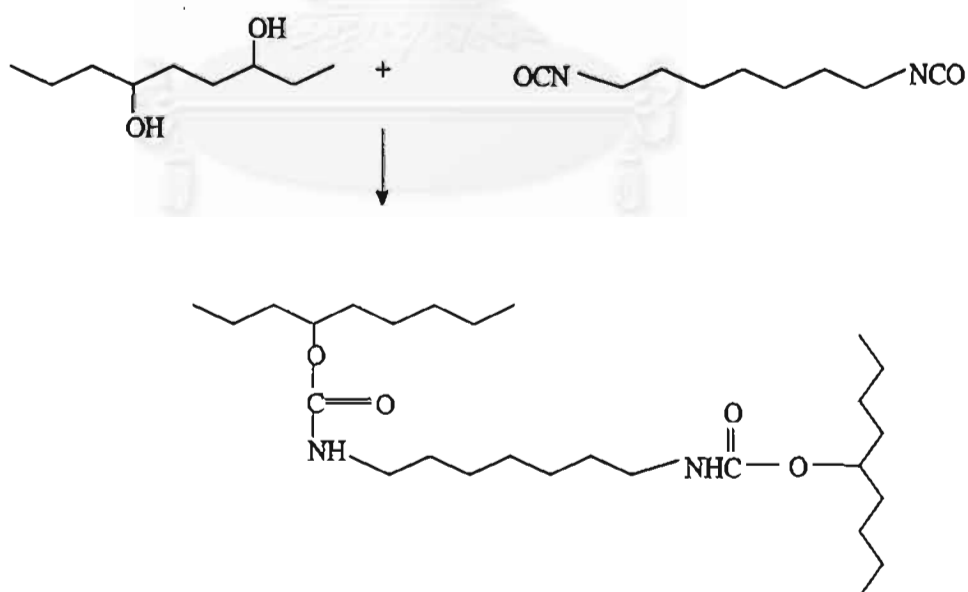


Figure 2.9 The crosslinking reaction between polyol and isocyanate¹⁹

Applications

Polyurethanes are used in a wide variety of applications, including fibers (particularly the elastic type), adhesives, coatings such as acrylic polyurethane top coat, elastomers and rigid foams²⁰.

2.2.1.4 Polyols

There are a variety of polyols that may be used with the polyisocyanate and melamine and selection will depend on their applications. The structure of the polyols plays a large part in determining the properties of the final coatings. Linear structure of difunctional polyol chains will lead to more flexible, less chemically resistant films. The crosslink density is influenced by the degree of functionality, leading to harder, less elastic, more chemically resistant and more thermally stable films. In addition, when the hydroxyl content increases, the resistance properties increase, but the rate of cure decreases¹². The crosslinking between melamine / polyol reaction in a film was seen in reference¹⁹. The difunctional polyols are mainly used as chain extenders or crosslinkers. Crosslinkers are used to obtain desired network structure in order to control the solvent resistance of the final coatings. The most widely chosen classes of polyols are polyethers, polyester, alkyd resins and acrylics. Other less popular polyols resins are epoxies, vinyls, cellulosics, poly (vinyl chloride), polyketone resins, castor oil and silicone resins. Takekuchi (1982) investigated the influence of molecular weights and the values of hydroxyl in acrylic polyols on crosslinking two-pack PU coating. They found more and more applications in PU coatings²⁰.

Acrylic polyols are usually obtained by copolymerizing hydroxyethyl and hydroxypropyl acrylate monomers with use of aliphatic polyisocyanates, this copolymer offers ambient curing and better properties such as exterior durability, high hardness, and high solvent resistance²¹.

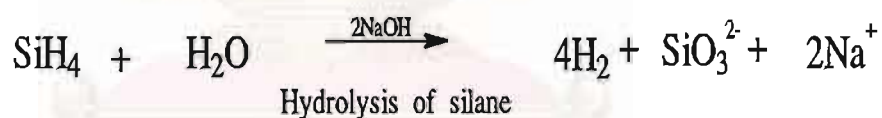
Applications

A wide range of polyols are used in polyurethane coatings which may belong to di- or polyfunctional polyols. Difunctional polyols are mainly used as chain extenders or crosslinkers. They are used as coatings, fibers, films, adhesives, potting compounds, and elastomers. Resilient polyurethane fiber (spandex) are used for foundation garments and swim suits¹⁵.



2.2.2 Inorganic Coating Materials

Inorganic coating materials are based on inorganic polymers of which their polymer chains are free of carbon atoms. The only elements which are capable of forming homopolymeric chains are sulphur, silicon, selenium, and tellurium; all of them can exist as polymer chains in elemental forms. Most inorganic compounds could be considered to be polymeric, at least in the solid state, due to the very strong ionic lattice forces that operate between the atoms and molecules¹. Most inorganic polymers, in particular the extremely abundant naturally occurring silicate minerals, are highly cross-linked and are therefore hard and strong, but brittle and hardly insoluble with high softening points. The stability of heteropolymeric chains of silicon and tin is higher than that of homopolymeric chains. For example, the strength of the silicon-carbon bond in the silicarbons is 58 kcal/mole, and that of the silicon-oxygen bond in the siloxanes is 89 kcal/mole. The higher degree of stability of the siloxane bond is also demonstrated by the formation of sodium silicate when silane is hydrolyzed in the presence of sodium hydroxide. The scheme of hydrolysis of silane is shown as below¹:

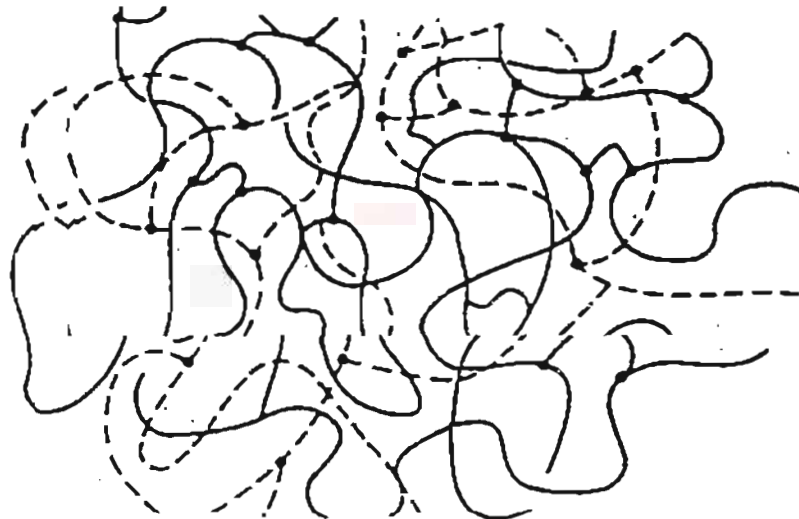


The abundance of stable mineral silicates is additional evidence of the stability of the silicon-oxygen linkage. The use of inorganic materials for coating application is limited due to their films tending to shrink easily. Due to their unique clarity properties, inorganic materials are found to improve clarity of organic polymeric materials and enhance other proportion of organic/inorganic materials^{22,23}.

2.2.3 Organic/Inorganic Coating Materials

2.2.3.1 Structure

An inorganic/organic material, a composite material is developed to an innovative composite material. Generally, a composite material has a heterogeneous structure containing two or more phases arising from its components⁵. The phases may all be continuous or more phases may be dispersed within a continuous matrix. The structure of inorganic/organic materials can form 'Interpenetrating Polymer Network's (IPNs). IPNs is a type of combination between two polymer to form the network structure. Polymers have been intimately mixed through synthesis or crosslinking reaction. Therefore, two different crosslinked polymers can be blended homogeneously. As a result, improved physical and mechanical properties of such materials significantly obtained. Example of schematic representation of an IPNs can be shown as below;²⁰



= polymer A ; ----- = polymer B

2.2.3.2 Processing

Since the advent of a sol-gel process, inorganic/organic hybrid could be prepared at relatively mild temperatures. Basically, the sol-gel process means the synthesis of an inorganic network by a chemical reaction in solution at low temperature⁶. The sol-gel process has the formation of an amorphous network at least in the first step. Most of the transition metals and the group III and group VI element can be precipitated as gel-link hydroxides in aqueous solution. The precursor which is able to form reactive inorganic monomers or oligomers can be used for sol-gel techniques. Even finely divided silica particles can be peptized and used for the preparation of sols. The most work in the sol-gel field has been performed by use of alkoxides as precursors. Alkoxides provide a convenient source for inorganic monomers which in the most cases are soluble for inorganic monomers which in the most cases are soluble in common solvents. Another advantage of the alkoxide route is the possibility to control rates by controlling hydrolysis and condensation. This equation can show as below.²⁴

HYDROLYSIS

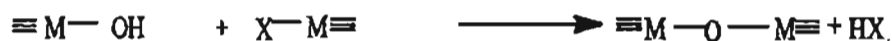


M = Metal or Si

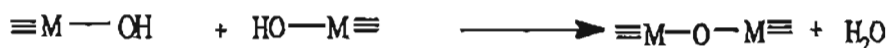
X = reactive ligand like halogen, OR, NR₂, acylate

CONDENSATION

ALCOHOL CONDENSATION



WATER CONDENSATION



This equation can present state-of-the-art in the sol-gel field clearly describing the basic feature of the sol-gel process: The hydrolysis rate in general depends on the type of precursors and the reactive monomers are produced at different rates. The condensation in general can not be separated from hydrolysis, the consumption in rate of reactive monomers by condensation can influence the production rate by equilibrium too. On the other hand, the condensation rate is determined by the production rate of monomers. The sol-gel process can be illustrated in Figure 2.9²⁶.

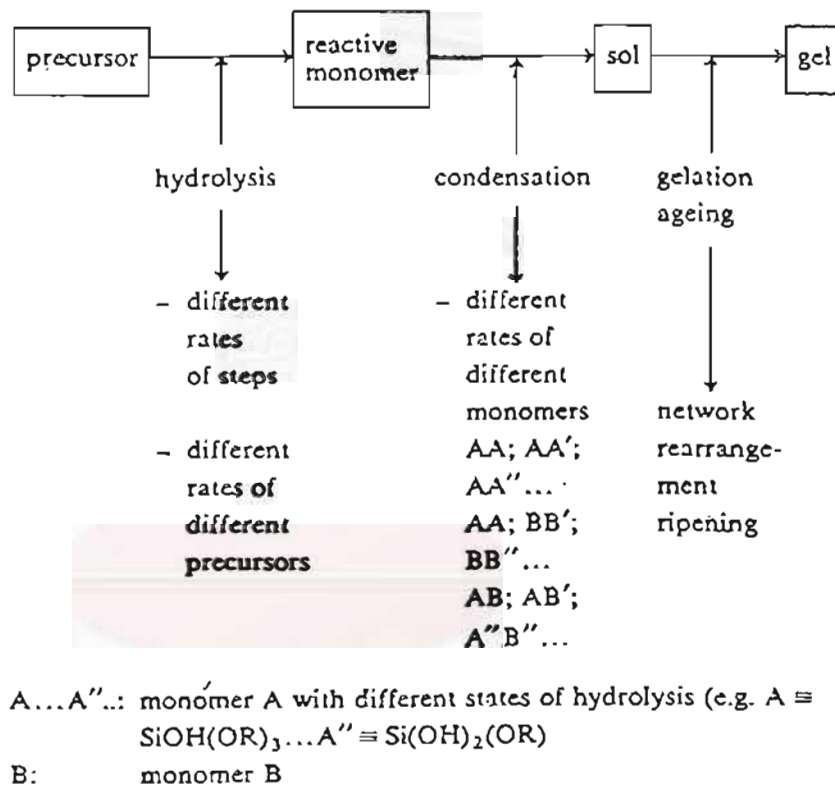


Figure 2.9 The sol-gel process²⁶

As already indicated in Figure 2.9, homogeneity of gels is very important for the further processing of material properties.

2.2.3.3 Advantage

The advantages of the sol-gel process for material synthesis which can be summarized as follows²⁷:

- An easy way to purify precursors
- An easy way to get homogeneous distribution of precursors
- An easy way to introduce trace elements
- Its possible use of chemistry to control reactions
- A pre-inorganic network formation in solution
- The introduction of permanent organic groupings in solution leading to prepare inorganic/organic hybrid material
- Allowing to adjustment of appropriate viscosity for coating

2.2.3.4 Example of applications

The novel inorganic/organic composites are useful in coating application, example transparent inorganic/organic copolymers by sol-gel process; Thermal behavior of copolymers of Tetraethyl Orthosilicates (TEOS), Vinyl Triethoxy silane (VTES) and Hydroxymethyl methacrylate (HEMA) monomers. Three types of inorganic/organic copolymers have been prepared in a one-step sol-gel process. The one step sol-gel process was carried out in mixtures of three monomeric components of HEMA-VTES-TEOS. They reported the synthesis of three component hybrid material that were prepared by an hydrochloric acid catalyzed sol-gel process. In one step, using co-condensation and co-polymerization of TEOS, VTES and HEMA monomer. Copolymers with HEMA, which is able to form a linear organic polymer that can be linked to silica. The HEMA molecule is small, it can be distributed throughout the silica network, The Si-OH network can form hydrogen bonding by hydroxyl groups together with carbonyl groups. A schematic diagram of the polymerization of HEMA-VTES-TEOS is shown in Figure 2.10²⁸.

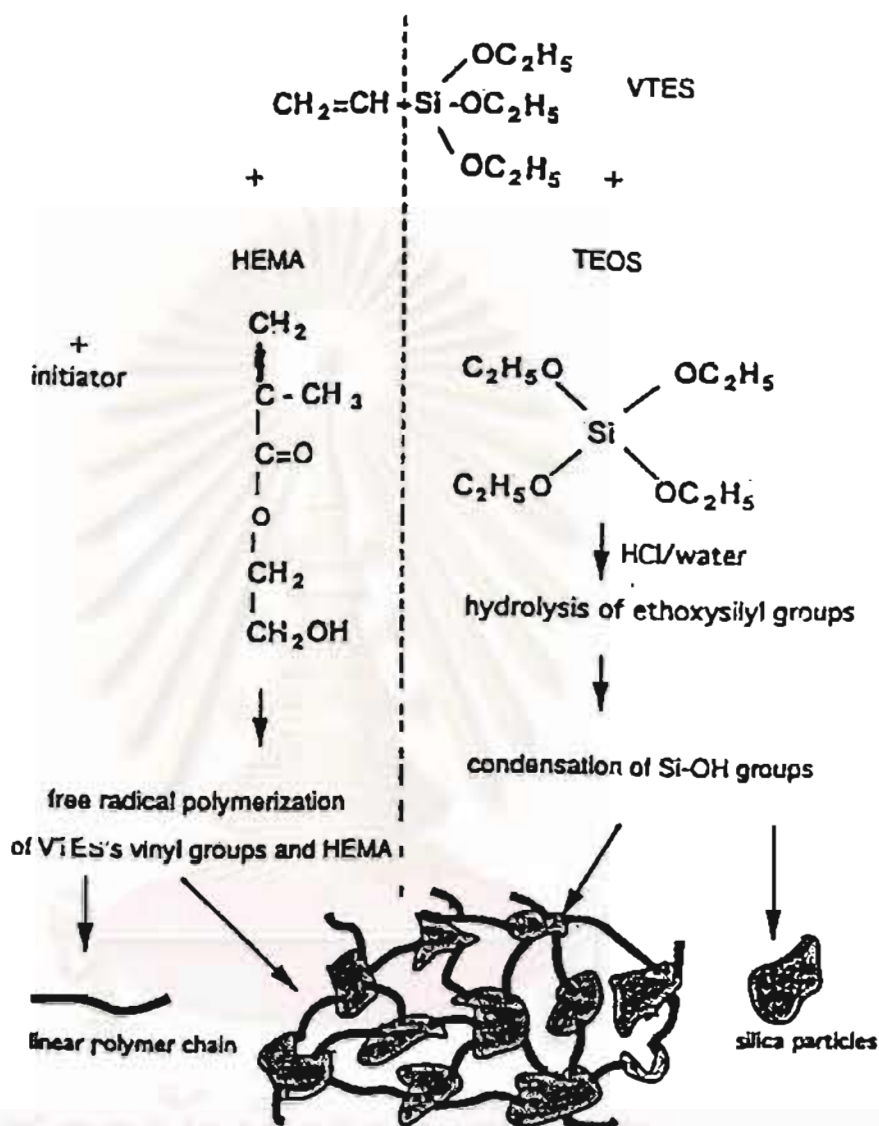


Figure 2.10 Schematic diagram of the polymerization of the three monomer system:HEMA-VTES-TEOS²⁸

Thermal analysis of the film can be characterized by TGA. The thermal stability's of three component inorganic/organic copolymers depend strongly both on the silica content and the type of organic monomer. The least thermal stability was exhibited by HEMA copolymers because of the linear structure of the organic components.

2.3 Relevant Literature Review

G. Michael and Lazzara [1984] studied techniques to measure melamine / polyol reactions in a film. These techniques use a Fourier Transform Infrared spectrometer (FT-I R), a solid state ^{13}C Nuclear Magnetic Resonance spectrometer (^{13}C NMR) and a flow oven gas chromatograph. These techniques continuously measure functional group changes and reaction volatiles produced while melamine / polyol films cure. The chemical changes that occur when a polyol reactions with a fully alkylated melamine, the resulting of these cure products were characterized by the endless transesterification reaction²¹.

T.Yamamoto,T.Nakamichi and O.Ore [1988] studied kinetic of carboxylic acid catalyzed melamine/polyol reaction in a film. This paper describes the reaction mechanisms of hexamethoxymethylmelamine (HMMM) with acrylic polyol under catalysis of carboxylic acid which was incorporated into the polyol. To investigate how the chemical reaction kinetically proceeds and the network formation progresses during cure, change in IR spectra by monitoring the disappearance of functional groups (OH, CH_3) and those in viscosity have been measure. The increase in viscosity was so small in the early stages of the reaction that the three-dimensional networks seemed not to be formed, which means that the functional group mobility was not constrained and it became possible to analyze the chemical reactions kinetically. In the present of a carboxylic catalyst, the chemical reaction for the primary hydroxylated polyol system was only transesterification at cure at temperatures of $140\text{ }^\circ\text{C}$ below, but at $160\text{ }^\circ\text{C}$ or above the self-condensation reaction completed³.

J.W Collette,P.Corcoran,H.P.Tannenbaum and W.S.Zimnt[1986] studied the mechanism and kinetic of the crosslinking of acrylic polyols with HMMM. In the crosslink reaction the solution became gel formation and methanol release are found to be

affected by the concentration of $-OH$ and CH_3O- groups and the nature of the catalyst (*p*-toluenesulfonic acid) to be proportional with the hydrogen ion concentration. Mechanism studies the primary chemical reactions is the release of methanol and occur regardless of stoichiometry, oligomer molecular weight, or functionality. The physical phenomena of gelation involves network formation through methylene bridges and occurs only if the stoichiometry and functionality are in the appropriate limits. Kinetics studies how the networks formation and transesterification between $-OH$ groups in acrylic polyols and CH_3O- groups in HMMM. The kinetics of the methanol could be compared with the gel forming reaction by means of a crosslink model. In order to obtain this kinetic capable of quantitatively measuring the instantaneous concentration of volatiles liberated as a function of time was developed².

H.Schmidt (1988) survey over the role of chemistry of materials preparation by sol-gel process. The basic chemistry of sol-gel process is complex due to the different reactivities of the network forming and the network modifying components and the wide variety of reaction parameters. These chemistry has to help to find out the important parameters for materials tailoring. Progress in this also involves the possible of incorporating organic into inorganic networks. Most work in the sol-gel field has been performed by the use of alkoxide as precursors alkoxide provide a convenient source for the inorganic monomers which in the most cases are soluble in common solvents. The advantage studied of sol-gel process were appropriate viscosity for coating application, an easy way to purify precursors and the densification to inorganic solids and comparatively low temperatures. The reaction mechanism was involved of hydrolysis and condensation, and as a result could investigate by FT-IR, NMR, GC, MS, Raman and SEM²⁹.

B.Wang, G.L.Wilkens, J.C Hedrick, S.C Liptak, and J.E McGrath[1991] have developed new high refractive index organic/inorganic hybrid materials from sol-gel processing. To study two series of novel hybrid materials have been prepared by using

titanium tetrapropoxide as the inorganic component to react with triethoxysilane-capped organic oligomer being either poly(acrylene ether ketone) or poly(acrylene ether sulfone). These hybrid materials with different ratio of organic/inorganic content relationship to structure property behavior. At higher inorganic composition they show a higher organic oligomer composition show a higher flexibility. Therefore appear that these new ceramer system may lean potential applicability for high refractive index optical coatings²².

Yen Wei, Pachun Yang and Ligang Tang [1993] studied synthesis, characterization, and properties of new polystyrene-SiO₂ hybrid sol-gel materials. An organic-inorganic hybrid materials has been prepare by incorporating polystyrene structure units covalently into the SiO₂ glass network via the sol-gel approach. The polymer precursors were synthesized by free-radical copolymerization of styrene with 3-(trimethoxysilyl)propyl methacrylate (MSMA) at various feeds. These copolymer were then hydrolyzed and co-condensed with tetraethyl orthosilicate in tetrahydrofuran (THF) at room temperature. The number average molecular weight of polymer precursor was 18700 to 26200, its characterized by GPC and the new hybrid materials were characterized with FT-IR, TGA, DSC, SEM and X-ray diffraction. The film hybrid materials have excellent optical transparency. For these it show well-defined glass transition temperature (T_g) in DSC. The bulk properties of the materials including density, hardness and refractive index were found to vary with the contents of SiO₂ and the polymer components between the values of the pure SiO₂ sol-gel glass and the pure polymer. Therefore, these properties can be designed and controlled quantitatively by changing the composition of the polymer and SiO₂ components²⁶.

B. Tamami, C. Betrabet and G.L. Willkers [1993] have developed new ceramer high optical abrasion resistant transparency coating materials based on functionalized melamine and tris(*n*-aninophenyl)phospine oxide compound. These synthesis of new high optical abrasion resistance coating reagent in DMF solution. The process was prepared by a sol-gel method and heating of this compound form crosslinked organic/inorganic

network. These highly functionalized compounds have been used for coating a bisphenol-A polycarbonate substrate. The thickness of these films was in the range of 1-3 μ m. The film shown the highly crosslinked materials based on sol-gel reaction of the alkoxy silane group exhibit optical transparency and good abrasion resistance⁴.

E.S Ntsihele and A.Pizzi [1995] investigated the crosslinked coatings by co-reaction of isocyanate-methoxymethylmelamine systems. They studied the two-components (isocyanate/methoxymethyl melamine) and three-components (isocyanate/methoxymethyl melamine/polyol) systems were found capable of producing high-solids, high-temperature coating by cross-linking reactions. The two components system showed that all the cross-linking reactions of melamine-acylic, urethane linkages as well as melamine-isocyanate through methylol and hydrolyzed methoxymethyl groups can occur. A blocked isocyanate was then used where by the methoxymethyl melamine reactions at an earlier stage and urethane formation is delayed. The overall result seem to be that use of high temperatures achieves improved cross-linking. This probably because high temperatures would promote the acylic/-NCO reactions producing the urethane cross-linking. The transesterification reaction occurred from -NCO groups in isocyanate and -OH groups in polyol. The cure films of the three-components were smooth, glossy and fairly strong. But, the cure films of two-components were quite brittle³⁰.

2.4 Purposed concept for this research

In this research, the organic/inorganic hybrid materials for clear coating application will be prepared. These materials are based on alkoxy silane functionalized acrylic copolymers. The preparation of this materials involves in two steps; the synthesis of poly(HEMA-co-HPA) and then functionalization of poly(HEMA-co-HPA) with IPSE. The chemical reactions can be written as follows;

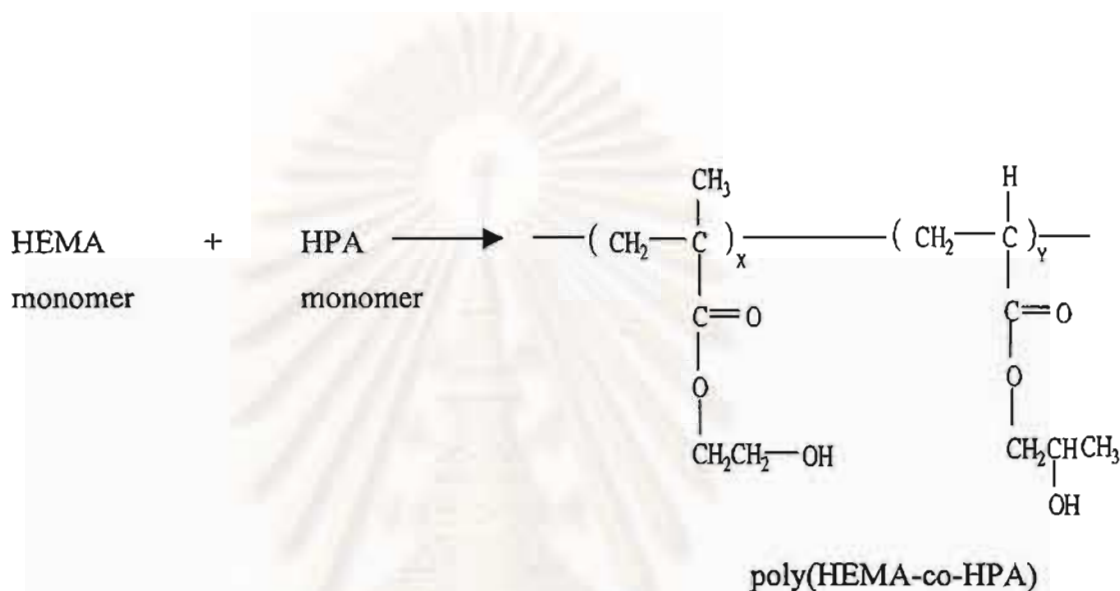


Figure 2.12 Synthesis of poly(HEMA-co-HPA)

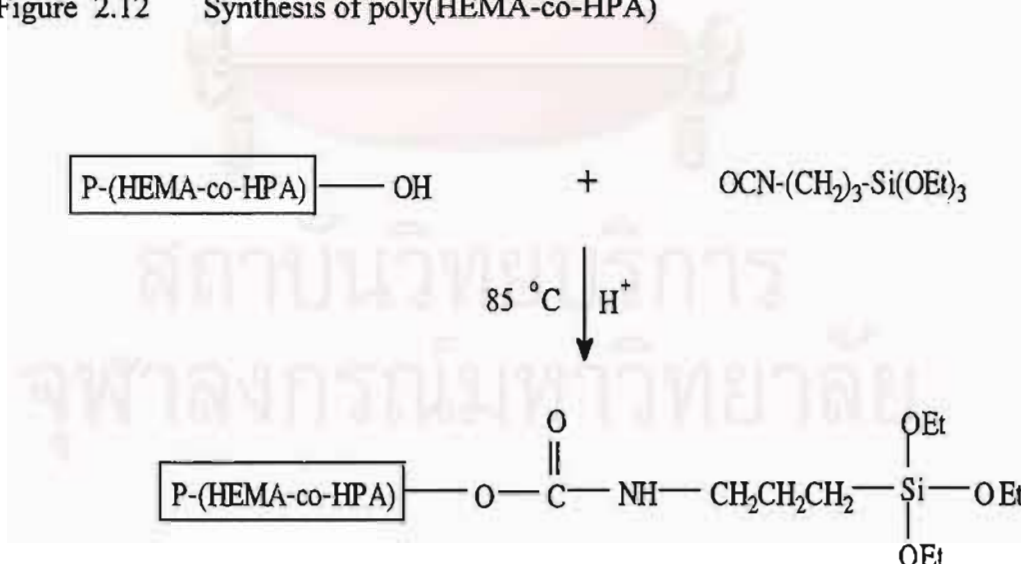


Figure 2.13 Functionalization of poly(HEMA-co-HPA) with IPSE

The molecular weight of poly(HEMA-co-HPA) will be controlled in the range of 10,000-15,000 g/mole. Characterization techniques including GPC, ^1H NMR and DSC, will be employed to obtain the desired compound. The functionalized acrylic copolymer has two functional groups, alkoxy silane group and hydroxyl group. The obtained polymer will be then used as clear coating by mixing with HMMM and /or TEOS in DMF medium. To the prepared coating formulation, p-TSA as a catalyst is added prior to coating. The coated substrate (PC sheet) is dried in vacuum before curing at 125 °C for 14 hours. It is expected that two types of crosslinking reaction occur during curing; the transesterification reaction between methanol groups of HMMM with of hydroxyl groups poly(HEMA-co-HPA) to produce organic network and sol-gel reaction of $-\text{Si}(\text{OEt})_3$ to produce inorganic network. The schemes of organic/inorganic network production of two-components and three-components systems represented in Figure 2.14 and Figure 2.15, respectively.

Two types of coating formulations will be studied; functionalized poly(HEMA-co-HPA)/HMMM system and functionalized poly(HEMA-co-HPA)/HMMM/TEOS system. The various ratios of coating composition will be carried-out in order to maximize the properties of coating films. It is anticipated that these films have good abrasion/scratch resistance as well as high transparency. The clarity of coating films is determined by the transmittance measurement using a UV/VIS spectrophotometer. The results after testing are compared with that obtained from an uncoated PC sheet. Finally, the coated films are evaluated for surface properties by abrasion testing and scratch testing. This measurement is to record the maximum load for causing line appearance on the PC surface.

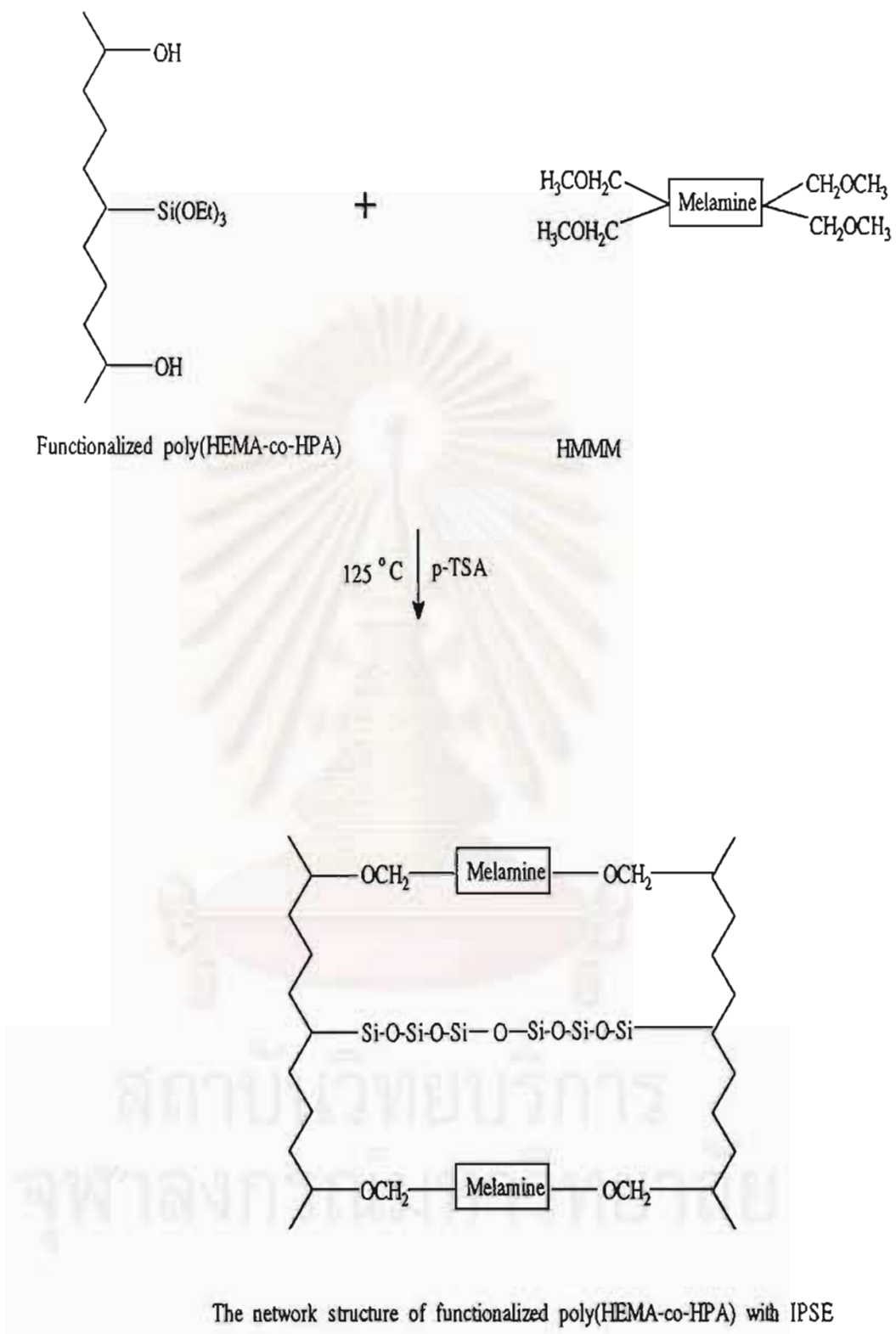


Figure 2.14 The network structure of organic/inorganic films
(Two- components system)

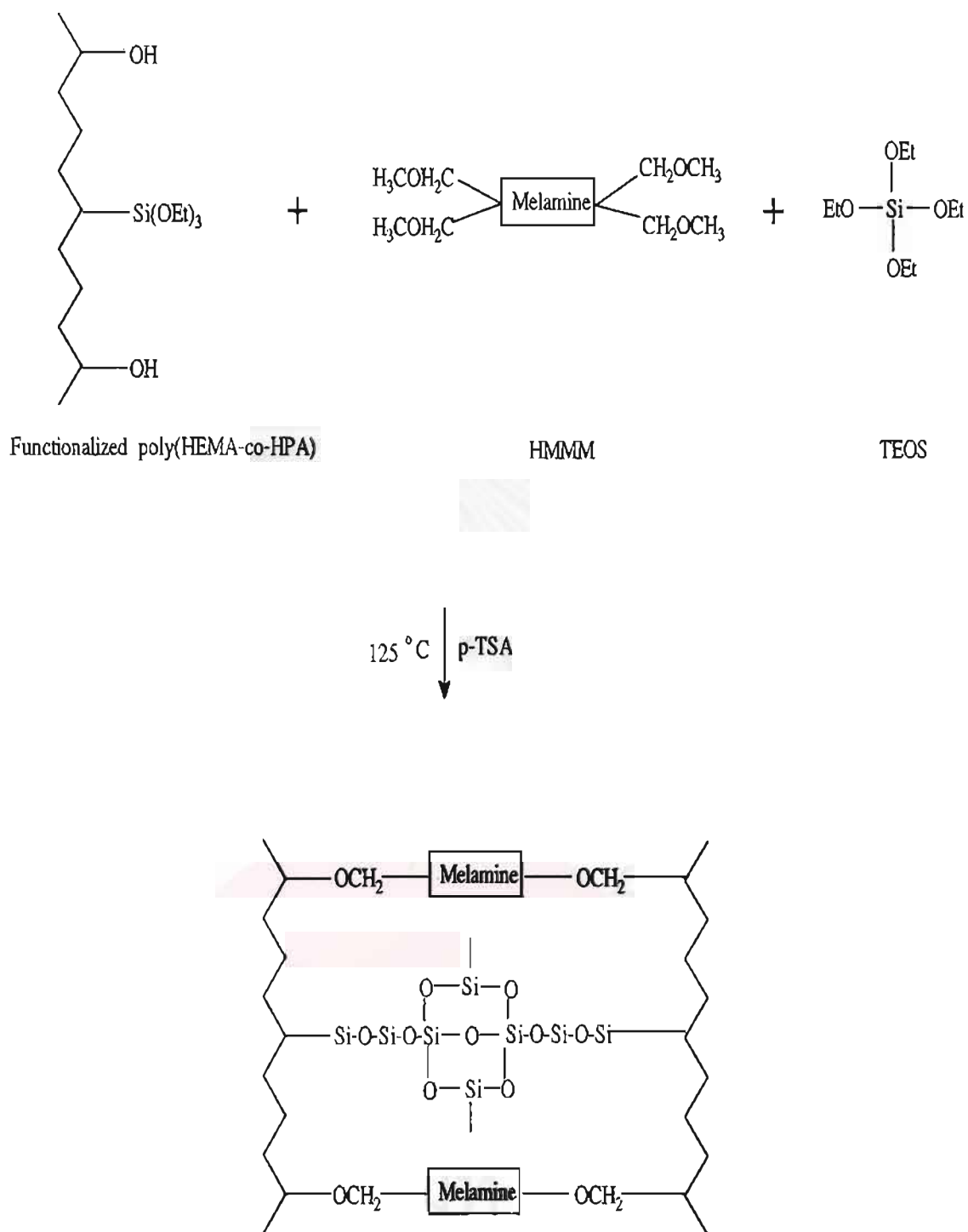


Figure 2.15 The network structure of organic/inorganic films (Three-components system)

CHAPTER 3

EXPERIMENTAL

3.1 Equipment

1	Nuclear Magnetic Resonance Spectroscopy (¹ H NMR)	Jeol INM A 500
2	Fourier Transform Infrared Spectroscopy (FT - IR)	Nicolet Impact 400 D
3	Gel Permeation Chromatography (GPC)	Milipore Model water 150 cv
4	Differential Scanning Calorimetry (DSC)	Perkin Elmer Model DSC 7
5	Thermogravimetric Analysis (TGA)	Perkin Elmer Model TGA 7
6	Scatch Test Apparatus	Sheen Instruments
7	Abrasion Scrub Tester	Sheen Instruments
8	UV / VIS Spectrophotometer	Macbeth Model ColorEye7000

3.2 Chemicals and Materials

1. benzene (Fluka)
2. benzoyl peroxide (BPO, Merck)
3. dimethyl formamide (DMF, Fluka)
4. ethanol (Fluka)
5. hydroxyethyl methacrylate (HEMA , Siam Chemical Industry Co.,Ltd)
6. hydroxypropyl acrylate (HPA , Siam Chemical Industry Co.,Ltd)
7. hexamethoxymethyl melamine (HMMM , Monsanto , Resimene 747)
8. hexane (Fluka)
9. 3 - isocyanatopropyltriethoxysilane (IPSE , Fluka)
10. laurylmercaptan (Fluka)
11. methanol (Fluka)
12. p - toluenesulfonic acid (p - TSA , Fluka)
13. tetraethyl orthosilicate (TEOS , Fluka)
14. Polycarbonate Sheets (Eastern Polymer Industry Co.,Ltd)

3.3 Synthesis of poly (hydroxyethyl methacrylate-co-hydroxypropyl acrylate), (Poly (HEMA-co-HPA))

Random copolymerization of HEMA with HPA initiated by benzoyl peroxide (BPO) and laurylmercaptan as a chain transferring agent was carried out in a 500 ml three-necked round bottom flask equipped with nitrogen gas inlet, The mixture of 50 wt % HEMA (18.3829 g) and 50wt% HPA(18.3825 g) BPO (2.0762 g, 5.5% based on total monomer content), and laurylmercaptan (0.1177 g 0.32% of total weight) were charged to reaction vessel contains 331 g of ethanol and the copolymerization was performed at 60 °C under nitrogen atmosphere for 24 hours. The obtained copolymer was purified by repeated precipitation in a mixed solution of benzene and hexane (1:1 v/v ratio). The copolymer was washed several times with a hexane/benzene mixture to remove unreacted monomers and other impurities and then was dried at 60 °C under vacuum for 24 hours.

The characterizations of the copolymer were performed by ¹H-NMR, FT-IR technique; the molecular weight was determined by GPC; and the glass transition temperature (T_g) was measured by DSC.

The reaction scheme of poly (HEMA-co-HPA) may be written as follows:

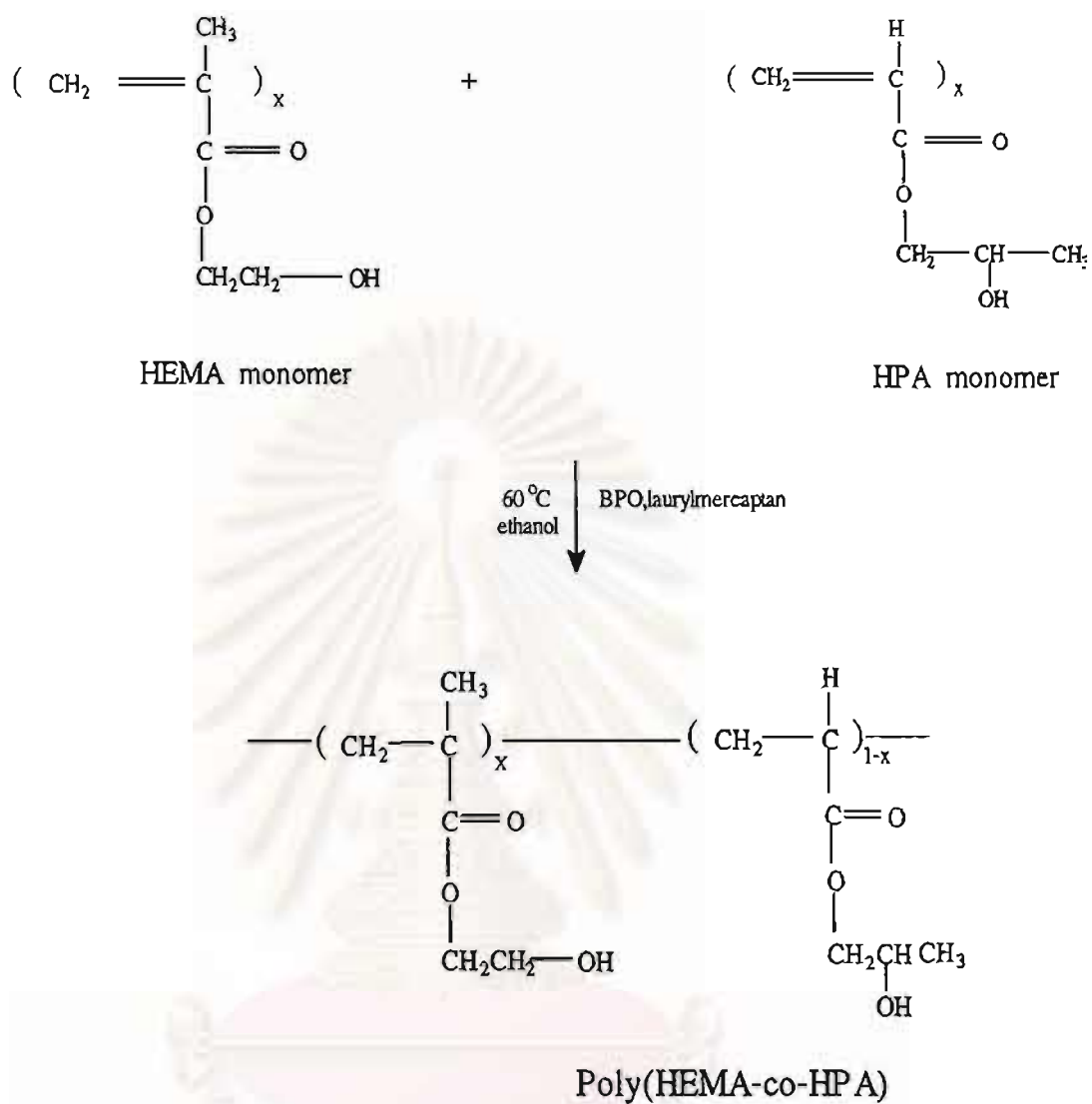


Figure 3.1 The synthesis reaction of Poly (HEMA-co-HPA) from HEMA and HPA monomers

3.4 The Functionalization of poly (HEMA-co-HPA) with Isocyanatopropyl-triethoxysilane.

The alkoxy silane functionalized copolymers were prepared by the reaction of poly (HEMA-co-HPA) with 3-isocyanatopropyltriethoxysilane (IPSE). A solution about 1.37 g of poly (HEMA-co-HPA) in dried DMF about 11.23 g was prepared in a 25 ml round bottom flask purged with nitrogen gas to remove dissolved oxygen. To this solution IPSE was added under vigorous stirring while the temperature was raised to 85 °C . The reaction was carried out at this temperature for 8 hours. The various amounts of IPSE were used as shown in Table 3.1

The progress of the reaction was monitored using FT-IR spectroscopy by analyzing the reaction solutions at every 4 hours until the isocyanate peak (about 2270 cm^{-1}) completely disappeared. A solution containing alkoxy silane functionalized poly (HEMA-co-HPA) was subsequently used without further purification. In this experiment, the copolymes with various degrees of functionalization were prepared as shown in Table 3.1

Table 3.1 Poly (HEMA - co - HPA) functionalized with IPSE at different mole ratios

Sample	IPSE*		Poly(HEMA-co-HPA) Weight (g)	DMF Weight (g)
	Mole %	Weight (g)		
AM1	10	0.2605	1.3745	11.2872
AM2	20	0.5212	1.3752	11.2864
AM3	30	0.7816	1.3762	11.2857
AM4	40	1.0421	1.3717	11.2826
AP3	30	0.7815	1.3732	11.2855
AP4	40	1.0421	1.3725	11.2832
AP5	50	1.3026	1.3744	11.2843
AP6	60	1.5632	1.3729	11.2839
AP7	70	1.8237	1.3718	11.2821

* based on mole % of hydroxyl groups of the copolymer

The reaction can be schematically represented by the following equation :

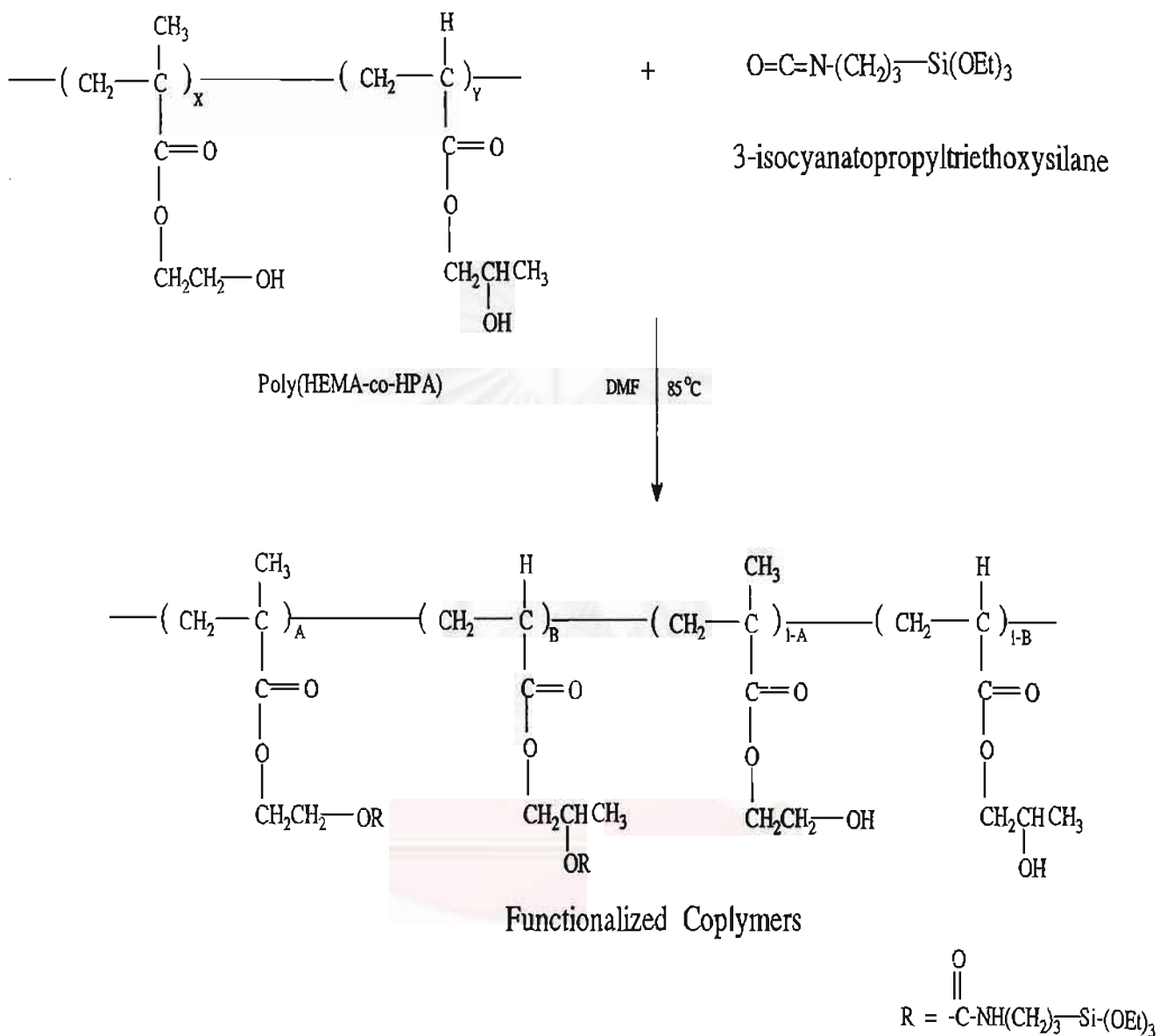


Figure 3.2 The synthesis reaction of copolymer functionalized with IPSE

3.5 Characterization

3.5.1 ^1H NMR Analysis

Proton NMR spectra were recorded on a Jeol JNM A 500 spectrophotometer operating at 500 MHz with deuterated acetone as a solvent and tetramethylsilane (TMS) as an internal reference. The chemical shifts (δ) reported are given in part per million.

3.5.2 Molecular Weight Determination by GPC

Gel permeation chromatography equipped with a Millipore model water 150 CV solvent delivery module, a refractometer as **detector**, and an Ultrastryagel linear column using tetrahydrofuran (THF) as eluvant was **employed** to measure the molecular weight of the copolymers. **The molecular weight** and molecular weights distributions were calculated against those of **monodispersed** polystyrene standards with molecular weights resolving range of **500-10,000,000**, flow rate of 1 ml/min and temperature at 30 °C.

3.5.3 Glass Transition Temperature (Tg) Determination by DSC

DSC analysis was performed on a Perkin Elmer model DSC 7 with a measuring **temperature range of** -100 to 220 °C and a heating rate of 10 °C/min.

3.5.4 FT-IR Spectroscopy

Fourier-transform infrared spectroscopic measurement was performed on Nicolet Impact 400D spectrometer. The samples of the functionalization of poly(HEMA-co-HPA) with IPSE were coated on KBr pellets. The parameters were used as follows: scanning range 4,000 400 cm^{-1} , scan number of 32 cm^{-1} , and resolution: 4 cm^{-1} .

3.6 Application of Organic / Inorganic Coating Composites onto PC Sheet

3.6.1 Preparation of a Coating Formulation

3.6.1.1 Preparation of Coating Solutions Containing TEOS (three components system)

A coating solution was prepared by mixing the solution of the alkoxy silane functionalized poly(HEMA-co-HPA), hexamethoxymethyl melamine (HMMM) and tetraethyl orthosilicate (TEOS). A p-toluenesulfonic acid (0.1 wt% of the total solid content) was then added. The coating mixture was stirred in a 20 ml beaker covered with parafin film under controlled temperature at 20 °C and not over 65% relative humidity. The resulting homogeneous solution was applied on to a PC substrate cleaned by ethanol. The coated PC sheet was dried at 60 °C before curing at 125 °C for 14 hours. In this experiment, coating formulas were prepared, and the amounts of coating compositions used were indicated in Table 3.2

Table 3.2 Composition of coatings formulations in organic/ inorganic coating composite contain TEOS

Copolymer		HMMM		TEOS		p-TSA	
Batch	Weight(g)	%weight ^a	Weight(g)	%weight ^b	Weight(g)	%weight	Weight(g)
AM1a	1.2764	50	0.4116	40	0.6586	0.1	0.0037
AM1b	1.2772	40	0.3458	50	0.8782	0.1	0.0041
AM2a	1.2518	40	0.3452	40	0.6587	0.1	0.0042
AM2b	1.2519	30	0.2742	50	0.8782	0.1	0.0042
AM3a	1.2284	30	0.2744	40	0.6586	0.1	0.0043
AM3b	1.2018	20	0.2055	50	0.8783	0.1	0.0044
AM4a	1.2280	20	0.2058	40	0.6586	0.1	0.0045
AM4b	1.2021	10	0.1375	50	0.8784	0.1	0.0046
AM4c	1.2019	50	0.3454	10	0.2196	0.1	0.0049

a = based on hydroxy groups, b = based on IPSE

3.6.1.2 Preparation of Coating Formulation without TEOS (two component system)

This experiment was carried out in order to compare the surface performance of coated films which contain free TEOS with those having TEOS. A coating solution was prepared by mixing the solution 12 g of alkoxy silane functionalized poly(HEMA-co- HPA) with HMMM. A p-TSA (0.3 wt% of the total solid content) was then added. The coating mixture was stirred in a 20 ml beaker at room temperature, The resulting homogeneous solution was applied onto a cleaned PC substrate. The coated PC sheet was dried at 60 °C before curing at 125 °C for 14 hours. The various coating formulas were prepared and the amounts of coating compositions used were indicated in Table 3.3.

Table 3.3 Composition of coatings formulations in organic/inorganic coating composite without TEOS

Copolymer		HMMM		p-TSA	
Batch	Weight(g)	wt %*	Weight(g)	wt%	Weight(g)
AP3	1.2261	70	0.4805	0.3	0.0079
AP4	1.2024	60	0.4112	0.3	0.0084
AP5	1.1813	50	0.3458	0.3	0.0090
AP6	1.1586	40	0.2740	0.3	0.0096
AP7	1.1370	30	0.2055	0.3	0.0102

* = based on copolymer hydroxy groups

3.6.2 Application of coatings

The coating solution from sections 3.6.1.1 and 3.6.1.2 were applied onto PC prepared substrates by a four-side coating applicator (Sheen Instrument). The coating layer obtained was approximately 90 μm . thick. The size of PC sheet used was 12x18 cm with the thickness of 0.3 mm. The PC substrate was cleaned with ethanol and dried with a hair drier. The coated PC samples were dried again at 60 $^{\circ}\text{C}$ for 1 hour in a vacuum oven to remove solvents and volatile substances. Curing was carried out in a vacuum oven at 125 $^{\circ}\text{C}$ for 14 hours. The sample was taken and cooled down at room temperature. The cured PC sheets were evaluated for scratch/abrasion resistance properties. The clarity of virgin PC, coated/cured PC, and PC after scratch/ abrasion test was measured and compared.

3.7 Thermal Analysis (TGA) of coated / cured coating films

TGA analysis of the coating film was determination of weight loss of cured film which was carried out using Perkin Elmer model TGA7. Heating rate was performed at 20 $^{\circ}\text{C}/\text{min}$ from the temperature range of 25 to 700 $^{\circ}\text{C}$.

3.8 Evaluations of surface properties of coated/cured PC Sheet

3.8.1 Abrasion Testing

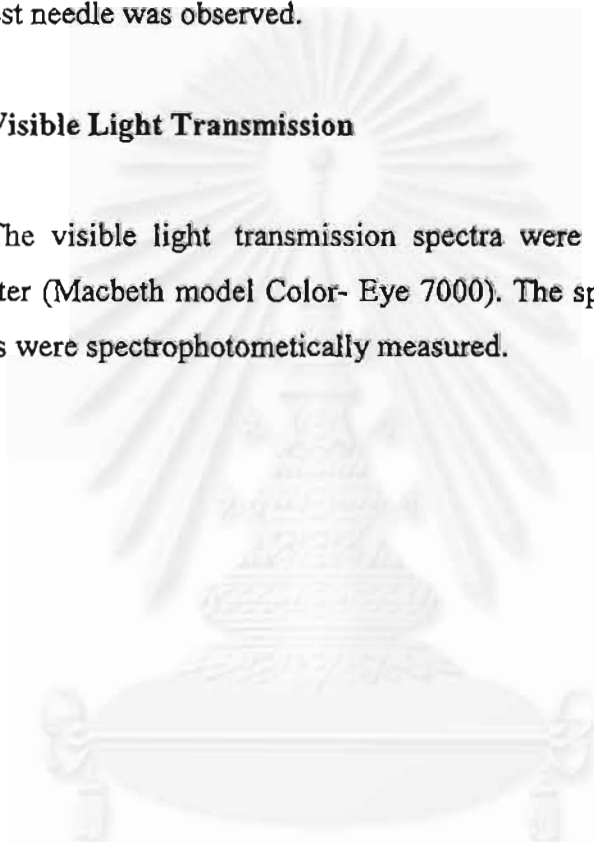
The abrasion resistance was performed by abrasion tester of Sheen Instruments Co., Ltd. Two brushes weighing 0.45 kg each were mounted on two holders. The testing samples were carried out under dry condition without of detergent or any other liquids. The measurement was recorded until the visible line appeared on the surface.

3.8.2 Scratch Testing

The scratch resistance was measured by scratch test apparatus Model Automatic Scratch test of sheen Instrument Co., Ltd. For the measurement, a scratch test steel needle loaded with a weight was moved on a testing sample surface. Measurements were carried out by gradually adding weights until a line on the specimen surface caused by the scratch test needle was observed.

3.8.3 Visible Light Transmission

The visible light transmission spectra were measured using UV/VIS spectrophotometer (Macbeth model Color- Eye 7000). The specimens were tested after abrasion testings were spectrophotometrically measured.



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterizations of Synthesized Poly(HEMA-co-HPA)

4.1.1 ^1H NMR Analysis

The proton NMR spectroscopy was employed to characterize the chemical structure of the copolymer by identifying the fingerprint of NMR spectrum. Figure 4.1 represents the ^1H NMR spectrum of poly(HEMA-co-HPA). It is common that methyl proton ($-\text{CH}_3$) should appear in the nearest region to the TMS reference. As can be seen from the spectrum, peaks at the region of 0.9-1.4 ppm can be assigned to methyl protons of HEMA as well as HPA's segments. Their surrounding electron environment is not entirely similar, resulting in appearing as overlapping signals. The signal shows up around 2 ppm corresponding to four methylene protons from polymer backbone. HEMA's ethylene protons and HPA's methylene protons are found further down field in the region of 3.5-5.0 ppm because of the electronegativity effect of surrounding oxygens.

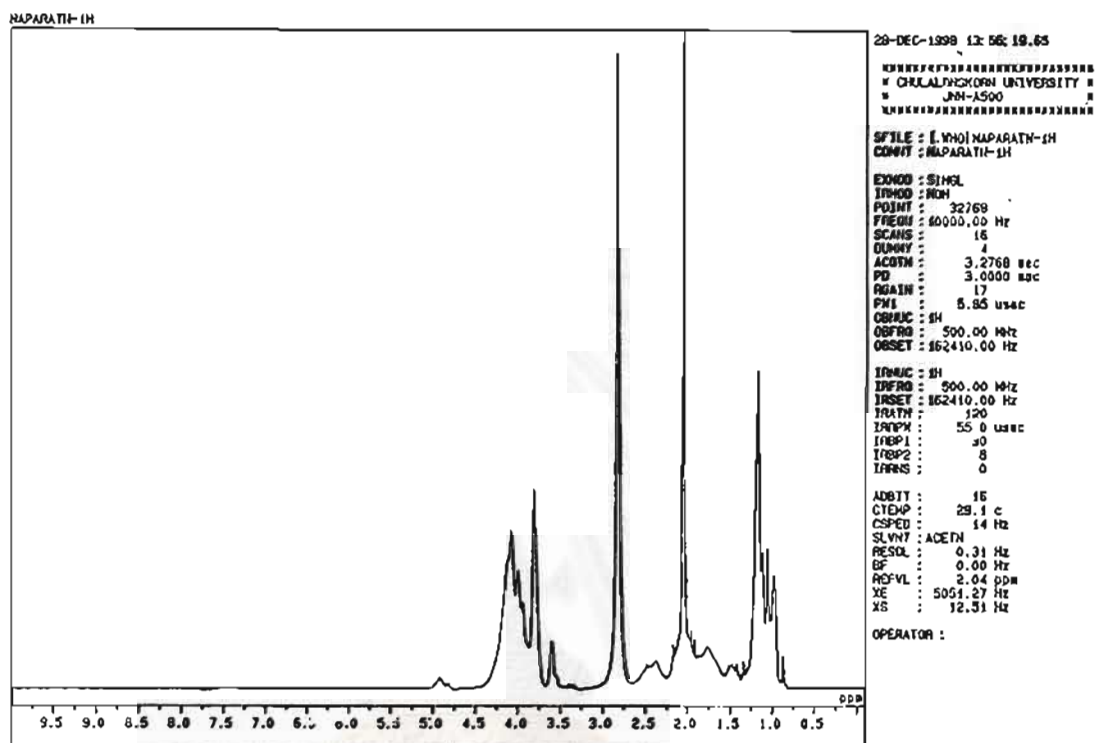
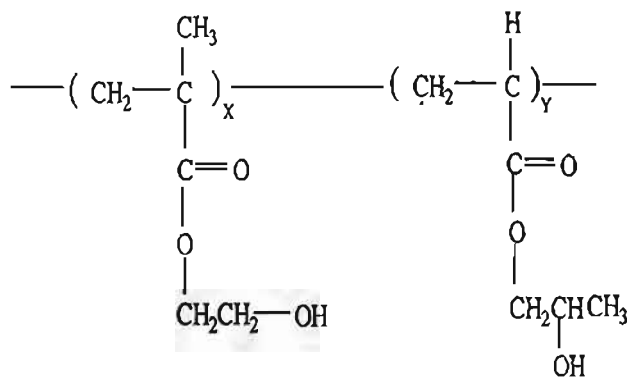


Figure 4.1 The ^1H NMR spectrum of poly(HEMA-co-HPA) in deuterated acetone solvent

The chemical structure of poly(HEMA-co-HPA) is shown below:



The chemical shifts of poly(HEMA-co-HPA) are summarized in Table 4.1

Table 4.1 The chemical shifts of poly(HEMA-co-HPA)

Assignment	Chemical shift(δ)
-CH ₃	0.9-1.4
-CH ₂ -, -CH-	1.4-2.5
-O-CH ₂ CH-, -O-CH ₂ CH ₂ -, -CH-O-	3.5-5.0

4.1.2 Determination of Molecular Weight Determine by GPC

The molecular weight of poly(HEMA-co-HPA) is characterized by GPC. The result is shown in Figure 4.2. Preferably, polymers having low molecular weights are suitable for coating applications for an easy control of the viscosity of coating formulation and obtaining better mixing when multicomponents are involved. The molecular weight of poly(HEMA-co-HPA) was determined as described in section 3.5.3. The average molecular weights of prepared poly(HEMA-co-HPA) determined by the GPC method were as follows; $M_n = 3,371$, $M_w = 13,215$, and $M_w/M_n = 2.07$. This copolymer was suitable for coating applications.

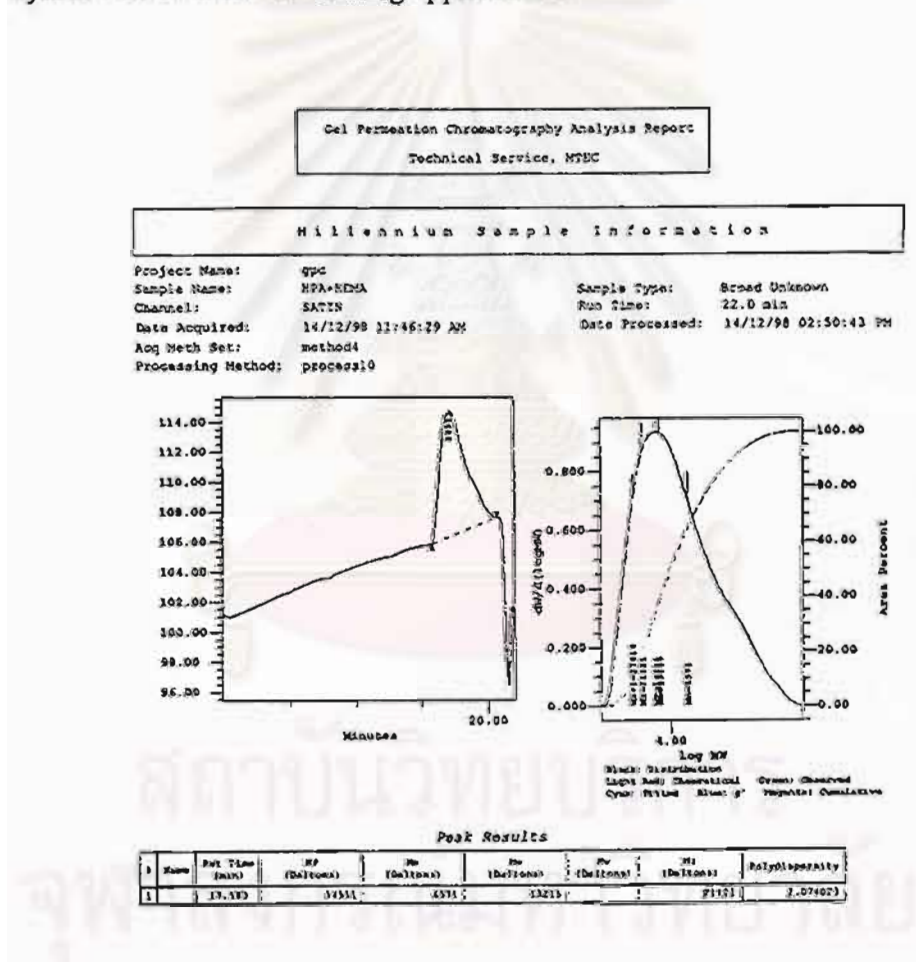


Figure 4.2 GPC chromatogram of poly(HEMA-co-HPA)

4.1.3 Measurement of Tg of Poly(HEMA-co-HPA) by DSC

For a comparison purpose, poly(HPA) and poly(HEMA-co-HPA) were prepared and characterized by DSC thermograms as given in Figure 4.3 and Figure 4.4, respectively.

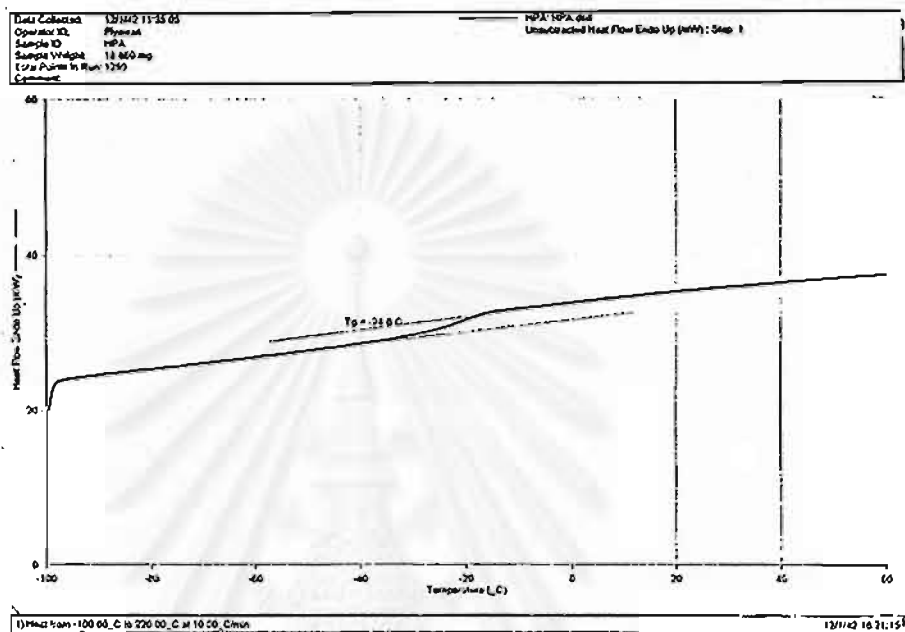


Figure 4.3 DSC thermogram of poly(HPA)

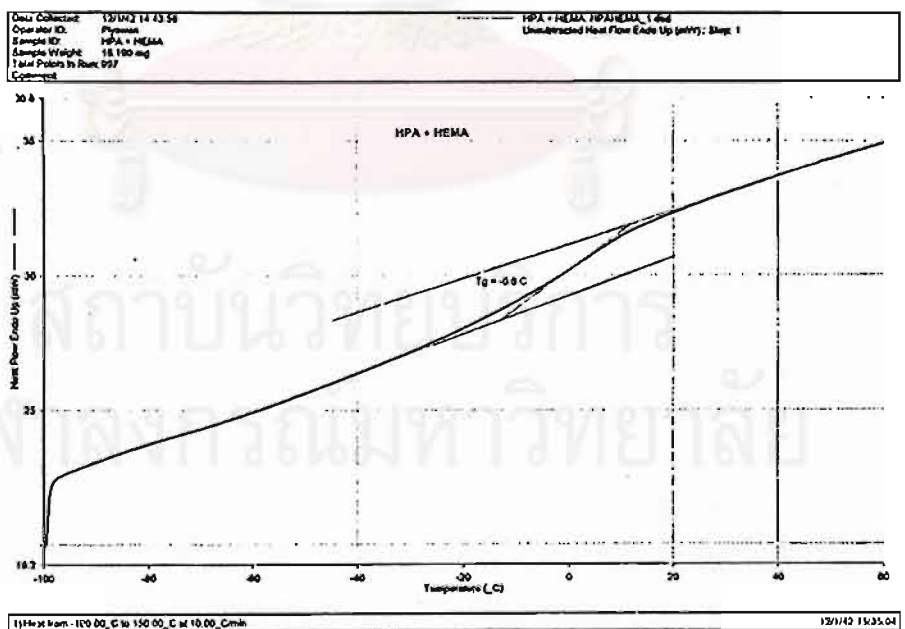


Figure 4.4 DSC thermogram of poly(HEMA-co-HPA)

Onset temperatures found at $-24.6\text{ }^{\circ}\text{C}$ (Figure 4.3) and $-0.6\text{ }^{\circ}\text{C}$ (Figure 4.4) are believed to be the T_g of poly(HPA) and poly(HEMA-co-HPA), respectively. From the literature, the poly(HEMA) homopolymer has a T_g value of $55\text{ }^{\circ}\text{C}$ (Polymer Science Dictionary,1996). T_g value of poly(HEMA-co-HPA) was higher than that of poly(HPA) but lower than that of poly(HEMA). According to T_g properties of polymers, T_g value of a copolymer is proportional to the composition of its homopolymer pairs. A measured T_g value of poly(HEMA-co-HPA) indicated that random copolymer was produced. The introduction of HPA segment into poly(HEMA) structure was to decrease the regularity of poly(HEMA) to obtain the suitable viscosity of coating formulation. A low T_g value of poly(HEMA-co-HPA) gave information that the prepared copolymer was rubber-like at room temperature.

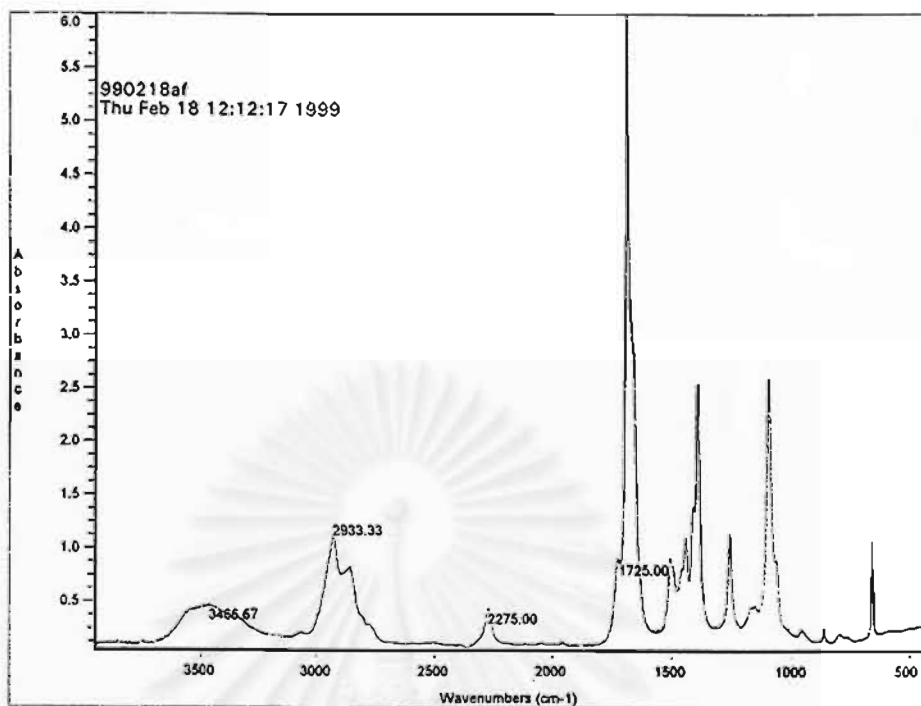


4.2 The functionalization of poly(HEMA-co-HPA) with IPSE.

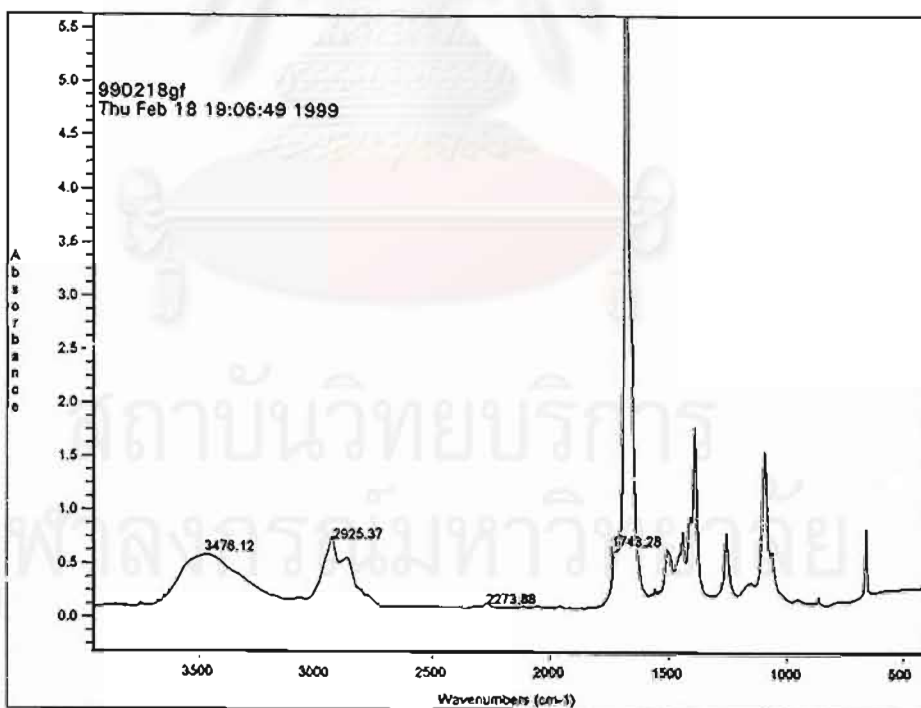
The reaction of poly(HEMA-co-HPA) with IPSE was monitored by FT-IR spectroscopy. The strong absorption band of isocyanate group of an IPSE showed up clearly at 2270 cm^{-1} . This reactive group readily underwent a chemical reaction with poly(HEMA-co-HPA) hydroxyl group to produce urethane linkage of which its absorption band appeared at 1528 cm^{-1} as the reaction proceeded. However, identification of this band was difficult due to the interference of solvent bands. The gradual disappearance of the isocyanate peak at 2270 cm^{-1} was mainly indicative of continuing reaction of isocyanate groups. An almost complete reaction could be observed when the peak at 2270 cm^{-1} nearly disappeared. The FT-IR spectra collected at various reaction times (shown in Figure 4.5 and Figure 4.6) confirmed the successful functionalization of poly(HEMA-co-HPA) with degree of alkoxy silane content of 30% and 40%, respectively. It is important to note that to prevent undesired gelling due to early hydrolysis and subsequent condensation of pendent silane groups, trace amount of water commonly found in the solvent must be completely removed prior to use. An assignment of absorption bands is summarized in Table 4.2 and the absorbance spectra of 30% IPSE and 40% IPSE functionalized copolymer are illustrated in Figure 4.5 and Figure 4.6, respectively. The overall chemical reaction of poly(HEMA-co-HPA) with IPSE may be written as shown in Figure 4.7.

Table 4.2 An assignment of the FT-IR spectra of functionalized poly(HEMA-co-HPA)

Substance	Chemical groups	Wave Number (cm^{-1})	Intensity	Tentative Assignment
IPSE	-N=C=O	2270	Strong	Isocyanate stretching
Poly(HEMA-co-HPA)	C=O	1727	Moderate	C=O stretching vibration
	-CH ₂	2929	Strong	C-H stretching vibration of CH ₃ -CH ₂ -
	-OH	3465	Strong	-OH stretching vibration
DMF	C=O	1679	Moderate	C=O stretching vibration

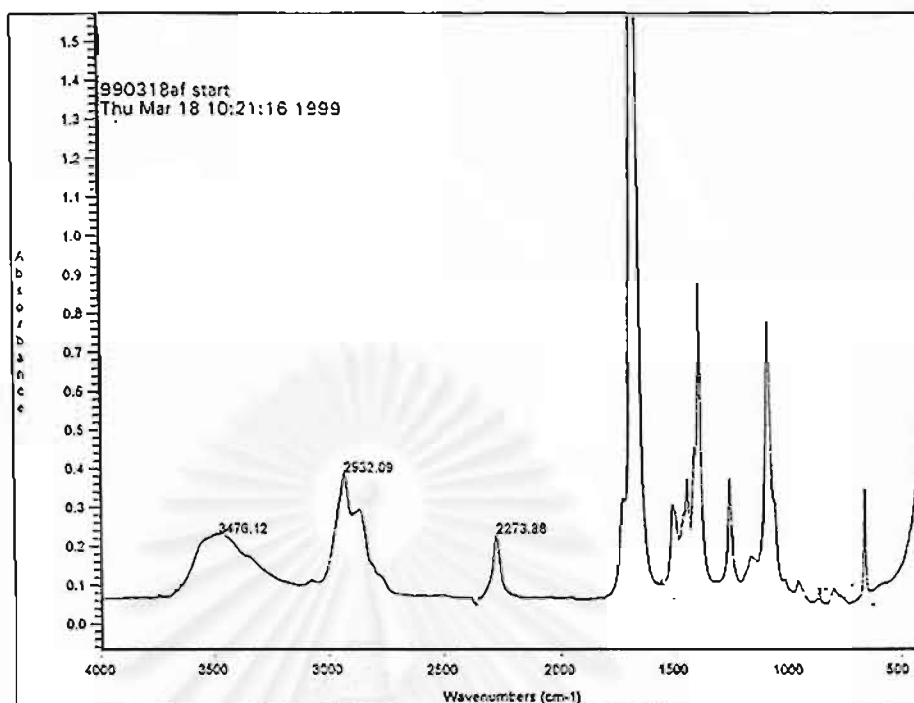


The absorbance spectrum of poly(HEMA-co-HPA) functionalized with 30% IPSE taken at the start of the reaction.

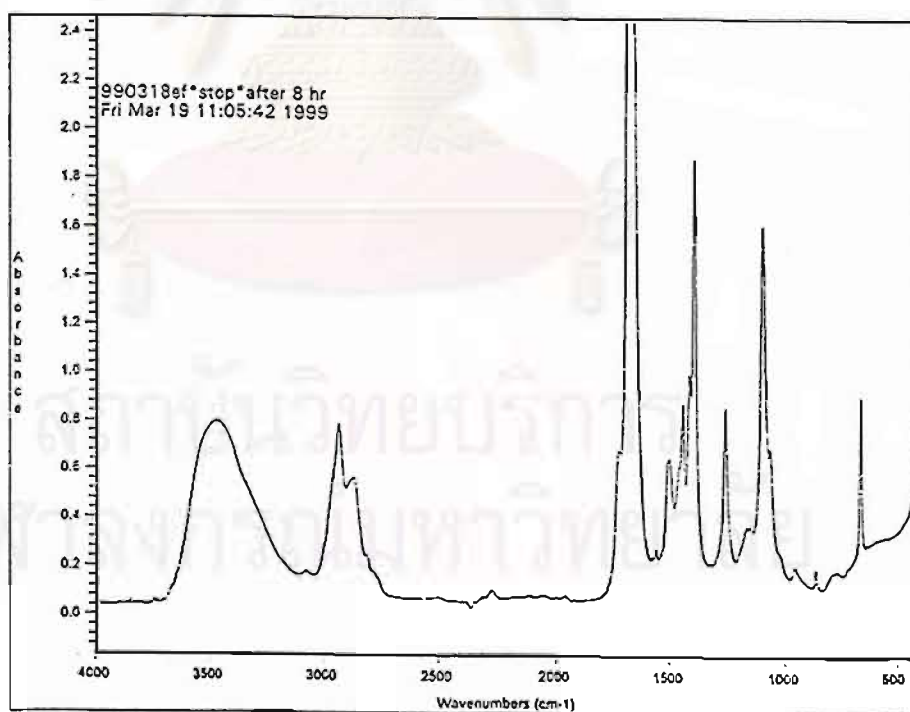


The absorbance spectrum of poly(HEMA-co-HPA) functionalized with 30% IPSE taken at the end of reaction.

Figure 4.5 FT-IR spectra of 30% IPSE functionalized poly(HEMA-co-HPA)



The absorbance spectrum of poly(HEMA-co-HPA) functionalized with 40% IPSE taken at the start of the reaction.



The absorbance spectrum of poly(HEMA-co-HPA) functionalized with 40% IPSE taken at the end of reaction.

Figure 4.6 FT-IR spectra of 40% IPSE at stop the functionalized reaction

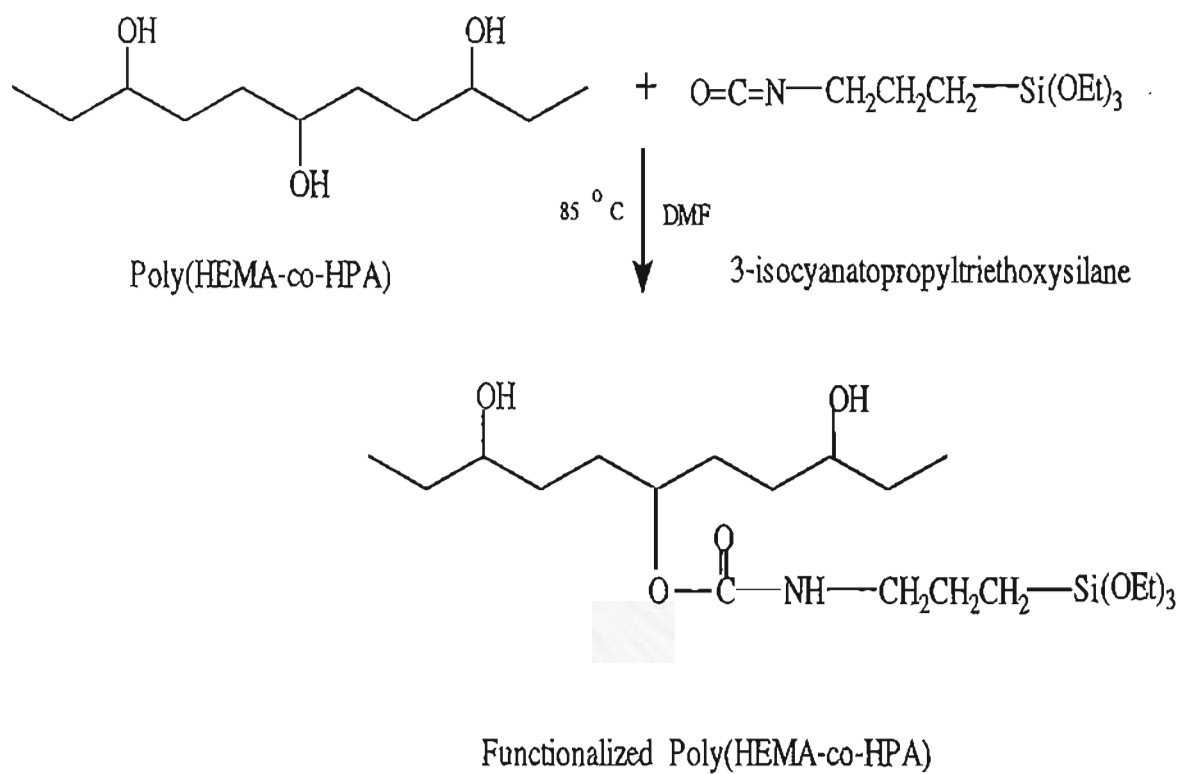


Figure 4.7 The overall chemical reaction of poly(HEMA-co-HPA) with IPSE

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4.3 Application of Organic/Inorganic Coating to PC Substrate

In this experiment, two coating systems were investigated. The first from now on referred as AP system, was based on two components and the latter referred as AM system was based on three components. The coating formulation of AP system was prepared by mixing the alkoxy silane functionalized copolymer and HMMM. For AM system, coating formulation was prepared by mixing the functionalized copolymer, HMMM, and TEOS. In the presence of p-toluenesulfonic acid as acid catalyst, these two systems could produce organic/inorganic cross-linked network when curing coating film in vacuum oven. The transparent network structure formed was derived from two different crosslinking reactions. Transesterification reaction between hydroxyl groups of poly(HEMA-co-HPA) and methylol groups ($-\text{CH}_2-\text{O}-\text{CH}_3$) of HMMM to produce organic network. The simple transesterification reaction was shown in Figure 4.8. The extent crosslinking reaction was performed by curing the coating film at high temperature for long period of times. In this experiment, curing temperature of 125 °C for 14 hours was used to prevent the deformation of PC substrate.

Inorganic network was achieved by sol-gel reactions which involved two step process; hydrolysis and subsequent condensation of alkoxy silane groups to produce siloxane (Si-O-Si) network. A typical sol-gel reaction was shown in Figure 2.9. The distinguished advantage of sol-gel process is that it produces inorganic crosslinked network at mild temperature, allowing possible combination of inorganic materials into organic matrix. However, the problem of gelation often arises during preparation of coating due to early formation of inorganic SiO_2 network. Hence, care must be taken during mixing of the coating composition. For AP system where two components are involved, the inorganic/organic network produced may be simplified as shown in Figure 4.9. Two types of inorganic crosslinks, intramolecular and intermolecular siloxane bonds was expected.

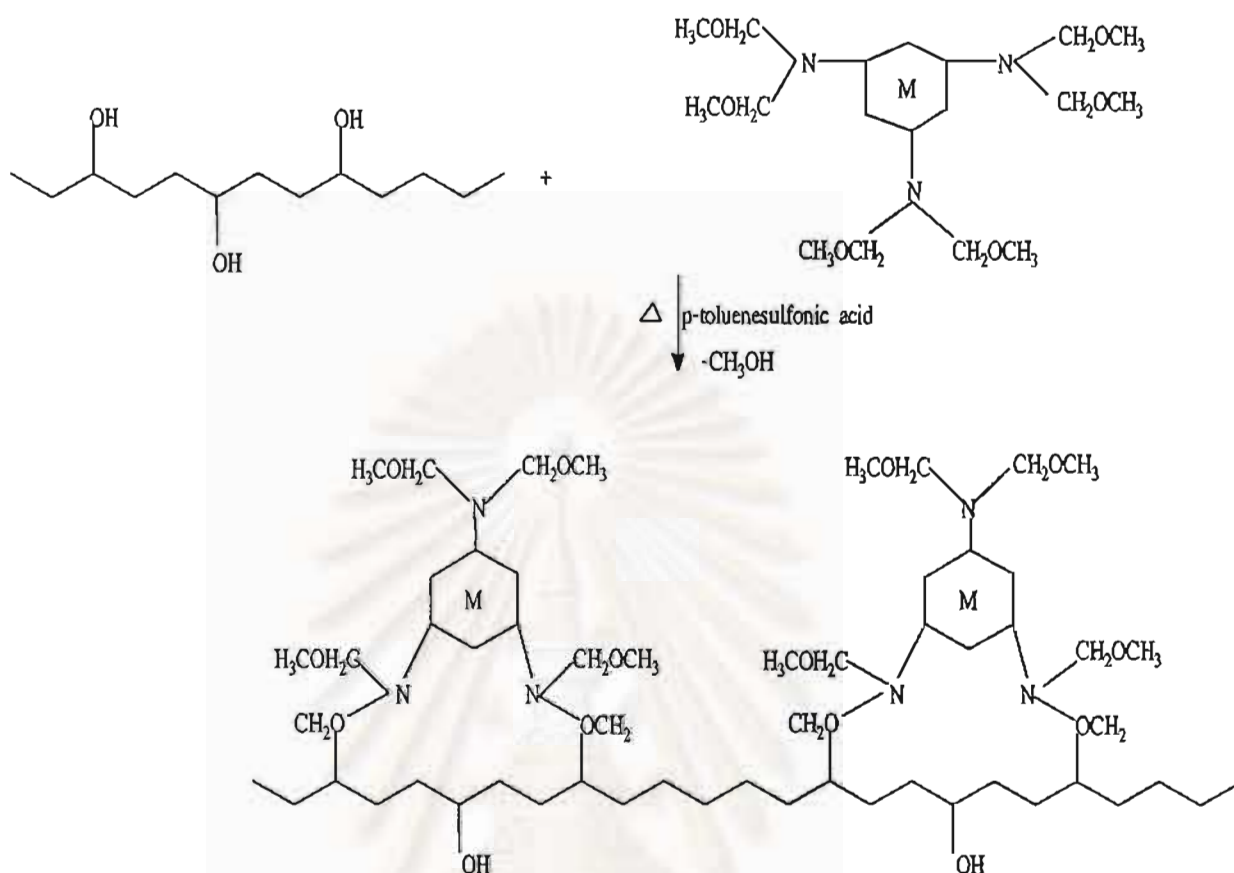


Figure 4.8 The transesterification between HMMM and pendent hydroxyl groups of copolymer

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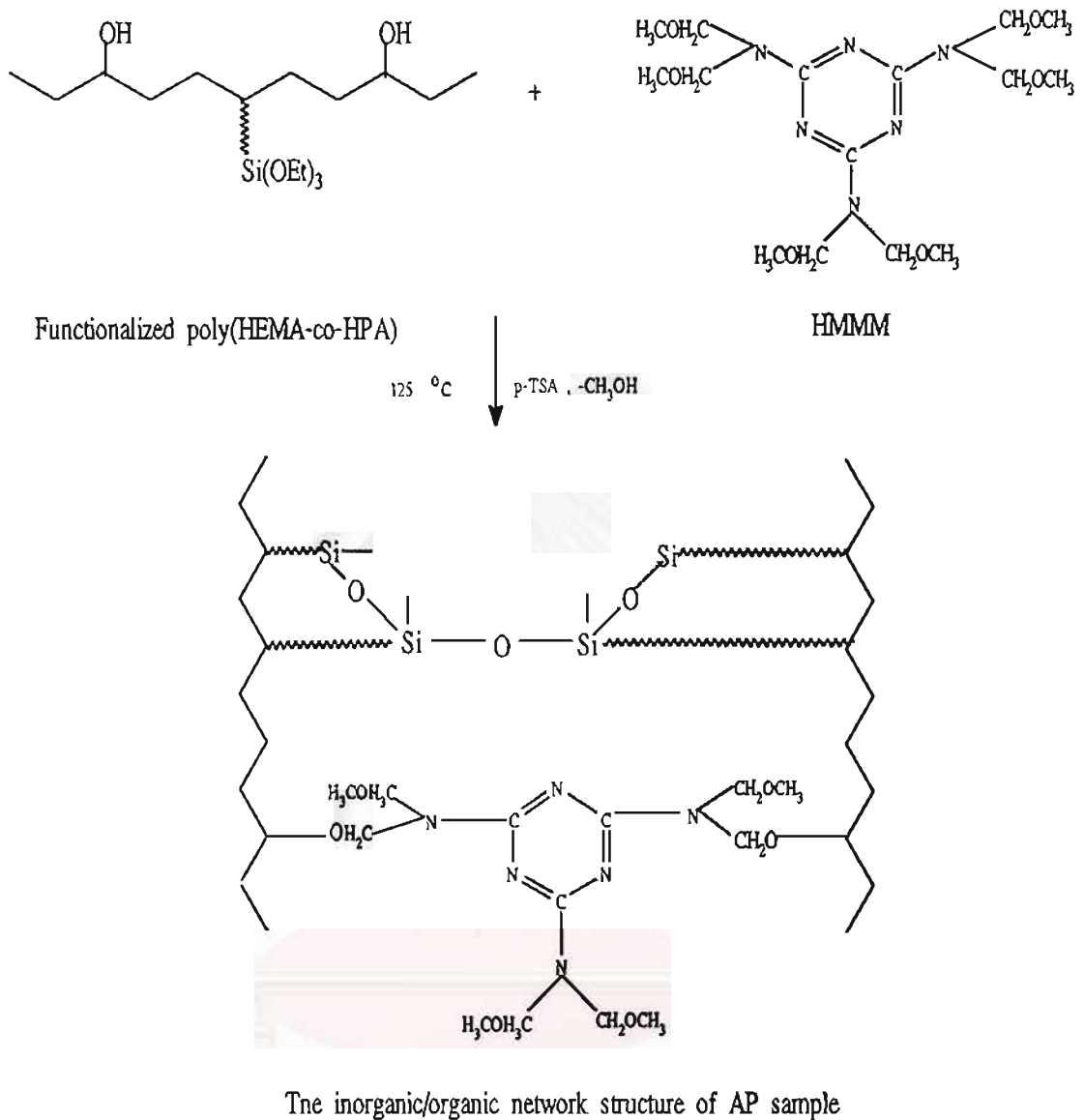
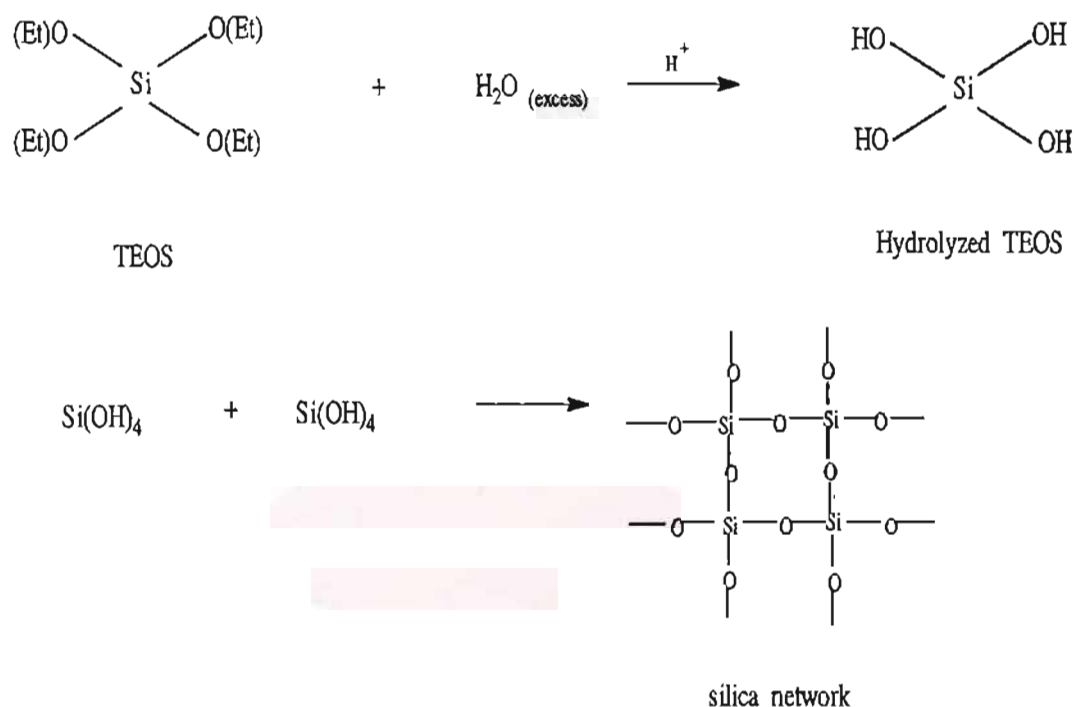


Figure 4.9 The inorganic/organic network produced by AP system

However, by using this system, the production of hybrid materials with a high degree of inorganic contents was limited. Moreover, the extent of sol-gel reaction to yield high density of inorganic network was restricted due to limited mobility of pendent siloxane groups.

The introduction of TEOS into AP system was investigated to improve transparency properties of hybrid materials. This system was referred to AM system. It was expected that TEOS, which is small in molecular weight and easy to be hydrolyzed, could form inorganic SiO₂ nanoparticles evenly distributed in organic network. The TEOS formed siloxane bonds through the p-TSA catalyst; this reaction is shown below:



Therefore, an optically transparent hybrid material without inorganic/organic phase separation could be achieved through siloxane bonds. The simplified inorganic/organic network produced from AM system could be illustrated as shown in Figure 4.10

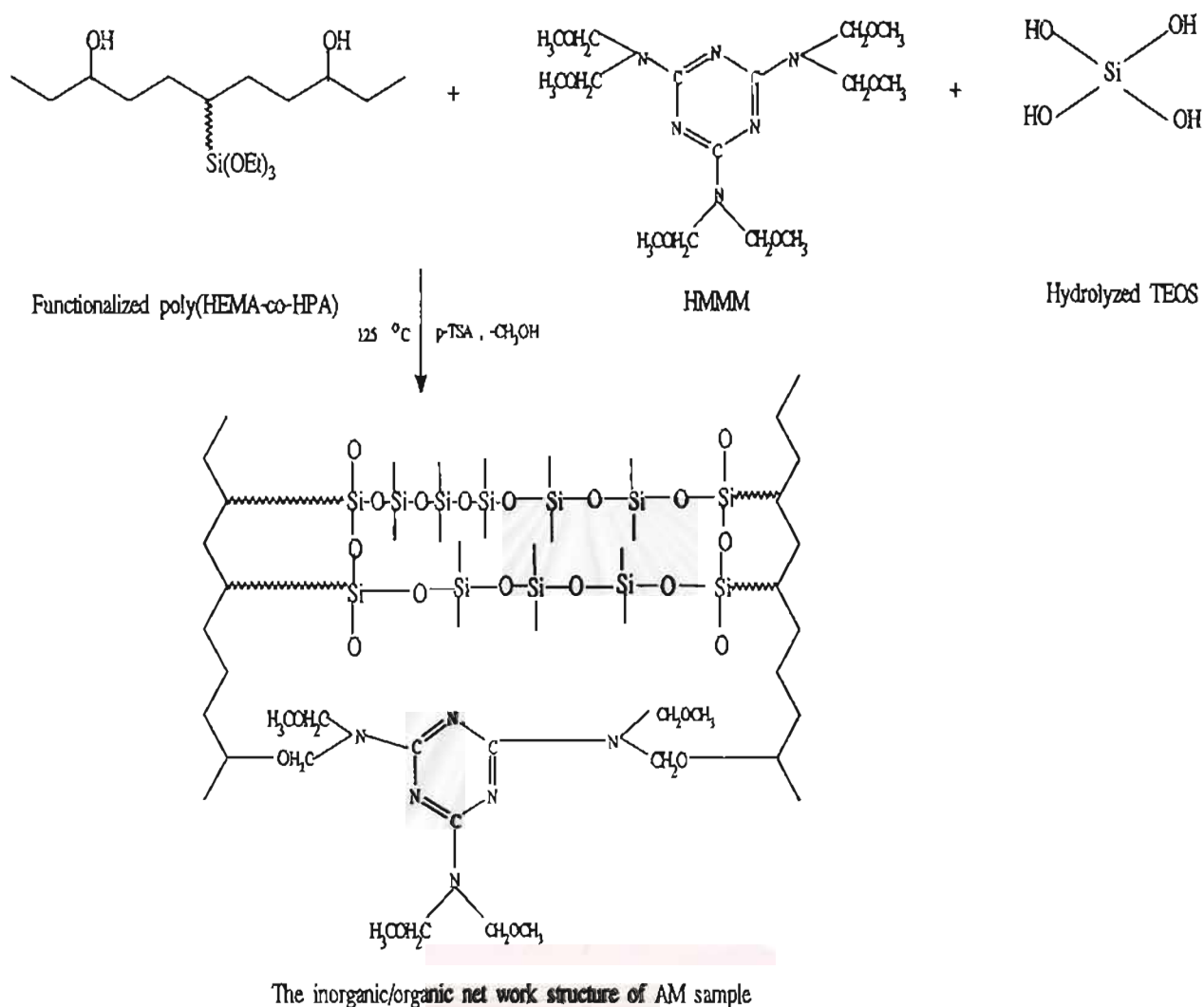


Figure 4.10 The inorganic/organic network produced by AM system

It should be noted that care must be taken during preparation of coating formulation due to early gellation. To avoid this problem, mixing of coating components should be carried out in a dried room, and solvents must be free of water trace.

4.4 TGA Analysis of Coated/Cured Organic/Inorganic Composites.

TGA analysis was used to determine the inorganic content (SiO_2) as well as the thermal stability of the composites. Percent weight loss of the sample plotted against temperature is shown in Figures 4.11 and 4.12 for AP system and AM system, respectively. The inorganic content determined by TGA and calculated value are shown in Table 4.3.

Table 4.3 Inorganic and organic contents of the inorganic/organic sol-gel copolymers.

Sample Code	Calculated value		TGA result	
	Organic Content (%wt)	Inorganic Content (%wt)	Weight Loss (%wt)	Silica Content (%wt)
AM1a	79.6	20.3	82.5	17.5
AM2a	72.7	27.3	76.0	24.0
AM3b	61.6	38.4	66.7	33.3
AP3	88.0	12.0	88.0	12.0
AP4	84.6	15.4	85.7	14.3
AP5	81.1	18.1	83.6	16.4

From Figure 4.11 and Figure 4.12, the decomposition process involves two main steps of weight loss rates. The weight loss observed at temperatures ranging from 500 °C to 750 °C could be attributed to the decomposition of unreacted HMMM and part of functionalized copolymer where the efficiency of crosslinking reaction was insufficient. The high density of organic crosslink brought about high heat resistance property to crosslinked network which could be stable up to 500 °C according to Mukhopadyay's report. Hence, the decomposition profile in the temperature range of 500-700 °C was presumably due to the decomposition of organic network. It was unlikely that this weight loss profile was attributed to the depolymerization of the functionalized copolymer chain as a result of pendent siloxyl groups undergoing intra- and intermolecular crosslinks between adjacent chains. The reason is that the percent weight loss tended to decrease with an increase in the degree of functionalization. From Figure 4.11, percent weight

loss in the temperature range of 500-650 °C were found to be, 9.5 and 8.2 % for sample AP4 and AP5 sample, respectively. The similar trend holds true for the AM system. The extent of the organically crosslinking reaction was affected by three major factors; the restricted mobility of pendent hydroxyl segment by siloxane bond and the inappropriate curing temperature due to a concern on thermal stability of the PC substrate as well as the availability of hydroxyl groups on the copolymer. Generally, the decomposite of organic network was completed at the temperature about 750 °C. Upon further heating, little change in weight loss was observed in all cases. The thermally stable residual was believed to be the inorganic SiO₂. The weight percentage of inorganic residual components in coating films varied accordingly with the amount of pendent alkoxy silane group and TEOS used in each formulation. The values measured by TGA were comparable to theoretical values. The presence of inorganic components in coating film played significant roles not only contributing to the thermal stability but also providing optical clarity to the materials. Those properties could be optimized by controlling the balance between the degree of pendent alkoxy silane groups and the amount of external TEOS added.

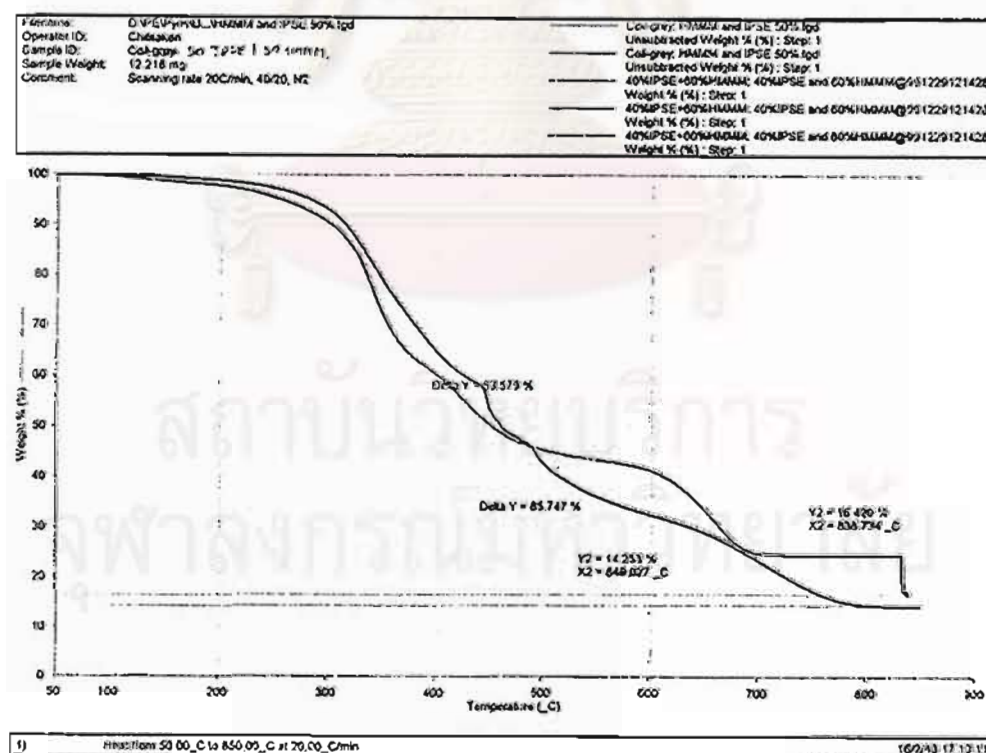


Figure 4.11 The decomposition curves of AP4 and AP5 formula

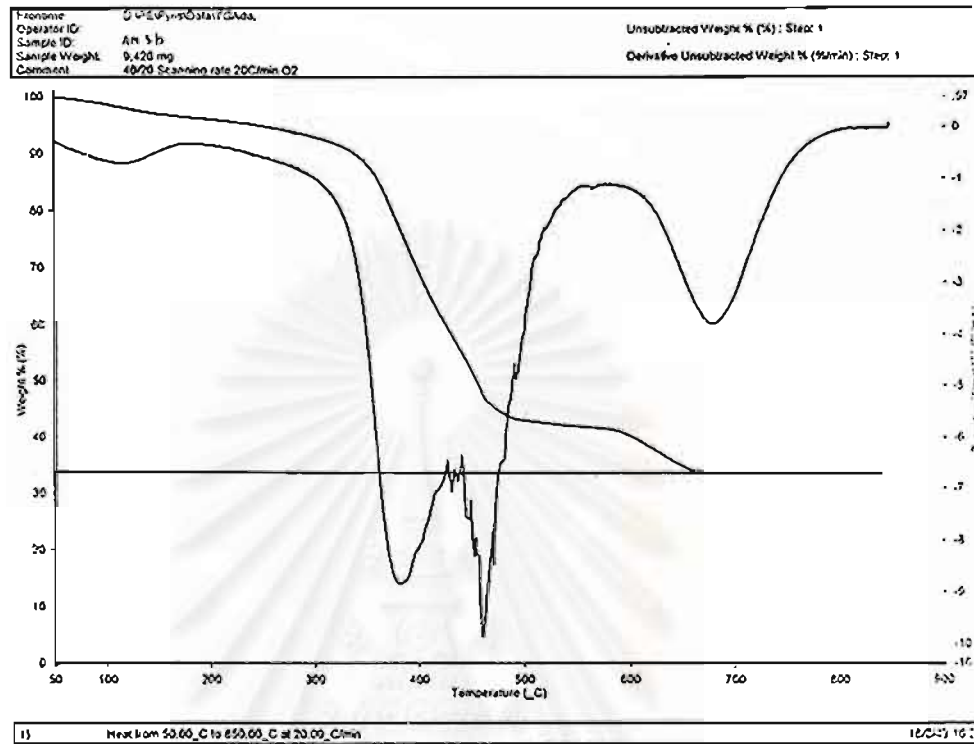


Figure 4.12 The decomposition behavior of AM3b sample

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4.5 Evaluation of Surface Properties of Coated/Cured PC Sheet.

4.5.1 The Results of Abrasion Testing

The coated and uncoated PC substrate samples were tested for abrasion resistance determined by the number of abrasion cycles. An abrasion cycle was recorded when the visible abrasion line appeared on the surface. The results are shown in Table 4.4 Mark x is the abrasion cycles required to produce a visible line on the coated/cured PC surface.

Table 4.4 The results of abrasion testing

Sample code	Abrasion cycle														
	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
PC	-	-	-	x	x	x	x	x	x	x	x	x	x	x	x
AM1a	-	-	-	-	-	x	x	x	x	x	x	x	x	x	x
AM1b	-	-	-	-	-	-	x	x	x	x	x	x	x	x	x
AM2a	-	-	-	-	-	-	x	x	x	x	x	x	x	x	x
AM2b	-	-	-	-	-	-	-	-	x	x	x	x	x	x	x
AM3a	-	-	-	-	-	-	-	-	-	x	x	x	x	x	x
AM3b	-	-	-	-	-	-	-	-	-	-	x	x	x	x	x
AM4a	-	-	-	-	-	-	-	-	-	-	-	x	x	x	x
AM4b	-	-	-	-	-	-	-	-	-	-	-	-	x	x	x
AM4c	-	-	-	-	-	-	-	x	x	x	x	x	x	x	x
AP3	-	-	-	-	-	-	-	x	x	x	x	x	x	x	x
AP4	-	-	-	-	-	-	-	-	-	x	x	x	x	x	x
AP5	-	-	-	-	-	-	-	-	-	-	x	x	x	x	x
AP6	-	-	-	-	-	-	-	-	-	-	-	x	x	x	x
AP7	-	-	-	-	-	-	-	-	-	-	-	-	x	x	x

From Table 4.4, it can be seen that number of abrasion cycles to make visible line on PC sheet, indicating poor surface performance of PC substrate. The comparison of abrasion cycles required to produce visible line on virgin PC and coated PC samples are graphically illustrated in Figure 4.13 and Figure 4.14 for AM system and AP system, respectively. The results show that abrasion resistance of virgin PC sheet is quite poor. After application of inorganic/organic hybrid materials on PC surface, abrasion resistance was significantly improved depending on to the composition of coating formula. It is interesting to point out that increased wear resistance was notably related to the presence of inorganic content.

In the case of AP system abrasion resistance of coated PC increased with an increase in the degree of alkoxy silane group. For AM system, the addition of TEOS could clearly improve the abrasion resistance of the coated substrate. Taken AM2 series as an example, sample AM2b which contained 40 wt% TEOS exhibited higher abrasion resistance than sample AM2a which has less amount of TEOS (30 wt%). The similar trend is observed in other series. Hence, it can be claimed that AM coating system gave better abrasion resistance than AP system which did not contain TEOS. However, the increase of TEOS amount could cause the coating shrinkage during the drying and curing process. As a result, it may be difficult to achieve a crack free coating system when higher amount of external TEOS applied.

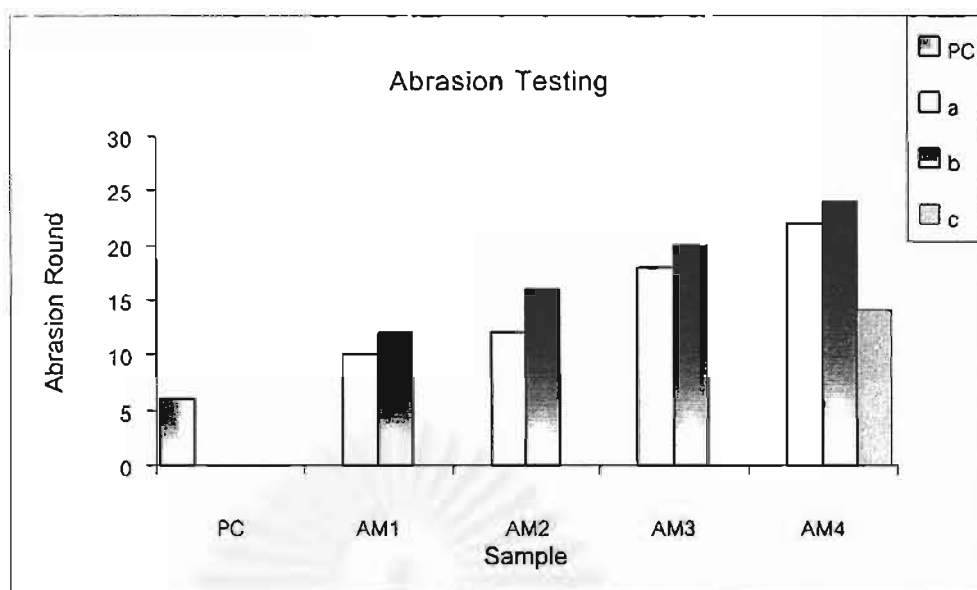


Figure 4.13 Comparison of abrasion cycles required to form a visible line on a coated/cured sample from AM system

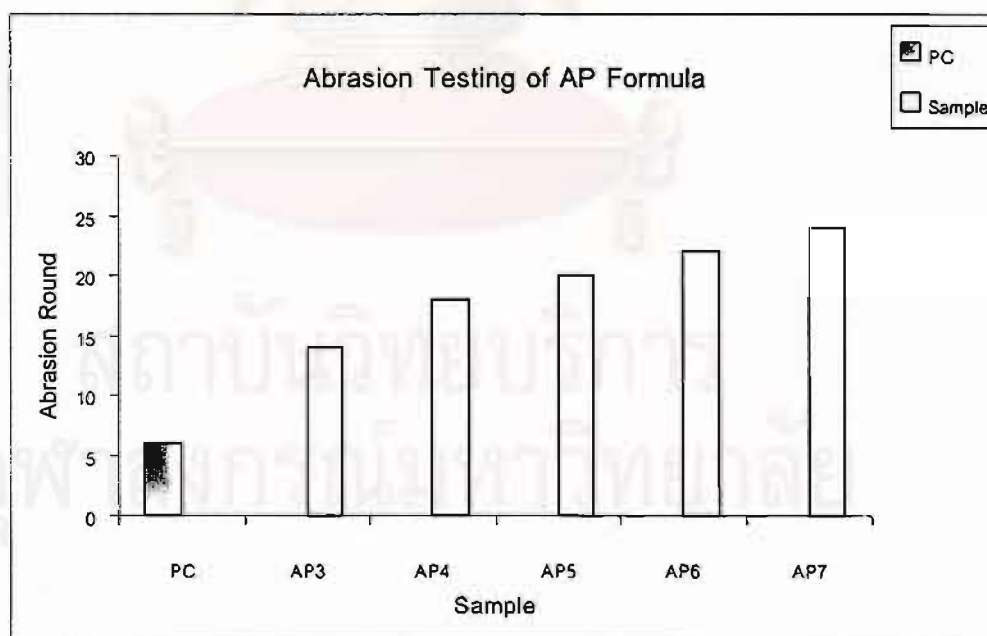


Figure 4.14 Comparison of abrasion cycles required to form a visible line on a coated/cured sample from AP system

4.5.2 The Results of Scratch Testing

Uncoated PC and coated PC were subjected to scratch resistance test. The minimum weight load required to make visible scratching line was indicated. The higher minimum load required, the better the scratch resistance property. The results are shown in Table 4.5

Table 4.5 The result of scratch testing

Sample Code	Minimum Weight Load Required (g)									
	100	200	300	400	500	600	700	800	900	1,000
PC										
AM1a	-	-	x	x	x	x	x	x	x	x
AM1b	-	-	-	x	x	x	x	x	x	x
AM2a	-	-	-	x	x	x	x	x	x	x
AM2b	-	-	-	x	x	x	x	x	x	x
AM3a	-	-	-	-	x	x	x	x	x	x
AM3b	-	-	-	-	-	x	x	x	x	x
AM4a	-	-	-	-	-	-	x	x	x	x
AM4b	-	-	-	-	-	-	-	x	x	x
AM4c	-	-	-	x	x	x	x	x	x	x
AP3	-	-	-	x	x	x	x	x	x	x
AP4	-	-	-	x	x	x	x	x	x	x
AP5	-	-	-	-	x	x	x	x	x	x
AP6	-	-	-	-	-	x	x	x	x	x
AP7	-	-	-	-	-	-	x	x	x	x

x = Minimum weight required to produce a visible line.

- = intact

Table 4.5 compares the results obtained from the scratch resistance measurement. The minimum weight which produced a appearance scratch line was recorded. For uncoated PC, the visible line was observed at 300 g load while coated PC could bear at 400 g load. The results of scratch resistance test could be graphically illustrated as shown in Figure 4.15 and Figure 4.16.

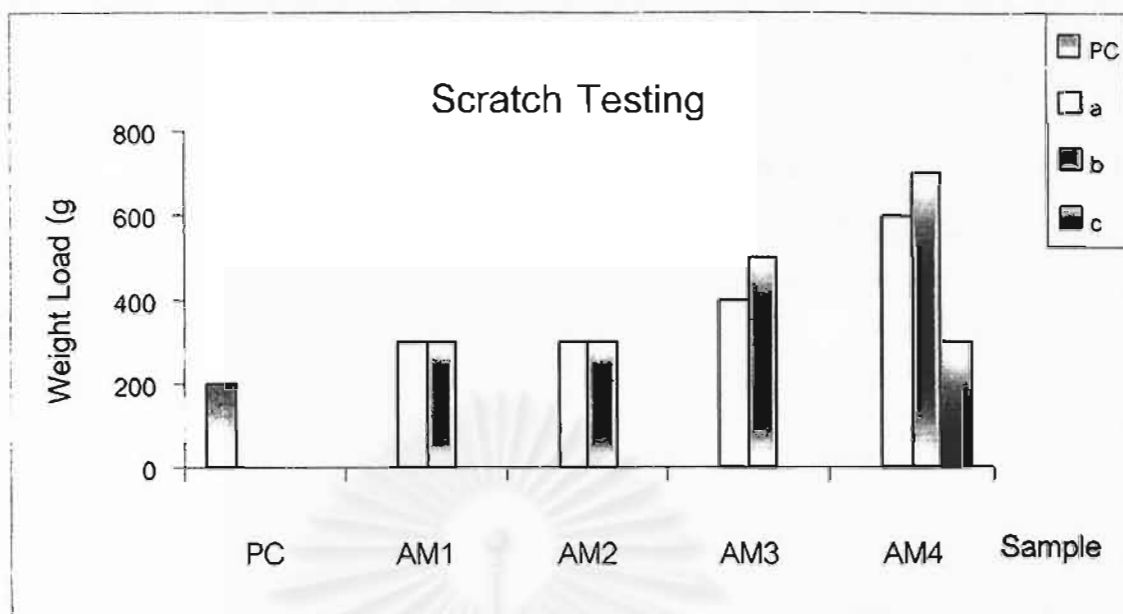


Figure 4.15 Comparison of minimum weight required to form visible line on a coated/cured sample from AM samples

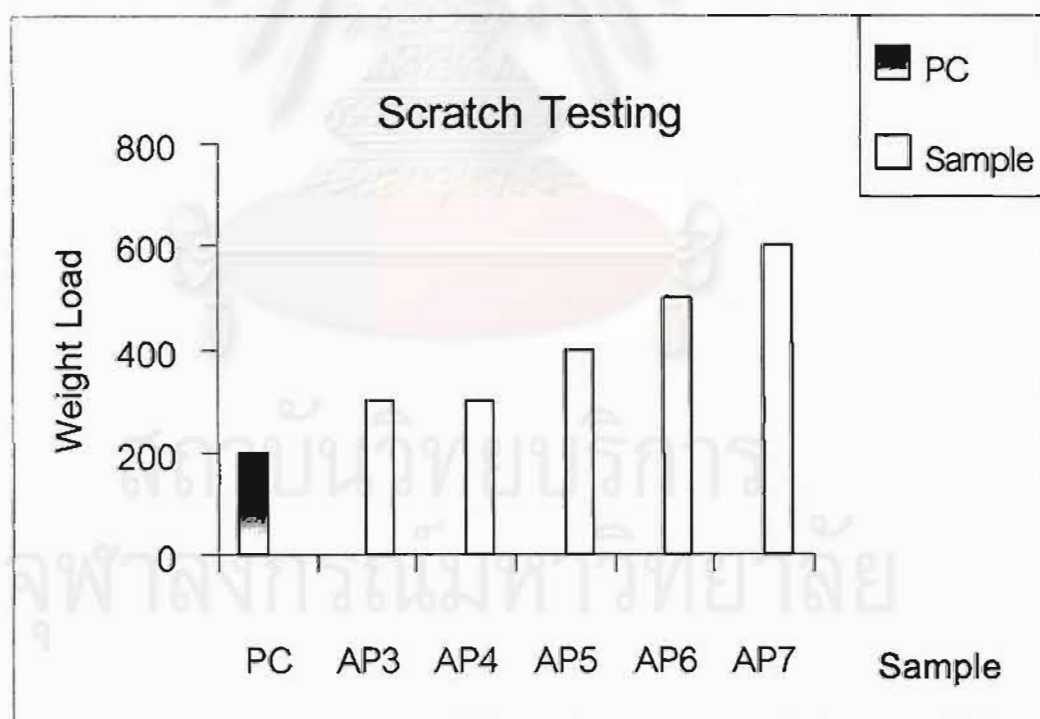


Figure 4.16 Comparison of minimum weight required to form a visible line on coated/cured sample from AP samples

The performance of coating films may be put in order as follows; AP coating system : AP7 > AP6 > AP5 > AP4 = AP3 and AM coating system: AM4b > AM4a > AM3b > AM3a > AM2b = AM2a = AM1b = AM1a = AM4c. Sample AM4b had the highest scratch resistance among those investigated formulas; this sample could be left unscratched up to load weight of 700 g. This result is in good agreement with those of the abrasion resistance test, confirming the influence of increased wt% of silica content (see Table 3.2).



4.6 Light Transmittance Measurement of Abraded Coated PC

Abrasion testing of 30 abrading cycles was carried-out on coated/cured samples. Afterthat, abraded samples were subjected to light transmittance measurement using UV/Vis spectrophotometer. Abrasive resistance property of inorganic/organic coating film was assessed by comparing the reduction in the degree of light transmittance among different coating films as well as uncoated PC. Figure 4.17 compares light transmittance obtained from AP series. It can be observed that abrasion resistance of coating film is closely dependent on the degree of ethoxy silyl groups in the functionalized copolymer. To be precise the formation of siloxane bond, which readily occurred, played an important role in an increase in surface performance of coating composites. This conclusion is drawn from the fact that an increase in pendent ethoxy silyl groups led to a decrease in copolymer hydroxyl groups, resulting in a decrease in organic network/inorganic network ratio. TGA evidence supports the above explanation in that the proportion of organic network decreased as the degree of ethoxy silyl increased. However, the presence of organic network was preferable in order to prevent film shrinkage and provide synergitic effect on abrasion resistant property to the coating.

Figure 4.18 compares the abrasion resistance among AM series. It is obvious that the addition of TEOS brought about higher abrasion resistance. It was believed that the introduction of TEOS resulted in increased proportion of inorganic network, hence providing better abrasion resistancy.

Finally, Figure 4.19 confirm the dominance of inorganic network on the surface performance of inorganic/organic coating.

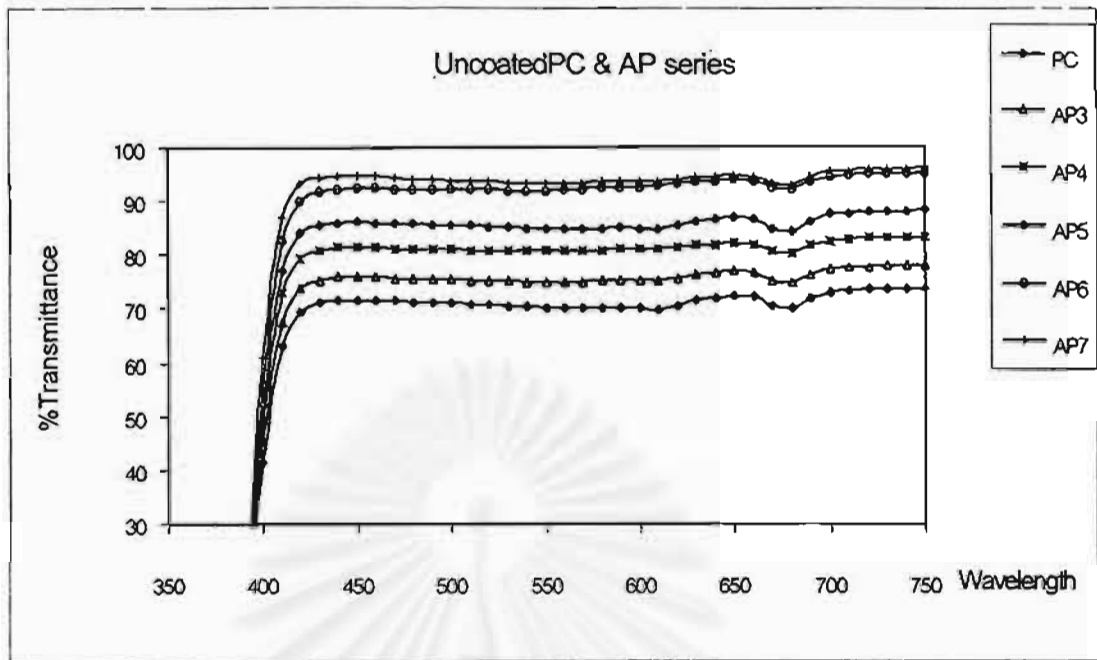


Figure 4.17 The compared transmission curves of uncoated PC and AP series

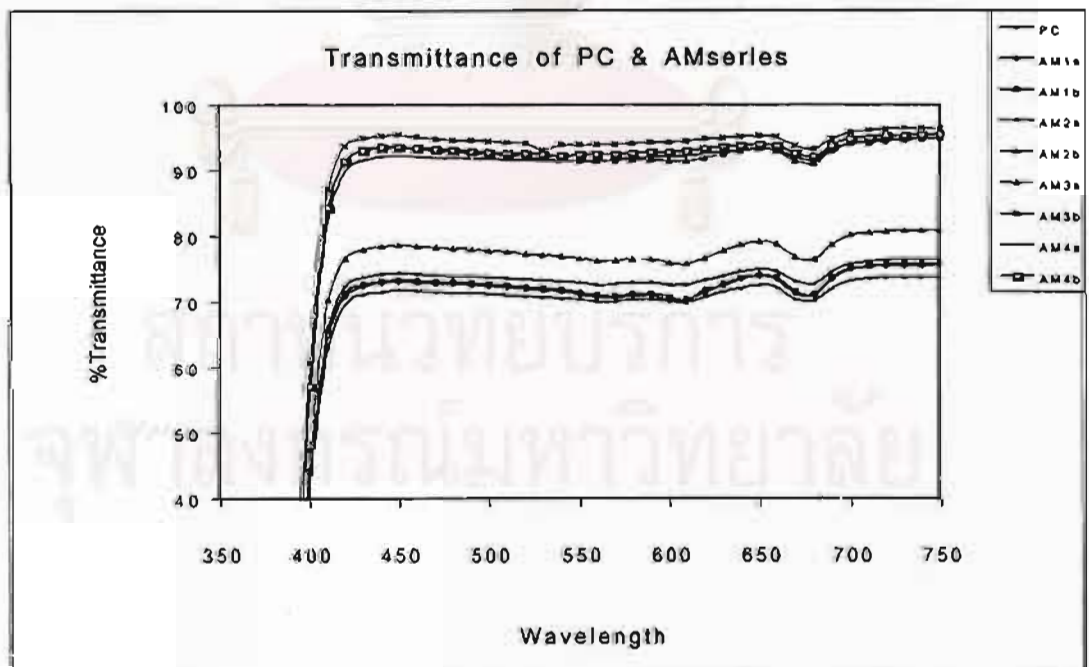


Figure 4.18 The compared transmission curves of uncoated PC and AM series

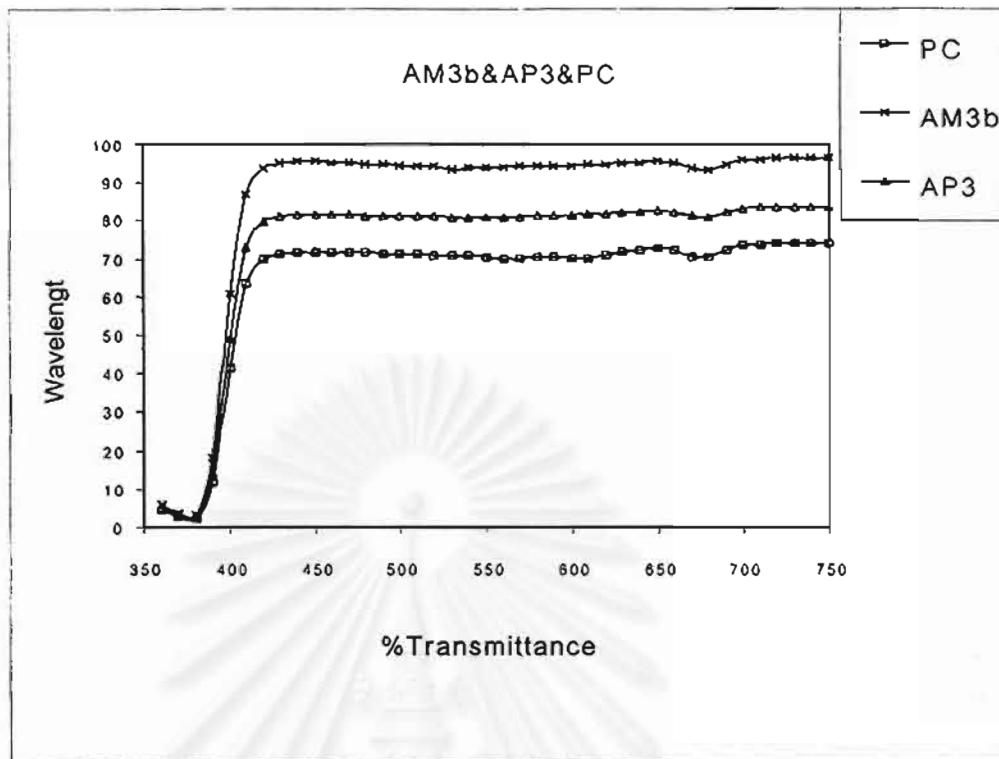


Figure 4.19 The compared transmission curves of uncoated PC, AP3, and AM3b

CHAPTER 5

CONCLUSIONS

A transparent organic/inorganic hybrid material has been developed for coating applications, and its surface performance was evaluated. The finding results can be concluded as follows:

- (1) The introduction of pendent siloxyl group into organic component was successfully carried out by functionalization of poly(HEMA-co-HPA) with IPSE. This functionalized copolymer could form an organic network film when cured with HMMM.
- (2) Transparent organic/inorganic coating was obtained by mixing the functionalized copolymer, HMMM (crosslinking agent) and TEOS and then curing at the desired temperature. The optical property of this material was dependent on the amount of added TEOS and the degree of functionalization. It was believed that pendent siloxyl groups played an important role in bonding the inorganic SiO₂ nanoparticles to organic network, hence reducing phase separation. A higher inorganic content contributed to better optical transparency.
- (3) Abrasion/Scratch resistance properties of coated PC sheets were markedly improved and closely related to the proportion of inorganic network.

CHAPTER 6

RECOMMENDATION FOR FUTURE WORK

- (1) TEOS is sensitive to hydrolysis and difficult to handle. An alternative compound may be helpful in order to solve this problem.
- (2) Generally, transesterification reaction between HMMM and polyol requires high curing temperatures in the range of 140-160 °C to achieve the high extent of organic crosslink density. However, due to a concern on the thermal stability of PC substrate such high temperature was avoided in this experiment. For the future work, it may be interesting to study other types of crosslinkers, for example diisocyanate based compound of which the crosslinking reaction take places at relatively milder conditions.
- (3) It was quite difficult to obtain uniformly speaded coating film on PC sample by the laboratory coating applicator. It is reccommended that alternative coating techniques should be sought.
- (4) Additional tests which are relevant to practical applications, such as in lenses production, should be done.

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APPENDIX

%Transmittance of AP and AM system

%TransmittanceAP system

(nm)	PC	AP3	AP4	AP5	AP6	AP7
360	4.32	4.64	4.98	5.21	5.62	5.77
370	2.75	2.97	3.26	3.37	3.62	3.77
380	2.28	2.47	2.69	2.84	3.048	3.27
390	11.55	12.91	14.11	15.02	15.99	18.4
400	41.65	45.34	49.28	52.21	55.76	60.86
410	63.37	67.56	72.97	77.15	82.58	86.99
420	69.62	73.85	79.55	84.03	90.02	93.43
430	71.24	75.36	81.02	85.64	91.79	94.62
440	71.61	75.88	81.51	86.17	92.41	94.97
450	71.86	76.04	81.66	86.32	92.64	94.98
460	71.78	75.91	81.47	86.17	92.53	94.68
470	71.57	75.81	81.34	85.97	92.42	94.39
480	71.44	75.74	81.29	85.89	92.38	94.22
490	71.33	75.67	81.17	85.8	92.35	94.08
500	71.22	75.55	81.07	85.64	92.27	93.89
510	71.45	75.44	80.99	85.48	92.21	93.76
520	70.88	75.31	80.92	85.33	92.13	93.65
530	70.68	75.19	80.81	85.17	92.03	93.44
540	70.55	75.09	80.75	85.03	91.99	93.34
550	70.35	74.99	80.69	84.88	92.03	93.21
560	70.32	74.91	80.74	84.74	92.11	93.35
570	70.21	74.96	80.84	84.79	92.25	93.44
580	70.32	75.17	81.01	85.03	92.48	93.58
590	70.35	75.26	81.16	85.14	92.62	93.67
600	70.15	75.17	81.22	84.95	92.73	93.72
610	69.95	75.19	81.32	84.93	92.92	93.84
620	70.63	75.72	81.67	85.51	93.28	94.18
630	71.56	76.35	81.96	86.22	93.57	94.43
640	72.18	76.67	82.09	86.68	93.77	94.57

650	72.58	76.98	82.35	86.99	94.04	94.78
660	72.25	76.74	82.13	86.75	93.82	94.55
670	70.44	75.29	80.99	85.01	92.54	93.24
680	70.15	74.93	80.63	84.62	92.12	92.85
690	72.19	76.51	81.97	86.49	93.60	94.42
700	73.25	77.54	82.86	87.69	94.57	95.44
710	73.58	77.83	83.13	88.00	94.86	95.75
720	73.75	78.00	83.36	88.25	95.10	95.94
730	73.78	78.11	83.44	88.31	95.18	96.02
740	73.85	78.15	83.51	88.37	95.29	96.11
750	73.86	78.17	83.55	88.41	95.34	96.16



AM system

(nm)	PC	AM1a	AM1b	AM2a	AM2b	AM3a	AM3b	AM4a	AM4b
360	4.33	4.43	4.43	4.53	4.74	5.64	5.87	5.59	5.66
370	2.75	2.86	2.86	2.89	3.15	3.65	3.84	3.57	3.65
380	2.28	2.39	2.39	2.44	2.58	3.09	3.26	3.02	3.11
390	11.55	12.48	12.66	12.71	13.6	16.44	18.21	16.03	16.53
400	41.61	43.69	44.17	44.55	47.48	57.15	60.66	55.85	57.25
410	63.34	64.97	65.52	66.33	70.31	84.11	87.06	82.42	84.17
420	69.62	70.92	71.39	72.34	76.53	91.36	93.65	89.77	91.44
430	71.25	72.35	72.78	73.76	78.15	92.91	94.93	91.46	93.02
440	71.61	72.86	73.25	74.19	78.45	93.38	95.29	92.04	93.48
450	71.82	73.01	73.39	74.33	78.61	93.41	95.34	92.22	93.65
460	71.78	72.93	73.27	74.21	78.44	93.16	95.09	92.21	93.37
470	71.59	72.76	73.07	74.03	78.23	92.86	94.82	91.87	93.14
480	71.44	72.68	72.99	73.93	78.11	92.72	94.66	91.84	93.03
490	71.37	72.56	72.88	73.86	78.01	92.52	94.54	91.76	92.87
500	71.25	72.39	72.72	73.66	77.81	92.34	94.36	91.67	92.72
510	71.00	72.19	72.53	73.55	77.63	92.18	94.21	91.61	92.61
520	70.81	71.93	72.26	73.35	77.36	91.97	94.05	91.53	92.51
530	70.62	71.75	72.03	73.21	77.16	91.74	93.05	91.41	92.38
540	70.54	71.46	71.79	73.02	76.95	91.55	93.84	91.33	92.28
550	70.35	71.06	71.44	72.84	76.62	91.45	93.85	91.35	92.29
560	70.05	70.61	70.97	72.62	76.25	91.29	93.88	91.43	92.31
570	70.02	70.52	70.88	72.63	76.19	91.29	93.96	91.52	92.44
580	70.34	70.82	71.18	72.83	76.43	91.48	94.13	91.71	92.57
590	70.35	70.79	71.15	72.87	76.46	91.58	94.23	91.82	92.66
600	70.01	70.22	70.62	72.62	76.01	91.41	94.25	91.97	92.75
610	69.95	69.94	70.37	72.55	75.82	91.36	94.41	92.11	92.84
620	70.64	71.89	71.33	73.15	76.56	91.86	94.75	92.49	93.21
630	71.55	72.31	72.66	73.97	77.88	92.43	94.99	92.77	93.51
640	72.12	73.33	73.63	74.53	78.62	92.86	95.15	92.99	93.66
650	72.54	73.88	74.15	74.92	79.11	93.21	95.33	93.24	93.91

660	72.28	73.47	73.76	74.64	78.76	92.96	95.1	93.11	93.7
670	70.45	71.18	71.54	73.03	76.77	91.54	93.74	91.88	92.4
680	70.11	70.81	71.19	72.72	76.36	91.04	93.53	91.52	92.1
690	72.14	73.34	73.67	74.56	78.72	92.86	94.85	93.04	93.6
700	73.24	74.85	75.13	75.75	80.15	94.06	95.77	94.09	94.6
710	73.54	75.22	75.47	76.21	80.51	94.06	96.06	94.43	94.9
720	73.78	75.38	75.65	76.26	80.71	94.54	96.25	94.67	95.2
730	73.75	75.45	75.71	76.36	80.78	94.65	96.36	94.76	95.3
740	73.84	75.55	75.76	76.39	80.85	94.71	96.39	94.89	95.4
750	73.83	75.53	75.79	76.45	80.91	94.88	96.44	94.96	95.4



VITAE

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