A STUDY TO IMPROVE ADHESION BETWEEN SURFACE GRAFTED POLYETHYLENE AND EPOXY RESIN

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ABSTRACT

This study was aimed to find methods to improve adhesion between surface grafted polyethylene and epoxy resin. PE film and fiber were grafted with two types of water soluble vinyl monomer. These were acrylamide (AAm) and acrylic acid (AA). Grafting was carried out using the 2-stage method. Hydroxylation by thermal decomposition of potassium persulfate ($K_2S_2O_8$) was first carried out to create hydroxyl groups on PE surface. The second stage was grafting of the monomers onto functionalised surface. The grafting reaction was carried out in aqueous solution by ceric ion technique. Thermogravimetric (TG) analysis, ATR-FTIR spectroscopy were used to investigate changes in surface properties. Surface structure of interface and surface rigidity were observed by atomic force microscopy (AFM). Interfacial adhesion of PE film and fiber with epoxy resin were measured by peel test and pull out test, respectively. The peel strength of PE film grafted with AA (AA-g-PE) was found to be over 2 times greater than that of PE film grafted with AAm (AAm-g-PE). This could be due to different extent of grafting and the nature of grafted chains. Reducing moisture content in both the AA and AAm grafted layers by drying in vacuum oven lowers interfacial adhesion with epoxy resin, attributable to reducing grafted chain mobility and increasing surface rigidity. However, when PE-g-AAm film was immersed in water at room temperature before assembling with epoxy resin, the peel strength was found to increase by 8 times. An improvement of about 40 times in peel strength was observed when using 80°C water. This significant improvement is likely to be due to an increase in chain mobility in swelled polyacrylamide. By contrast, swollen PE-g-AA film exhibited lower peel strength with epoxy resin. Since AA grafted chain had already high flexibility, adhesion of AA could not be improved by increasing grafted chain mobility through swelling. The extent of reaction, investigated with ATR-FTIR, in swollen grafted chains was not clearly observed. This result suggested that swelling increases interfacial adhesion through increasing physical interaction of grafted chains and epoxy resin.

KEY WORDS: POLYETHYLENE/ SURFACE GRAFTING/ GRAFTED CHAIN MOBILITY/ ADHESION

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การศึกษาเพื่อปรับปรุงการยึดติดระหว่างพอลิเอทิลีนที่ทำการกราฟท์แล้วกับอีพอกซีเรซิน
(A STUDY TO IMPROVE ADHESION BETWEEN SURFACE GRAFTING POLYETHYLENE AND EPOXY RESIN)

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บทคัดย่อ

การศึกษานี้ทำเพื่อหาวิธีเพื่อปรับปรุงการยึดติดระหว่างพื้นผิวของพอลิเอทิลีนทำการกราฟท์แล้วกับอีพอกซีเรซิน โดยการใช้พอลิเอทิลีนที่ทำการกราฟท์ด้วยไวนิลมอนอเมอร์ที่ละลายน้ำได้ 2 ชนิด คือ อะคริลาไมด์และกรดอะคริลิก โดยใช้วิธีแบบ 2 ขั้นตอน ขั้นแรกคือการทำปฏิกิริยาไฮดรอกซิเลชันเพื่อเพิ่มหมู่ไฮดรอกซิลลงบนผิวของพอลิเอทิลีน โดยการสลายโพแทสเซียมเปอร์ซัลเฟตด้วยความร้อน ขั้นที่ 2 คือการทำปฏิกิริยาการกราฟท์ด้วยมอนอเมอร์ที่มีขั้วลงบนผิวของพอลิเอทิลีนที่ทำการเพิ่มหมู่ฟังก์ชันแล้ว โดยใช้เทคนิคซีริกไอออน เทอร์โมกราวิเมทริก และ อินฟราเรดสเปกโตรสโคปีติดตาม การเปลี่ยนแปลงของสภาพผิว ใช้เครื่องอะตอมมิกฟอร์สไมโครสโคป (AFM) ในการศึกษาสมบัติของพื้นผิวและความแข็งของผิว ทดสอบการยึดติดที่ผิวของฟิล์มกับอีพอกซีเรซินด้วยเทคนิคพุลเอาท์เทสท์และทดสอบการยึดติดที่ผิวของเส้นใยพอลิเอทิลีนกับอีพอกซีเรซินด้วยเทคนิคพีลเทสท์พบว่าค่าการยึดติดของฟิล์มที่ผ่านการกราฟท์ด้วยกรดอะคริลิกจะสูงกว่าฟิล์มที่ผ่านการกราฟท์ด้วยอะคริลาไมด์ประมาณ 2 เท่าซึ่งน่าจะมีสาเหตุมาจากปริมาณการกราฟท์และธรรมชาติของสายโซ่ที่ต่างกัน การลดปริมาณความชื้นในชั้นกราฟท์ของทั้งพอลิอะคริลาไมด์ และพอลิอะคริลิกแอซิดโดยการอบในตู้อบสูญญากาศทำให้ค่าการยึดติดกับอีพอกซีเรซินลดลงซึ่งน่าจะเป็นผลมาจากการลดความสามารถในการเคลื่อนที่ของสายโซ่พอลิเมอร์และความแข็งที่ผิวที่เพิ่มขึ้น แต่เมื่อทำให้พอลิอะคริลาไมด์บนพื้นผิวของพอลิเอทิลีนบวมตัวด้วยน้ำที่อุณหภูมิห้อง จะพบว่าค่าการยึดติดเพิ่มขึ้นถึง 8 เท่าจากฟิล์มที่ไม่ได้ทำการบวมตัว และเพิ่มขึ้นสูงถึง 40 เท่าเมื่อทำการบวมตัวในน้ำร้อนที่อุณหภูมิ 80 °C การเพิ่มขึ้นของการยึดติดนี้ คาดว่าจะเป็นผลมาจากความสามารถในการเคลื่อนที่ที่เพิ่มขึ้นของสายโซ่ของพอลิอะคริลาไมด์หลังการบวมตัว ในขณะที่การบวมตัวของพอลิอะตริลิกแอซิดบนพื้นผิวของพอลิเอทิลีนมีผลให้การยึดติดลดลงเนื่องจากสายโซ่ของพอลิอะคริลิกแอซิดสามารถเคลื่อนที่ได้ดีอยู่แล้วการบวมตัวจึงไม่ช่วยเพิ่มความสามารถในการยึดติด จากการศึกษาปริมาณการเกิดปฏิกิริยาของสายโซ่ของพอลิอะคริลาไมด์ที่บวมตัวแล้วกับอีพอกซีเรซินด้วยอินฟราเรดสเปกโตรสโคปี พบว่าการบวมตัวไม่ทำให้ปริมาณของปฏิกิริยาทางเคมีระหว่างสายโซ่ของพอลิอะคริลาไมด์กับอีพอกซีเรซิน เพิ่มขึ้น จึงอาจสรุปได้ว่าการเพิ่มการยึดติดโดยการบวมตัวเป็นผลมาจากการเพิ่มอันตรกิริยาทางกายภาพ

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LIST OF ABBREVIATIONS

PE	= Polyethylene
HDPE	= High density polyethylene
LDPE	= Low density polyethylene
AA	= Acrylic acid
PAA	= Polyacrylic acid
AAm	= Acrylamide
PAAm	= Polyacrylamide
AAm-g-PE film	= Polyacrylamide grafted film
AA-g-PE film	= Polycarylic acid grafted film
AFM	= Atomic force microscope
ATR-FTIR	= Attenuated total reflection fourier transform infrared spectroscope
RI	= Relative intensity
TGA	= Thermal gravimetric analysis
HT	= Hydroxylation temperature
Ht	= Hydroxylation time
GT	= Grafting temperature
Gt	= Grafting time

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CHAPTER 1
INTRODUCTION

Polyethylene (PE) is one of the most widely used polymers in industry as fiber, film and bottle because it has many advantageous properties such as ease of processing, high chemical resistance, flexibility, low density and adequate mechanical properties and low cost. However, PE exhibits poor interfacial adhesion with most matrices, such as epoxy resin. This is due to its chemical inertness and smooth surface, which prevent chemical as well as mechanical bonding. Therefore, adhesion improvement of PE becomes important field of study. In order to improve adhesion of PE, it is necessary to understand the mechanism of adhesion. Several theories have been proposed in an attempt to provide an explanation for adhesion phenomena. The bonding of an adhesive to an object or a surface is the sum of a number of mechanical, physical, and chemical forces that overlap and influence one another. It can be distinguished into variety of theoretical models of adhesion. These include mechanical interlocking, electrostatic forces and the other chemical adhesion mechanism. This chemical adhesion mechanism can be divided into the intermolecular forces by the adsorption theory which are resulted from intimate intermolecular contact between two materials, and in the case of chemical interactions by the chemisorption theory in which primary chemical bonds form across the interface. The processes that play a role in the inter-penetration of polymeric chains at the interface is determined by diffusion. From these theories, there are many factors that influence the adhesion. Therefore to raise adhesion of polymer surface, it is sometimes necessary to carry out physical and/or chemical treatment.

Since PE exhibits low adhesion to most matrices, many methods for modification of PE surface have been developed to overcome this problem, such as plasma treatment [1-4], surface oxidation by corona discharge [5-6] and irradiation technique [7-9]. One of the best ways to modify PE surface is surface grafting, which is introducing new selective functional groups onto PE surface [10-12]. This

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modification technique allows the molecular redesign of polymer surfaces to optimize the PE-matrix interaction and the permanent improvement of PE whereas it does not deteriorate the bulk properties of PE. Many monomers such as glycidyl methacrylate (GMA) [12, 13], methyl methacrylate (MAA) [14], acrylic acid (AA) [15, 16], and acrylamide (AAm) [17, 18] were used as vinyl monomer for surface grafting. Among them, AA and AAm were widely used due to its water soluble property. However, there are the discrepancies between the adhesion of AA and AAm with epoxy resin [19, 20]. In addition, surface grafting with AAm showed the limitation of adhesion with epoxy resin [21-13]. This may be due to nature of AAm. In order to solve these problems, we have been studying the nature of each monomer and proposing a method for adhesion improvement of grafted surface. Increasing grafted chain mobility by swelling has received attention for adhesion improvement [16, 24]. Therefore, for better understanding of improving adhesion by swelling, it has estimate the interfacial adhesion between swelled PE surface and epoxy resin matrix as well as to identify the fundamental mechanisms responsible for the interfacial adhesion.

In this study, we used 2-stage method proposed by Bamford et al [10] to modify PE surface. This method was used in this work due to its many advantages such as less degradation effect and low amount of unwanted homopolymer. The first stage is hydroxylation of polymer to generate hydroxyl groups on surfaces by thermal decomposition of potassium persulface ($K_2S_2O_8$). The second stage is grafting of polar monomers that are AA and AAm onto functionalised polymers. The grafting reaction is subsequently carried out in aqueous solution by ceric ion technique. The grafted surface was subjected to further study of grafted chain mobility. Epoxy resin is attached to grafted PE films to give peel specimens. Adhesion of untreated and treated samples was evaluated using T-peeling test. ATR-FTIR and AFM were used to characterise the chemical structure of PE film surface. The percentage of moisture content in homopolymer was measured by TG analysis.

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CHAPTER 2
OBJECTIVES

In this present work, PE was modified with 2-stage method of hydroxylation via thermal decomposition of potassium persulfate ($K_2S_2O_8$) and subsequently grafting with acrylic acid (AA) and acrylamide (AAm) by ceric (IV) ion technique. Various techniques were used to analysis and compare the nature of AA and AAm grafted chain to gain an in-depth understanding of interfacial adhesion of AA and AAm grafted chain and epoxy resin matrix. The methods to improve adhesion between surface grafted PE and epoxy resin matrix were offered. The effects of moisture content, chain mobility and temperature on adhesion strength between grafted PE and epoxy resin matrix were studied. Moreover, the natural of chemical structure and surface structure of interface between grafted polyethylene and epoxy resin were investigated. Attempt was also made to study the fundamental mechanism responsible for the interfacial adhesion by estimating the extent of reaction with epoxy resin.

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CHAPTER 3
LITERATURE REVIEW

3.1 Polyethylene

Polyethylene (PE) has been widely used since it has many good properties such as high chemical resistance, high impact strength, ease of processing and flexibility with low cost. However, chemical inertness and smooth surface properties of PE limit the applications in composites and coating owing to the lack of adhesion.

It is well known that the basis structure of PE is the chain, which consists of only carbon and hydrogen atoms. Polyethylene is classified into several different categories based mostly on its mechanical properties. The mechanical properties of PE depend significantly on variables such as the extent and type of branching, the crystal structure, and the molecular weight. The formation of various possible chain structures depends upon the catalysts and the polymerization process techniques. Figure 3.1 illustrates the chemical structure of different type of PE.

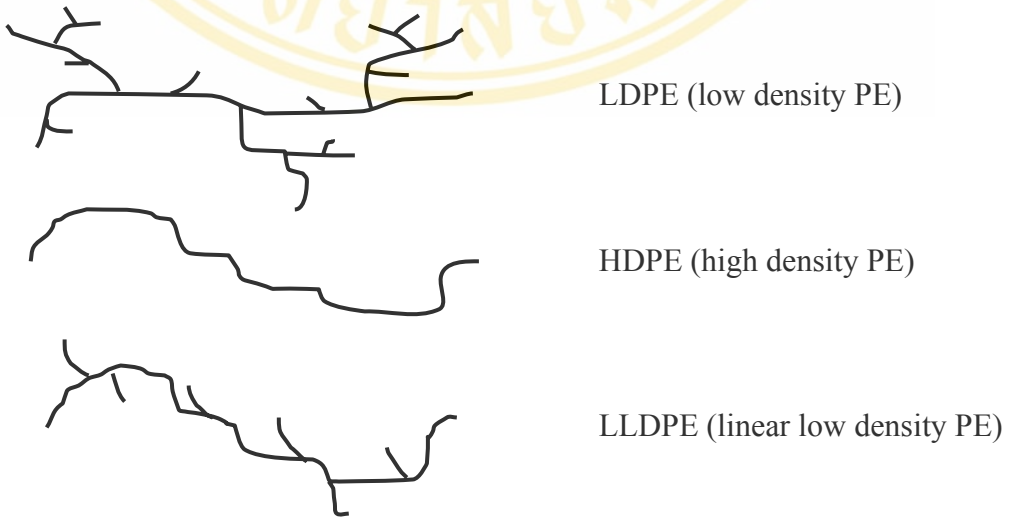

Figure 3.1 Scheme of polyethylene designation

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3.2 Surface Modification [25]

Because PE is inert and has low surface energy, the key problems with this material lie in its adhesion. To overcome these difficulties, surface modifications are employed to enhance the adhesion of PE without altering bulk properties.

There are two distinct types of surface modification: physical and chemical method. In physical method, the surface is irradiated by high-energy radiation to change the surface. In chemical method, the polymer surface is placed in contact with a reactive species, like a liquid, a solution or sometime gas. This provides surface chemical changes.

3.2.1 Physical Modification

The activities aimed at physically modifying polymer surfaces can be divided into two main categories, the first involved with chemically altering the surface layer, the second with depositing an extraneous layer on top of the existing material, thereby generating a sharp interface.

3.2.1.1 Flame Treatment

Flame treatments are widely applied in surface modification to introduce oxygen-containing functions at polymer surface. Active species formed by the high temperature include radicals, ions and molecules in excited states.

3.2.1.2 Corona Treatment

Corona treatments exploit the corona effect, i.e. the formation of high energy electromagnetic fields close to charged thin wires or points, with consequent ionization in their proximity, even at atmospheric pressure and relatively low temperature. In the ionized region, excited species (ions, radicals, electrons, molecules in excited states, etc.) are present and latter are active in surface modification, typically introduction of oxygen-containing functions.

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Oosterom et al [6] studied adhesion performance of UHMWPE after different surface modification techniques. Corona treatments were found to activate the surface by an increase in surface energy of over 100% in an order of less than a minute, corresponding to an increase in ultimate shear stress from 0.12 to 0.40 MPa.

3.2.1.3 Plasma Treatment

Plasma treatment has been widely applied to modify the polymer surface to improve the adhesion strength. When a gas is electromagnetically excited or electrically charged at low pressure (0.1-10 torrs), a glow discharge similar to corona discharge in air, refer to as plasma, is produced. Plasma contains free radicals, an equal number of positive ion and electrons and neutral species. The activated species can readily react with polymer substrate in contact.

Tahara et al [2] investigated improvement of adhesion of polyethylene by glow-discharge plasma. Plasma treatment enhances the adhesion of PE with epoxy resin, relating to an increase in surface energy and the anchor effects imparted by plasma etching. Peel strength increased up to 120 N/m or 6 folds higher than that of the untreated surface.

Tissington et al [3] studied the effects of oxygen plasma treatment on the adhesion behavior of polyethylene fibers. The adhesion to epoxy resin was monitored by pull out test. The effect of the oxygen plasma on the PE surface, and the subsequent increase in bond strength with epoxy resin, can be described in terms of three separate mechanisms. First, exposure to oxygen plasma results in the rapid oxidation of the PE surface, with the formation of active oxygen-containing groups. These are capable of strong polar interaction with the epoxy resin and produce the high degree of contact necessary for strong bonding. Secondly, at intermediate treatment times cross-linking of surface occurs, which increases the cohesive strength of the fibre surface. Finally, at long exposure times there causes extensive pitting of the fibre surface, which can improve adhesion by a mechanical adhesion by a mechanical keying effect.

Moon and Jang [4] studied the factors affecting the interfacial adhesion of ultrahigh-modulus polyetrheylene fibre-vinylester composites using gas plasma treatment. It was found that wettability enhancement by the chemical functional group

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formation and the mechanical interlocking due to the micropits were important factors in improving the interfacial adhesion.

3.2.2 Chemical Modification

Chemical modifications is the treatment that modified the chemical composition of polymer surface either by direct chemical reaction with a given solution (surface oxidation) or by the covalent bonding of suitable macromolecular chains to the sample surface (surface grafting).

3.2.2.1 Surface Oxidation

Surface treatment of various polymers by oxidizing solution displays surface roughness and the introduction of oxygen containing functional group. Chromic acid treatment on PE surface has been extensively studied. Nardin and ward studied the effect of chromic acid ($K_2Cr_2O_7/H_2S_2O_4/H_2O$) on PE surface. PE fiber was immersed in chromic acid for 1 min. It was found that chromic acid treatments seem to modify only the chemistry of the surface roughness unchanged. It was purposed that the treated surface contained carboxylic acid or ketone group.

3.2.2.1 Surface Grafting [26]

Surface modification via surface graft polymerization has been widely studied. It is a very simple method to obtain functionalized polymers with specific properties, by introducing specific monomers only on polymer surface. The surface graft polymerization of monomers can be initiated by trapped free radicals or polymeric peroxides generated in the surface region of the substrate polymer. Various commonly used grafting methods are illustrated in Figure 3.2. The key advantage of these techniques is that the surface of the same polymer can be modified to have very distinctive properties through the choice of different monomers.

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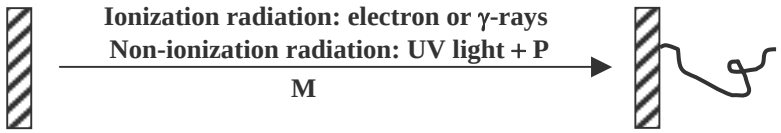
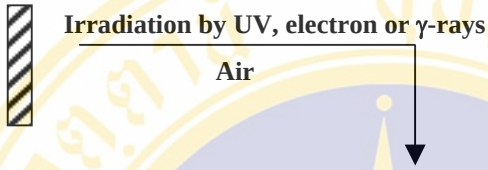
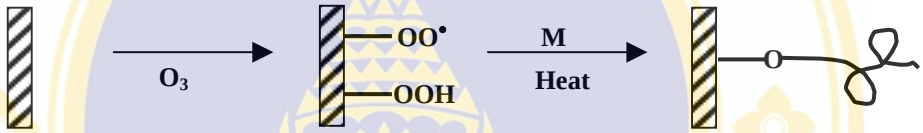
Mutual-Irradiation grafting



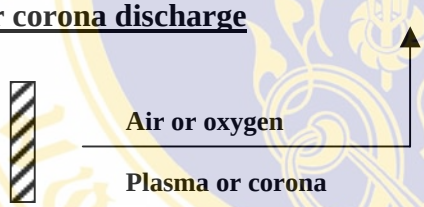
Pre-irradiation grafting



Chemical grafting



Plasma or corona discharge



M = monomer
P = photosensitizer or photoinitiator

Figure 3.2 Various surface grafting methods.

It is known that surface grafting may proceed by a free radical abstracts hydrogen atom from the polymer. Macroradical are then formed and there radical can act as grafting site for vinyl polymerization. Therefore, a fundamental step in grafting is the creation of active site on the polymer surface. This can be done using either peroxide initiator or irradiation technique.

- Peroxide-initiation

In the peroxidation grafting method, polymers were subjected to high-energy radiation in the presence of air or oxygen. The peroxy products are then treated with a

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monomer at a higher temperature, hence the peroxides undergo decomposition to radicals and initiate grafting. The peroxidation grafting process is represented through a simple mechanism below.

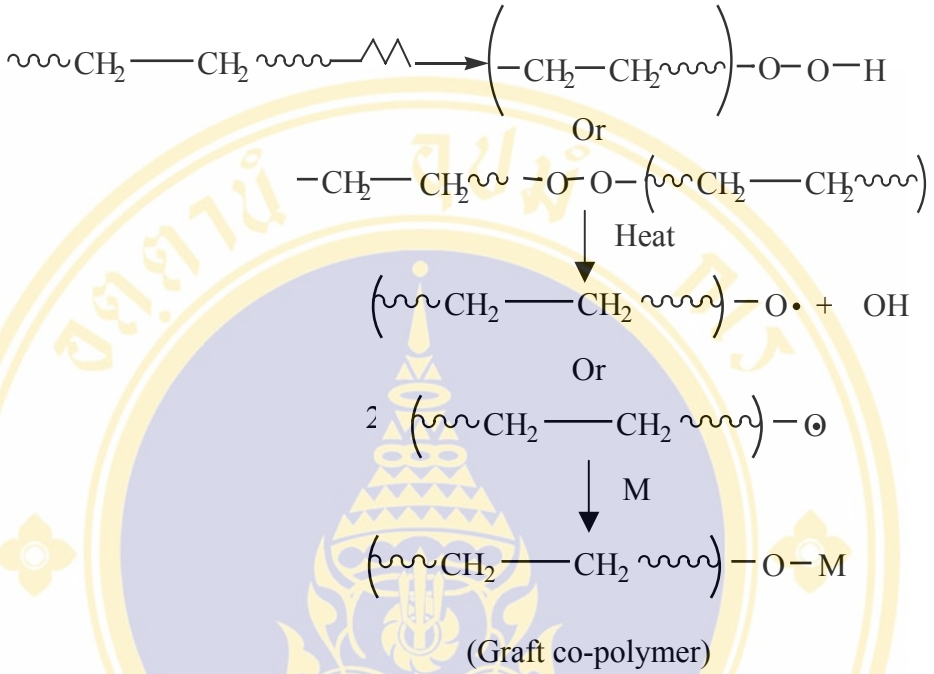

Figure 3.3 Grafting by peroxidation technique

Kidal et al [27] studied peroxide-initiated grafting of acrylamide on to PE surfaces. Organic peroxide, tert-butyl peroxide-nedecanoate was swollen into the film from cyclohexane. At elevated temperature, the oxygen-oxygen bond of peroxide is homolytically cleavage to from radical. The radical site in PE surface was created via H-abstraction. The grafted yield increased with reaction time. The presence of air was found to retard the grafting reaction.

- Irradiation technique

In the pre-irradiation technique, first polymer main chain is irradiated in vacuum or in the presence of an inert gas to from free radicals. Irradiated polymer substrate is then treated with a monomer, which is either liquid or vapor or as a solution in a suitable solvent. The pre-irradiation grafting process is represented through a simple mechanism below.

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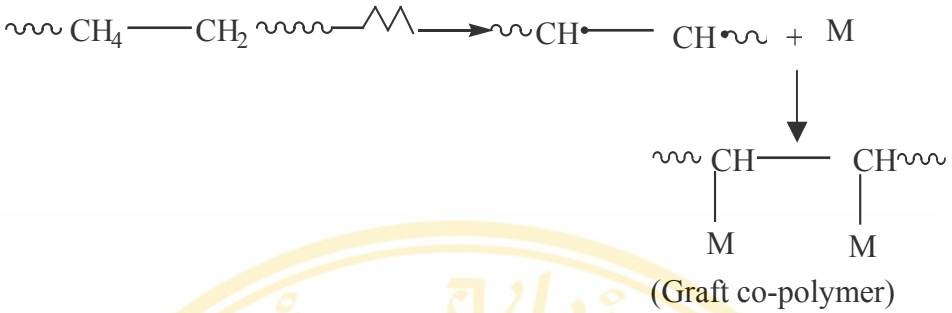

Figure 3.4 Grafting by pre-irradiation technique

Modification of PE by irradiation technique has been achieved [7, 8]. Balamurugan S. et al [7] and Chanunpanich N. et al [8] modified the surface of polyolefin by photochemical bromination. Polyolefin films were modified by photochemical bromination and subsequent to substitution reaction. It was seen that the modified polymer surfaces showed higher surface energy, leading to the improvement of wettability. Wang T et al [9] studied surface modification of LDPE films by UV-induced graft copolymerization and its relevance to photolamination. The LDPE films were pretreated by ozone treatment and monomer solution was introduced between the two ozone-pretreatment LDPE films. The LDPE/monomer/LDPE assembly was illuminated by UV light and then subjected to determination of lap shear adhesion strength. It was found that lap shear photolamination strength gradually and continuously increased after UV illumination.

3.3 Two-Stage Surface Modification

Many conventional surface treatments have been used to modify the surface properties of PE. Some of these methods have disadvantages of degrading polymers and the use of non-aqueous media may be necessary. Moreover, some techniques are complicated, require special equipment and produce large quantities of unwanted homopolymer.

Bamford et al [10] proposed a simple chemical modification for functionalisation and grafting of polar monomers onto polymer substrates. It is a 2-stage process in which the first is hydroxylation of polymer to generate hydroxyl

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groups on surfaces and the second grafting of polar monomers onto functionalised polymers.

3.3.1 Hydroxylation Stage

Hydroxylation of polymers is a method which comprises of the polymer in an aqueous media with an oxidizing agent capable of producing oxygen-centre radicals which are ultimately responsible for introducing hydroxyl groups on PE surfaces.

The oxidizing agent usually is a peroxy salt, preferably a peroxy-disulfate or monosulfate. The order of effectiveness in hydroxylation was studied and shown as the following [28]:

$K_2S_2O_8 \approx Na_2S_2O_8 \approx KHSO_5 \approx NaClO_4 > NaIO_4 > (H_2O_2+Fe\ (II)) > NaBO_3.4H_2O$

Thus it is clear that peroxy-disulfate shows highest effect for hydroxylation. It is well known that persulfate is a strong oxidizing agent and a radical source in aqueous solution that is frequently used as an initiator for free radical polymerisation. Bartlett et al [29] studied and purposed mechanisms for thermal decomposition of persulfate. It is a first order reaction and the mechanism is shown below.

$$^{-}O_3SO{-}OSO_3^{-} \longrightarrow 2\,SO_4^{\cdot-} \quad (1)$$

$$SO_4^{\cdot-} + H_2O \longrightarrow HSO_4 + {}^{\cdot}OH \quad (2)$$

$$2\,{}^{\cdot}OH \longrightarrow H_2O + 1/2\,O_2 \quad (3)$$

Kolthoff and Miller [30] confirmed this mechanism. The decomposition was carried out in ^{18}O-labeled water. It was found that the oxygen generated in the reaction originated from water. These reactions appear to be responsible for hydroxylation of polymer by the abstraction of relatively reactive hydrogen atoms from polymer substrate as shown below.

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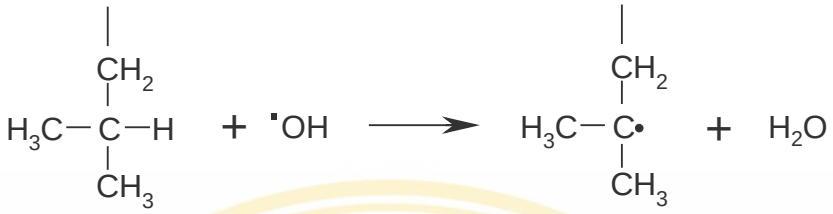
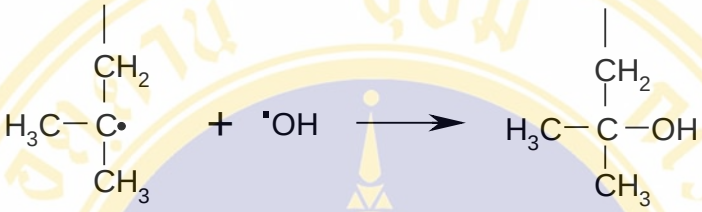
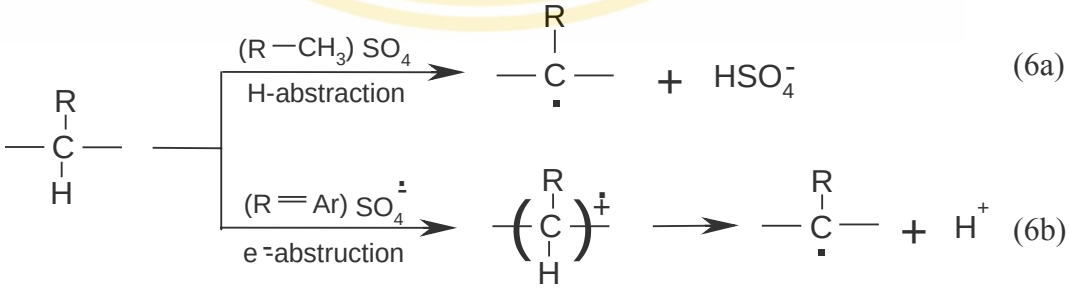


(4)



(5)

In thermal decomposition reactions (1)-(3), it is assumed that hydroxylation of the polymer occurs through interaction with hydroxyl radicals. However, the system contains three reactive species, i.e., OH, $SO_4^{\bullet -}$ and $^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-}$. Gaylord et al [31] studied the reaction of the sulphate anion-radicals. It was concluded that sulphate anion-radicals could react with organic compound in at least three different ways: by hydrogen abstraction, electron abstraction and addition to double bond. Bamford et al [10] purposed the mechanism that possibly leaded to functionalised polymer based on both sulphate anion-radicals and peroxy-disulfate dianions. These are shown in reaction (6a)-(6e). Reactions (6a) and (6b) depend on the nature of substituent R.



(6a)

(6b)

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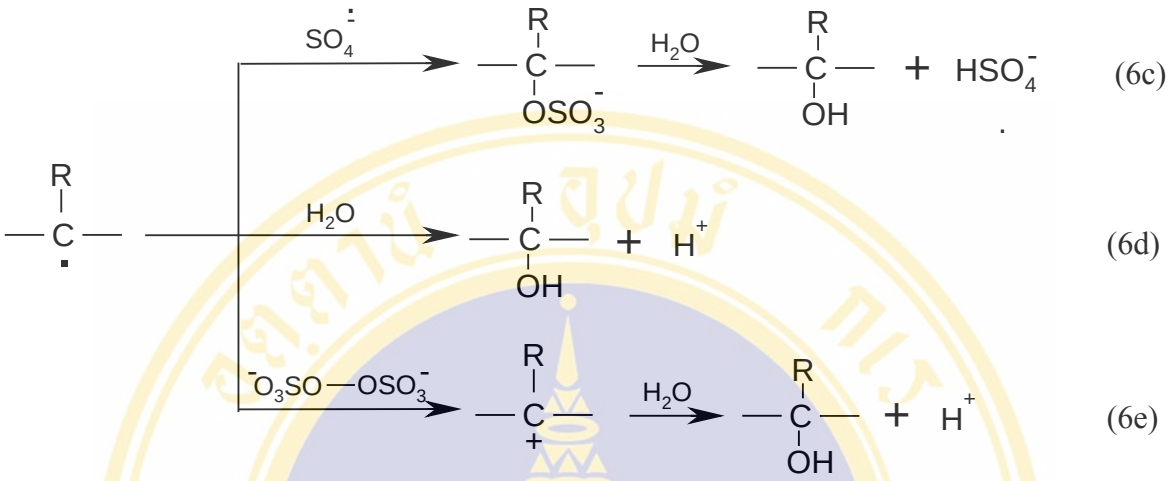
Reactions (6c)-(6e) show the possible paths for polymer radicals to change to functionalised polymers.



(6c)

(6d)

(6e)

It may be expected that functionalised samples should show hydroxyl groups on polymer surfaces after reaction.

3.3.2 Grafting Stage

It is well known that ceric salt can be used as an initiator for vinyl functionalized [30, 32, 33]. It also forms a very effective redox system in the presence of an organic reducing agent such as alcohol. This method has an advantage of performing reasonable rate at moderate temperatures. In addition, the ceric method has been extensively used in grafting of hydroxyl polymer substrates such as agar [34], starch [35, 36] and kenaf fibres [37]. These polymers have hydroxyl groups on polymer backbone. So, it shows very effective grafting.

The second stage of 2-stage method is grafting of vinyl monomers onto functionalized substrates. The grafting reaction is subsequently carried out in aqueous solution by conventional ceric ion technique. Such a reaction would proceed as follows:

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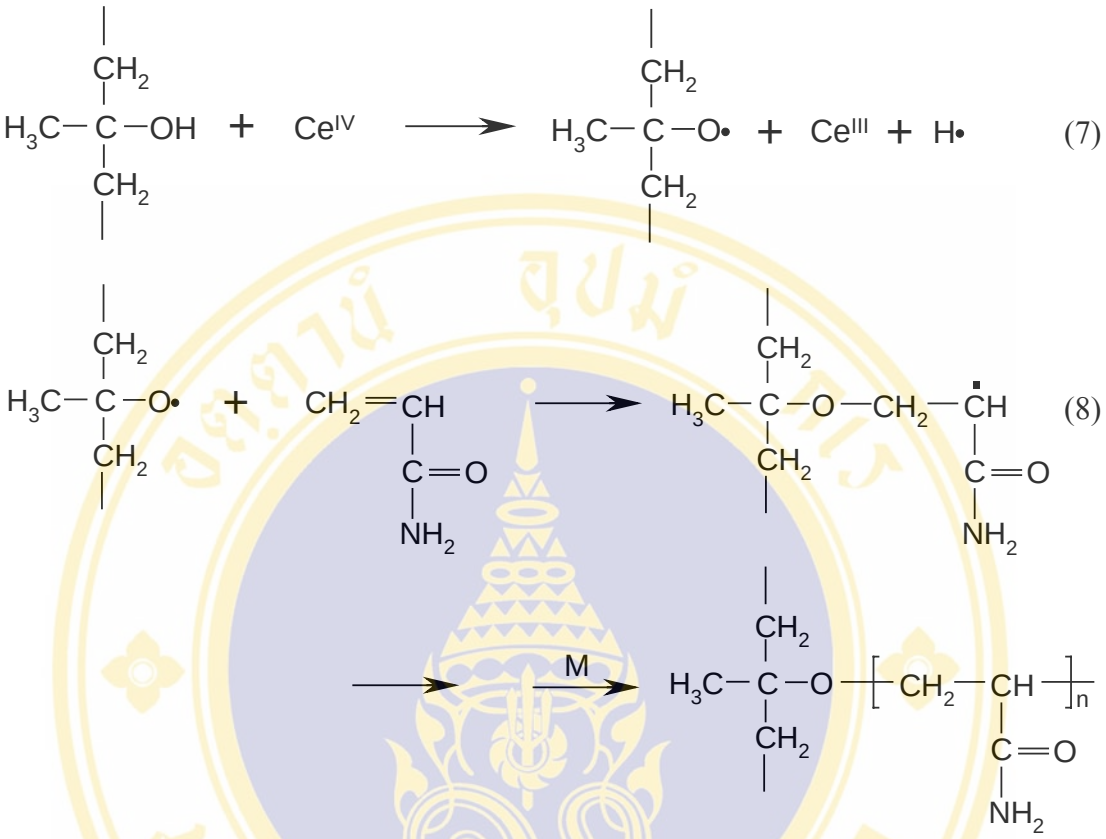

(7)

(8)

Many papers [10, 36] reported that non-functionalised samples did not show any grafting. Additionally, grafting of AAm by 2-stage method may be followed by hydrolysis of amide groups to carboxyl groups to provide an increase in polarity. Compared to other methods of surface grafting, 2-stage method possesses a number of technical and theoretical advantages. It generates reactive sites on polymer backbone. So, the side reaction could be minimized.

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3.4 Theories and Mechanism of Adhesion [38]

Adhesion mechanisms refer to the various types of intrinsic forces, which can operate across the adhesive/substrate interface. There are six possible mechanisms of adhesion.

3.4.1 Mechanical interlocking

3.4.2 Electronic theory

3.4.3 Theory of boundary layers and interphases

3.4.4 Adhesion (or Thermodynamic) theory

3.4.5 Diffusion theory

3.4.6 Chemical bonding theory

Among these models, one usually distinguishes rather arbitrarily between mechanical and specific adhesion, the latter being based on the various types of bonds (electrostatic, chemical) that can develop between two solids. Actually, each of these theories is valid to some extent, depending on the nature of the solids in contact and the condition of formation of the bond system. Therefore, they do not negate each other and their respective importance depends largely on the system chosen.

3.4.1 Mechanical interlocking

The mechanical interlocking model conceives of mechanical keying, or interlocking, of the adhesive into the cavities, pores, and asperities of the solid surface to be the major factor in determining adhesive strength. The enhancement of adhesion by mechanical keying can be attributed simply to the increase in interfacial area due to surface roughness, insofar as the wetting conditions are fulfilled to permit penetration of the adhesive into pores and cavities.

3.4.2 Electronic theory

The electronic theory of adhesion involves an electron transfer mechanism between the substrate and the adhesive, having different electronic band structures.

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This phenomenon could induce the formation of a double electrical layer at the interface. The results electronic forces can contribute significantly to the adhesive strength. Therefore, the adhesive-substrate junction can be analyzed as capacitor. During interfacial failure of this system, separation of the two plates of the capacitor leads to an increasing potential difference until a discharge occurs. Consequently, it is considered that adhesive strength results from the attractive electrostatic forces across the electrical double layer.

3.4.3 Theory of boundary layers and interphases

The cohesive strength of a weak boundary layer can always be considered as the main factor in determining the level of adhesion, even when the failure appears to the interfacial. This theory is based primarily on probability considerations showing that the fracture should never propagate only along the adhesive-substrate interface for pore statistical reasons and that cohesive failure within the weaker material near the interface is a more favorable event. Therefore, several types of weak boundary layers were proposed, such as those resulting from the presence at the interface of impurities or short polymer chains.

3.4.4 Adsorption (or Thermodynamic) theory

This theory is based on the belief that the adhesion will adhere to the substrate because of interatomic and intermolecular forces established at the interface, provided that an intimate contact is achieved. The most common interfacial forces result from Van der Waals and Lewis acid-base interactions. The magnitude of these forces can generally be related to fundamental thermodynamic quantities, such as surface free energies of both adhesive and adherend. Generally, the formation of an assembly goes through a liquid-solid contact step, and therefore criteria of good adhesion become essentially criteria of good wetting, although this is a necessary but not sufficient condition.

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3.4.5 Diffusion theory

The diffusion theory of adhesion is based on the assumption that the adhesion strength of polymer to themselves (autohesion) or to each other is due to mutual diffusion (interdiffusion) of macromolecules across the interface, thus creating an interphase. Such a mechanism implies that the macromolecular chains or chain segments are sufficiently mobile and mutually soluble. Therefore, if interdiffusion phenomena are involved, the joint strength should depend on different factors, such as contact time, temperature, nature and molecular weight of polymer, and so on.

The diffusion phenomena do actually contribute greatly to the adhesive strength in many cases involving polymer-polymer junctions. Nevertheless, the interdiffusion of macromolecular chains requires both polymers to be sufficiently soluble and the chains to possess a sufficient mobility. These conditions are obviously fulfilled for autohesion, healing, or welding of identical polymer processes. However, diffusion can become a most unlikely mechanism if the polymers are not or only slightly soluble, if they are highly cross-linked or crystalline, or put into contact at temperatures far below their glass transition temperature.

3.4.6 Chemical bonding theory

It is easily understandable that chemical bonds formed across the adhesive-substrate interface can greatly participate to the level of adhesion between both materials. These bonds are generally considered as primary bonds in comparison with physical interactions, such as Van de Waals, which are called secondary force interactions. The terms primary and secondary stem from the relative strength or bond energy of each type of interaction. The formation of chemical bonds depends on the reactivity of both adhesive and substrate.

In this section, mechanisms of adhesion that have laid the basis for the way to connect interfacial adhesion were proposed. In general, special surface properties such as chemical composition, hydrophilicity, roughness, crystallinity, conductivity, lubricity, and crosslinking density are required for the success of this proposal. PE does not possess the surface properties needed for this proposal. Thus, improvement of

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interfacial adhesion between surface grafted PE and epoxy resin depends significantly on quality of the interface which is based on these adhesion mechanisms.

3.5 Grafted Chain Mobility

Surface grafting has been one of the widely used methods to improve interfacial adhesion of polymer because it has advantages over other methods in several points, including controllable introduction of grafted chains with exact localization of grafted chains to the surface with the bulk properties unchanged. Furthermore, covalent attachment of graft chains onto a polymer surface avoids their delamination, and assures long-term chemical stability of introduced chains. There are numerous literatures that reported adhesion improvement by surface grafting [13, 16, 18, 19, 39, 40]. It was found that the adhesion of grafted surface depended on many factors, such as surface graft density, type of monomer, microstructure of the grafted surface and nature of the interfacial adhesion. However, the limitation of adhesion improvement could be observed when the grafted density exceeded a critical value [21, 22, 23]. From the theory of adhesion as describe in previous section, there are many ways to participate in adhesion strength of grafted chain and adhesive, including enhancement of the level of interdiffusion of grafted chain and adhesive. Nevertheless, the interdiffusion of grafted chains requires a sufficient mobility. It was known that grafted chain mobility can be increased by swelling in the presence of water [16, 24]. Therefore, study of increasing grafted chain mobility by swelling for improving adhesion becomes attractive.

Karlsson and Gatenholm [24] studied surface mobility of grafted hydrogels. Poly(2-hydroxyethyl methacrylatte) (PHEMA) was grafted onto PP substrate through ozone-induced graft polymerization. Angle-dependent ESCA and dynamic contact angle measurements (DCA) revealed that the grafted layer is probably swelled in the wet state and the grafts are relatively stretched. The drying process results in collapsing of the grafted layer, while at the same time the more hydrophobic parts of the polymer backbones are oriented to the hydrophobic environment. This finding indicated that swelling could increase grafted chain mobility. Figure 3.5 illustrates the

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schematic of proposed model of the difference between the grafted layer in wet state and in the dry state.

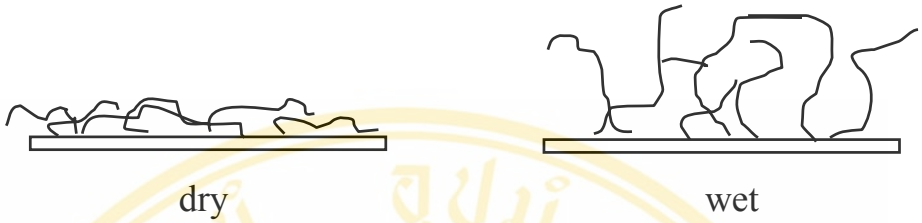

Figure 3.5 Proposed model of grafted chains in wet state and dry state

Kang et al [16] studied the surface modification of polymer films by graft copolymerization for adhesive-free adhesion. It was found that swelling of grafted chains in the presence of water resulted in enhancement adhesion strength of PE film. They found that two surface grafted films are capable of exhibiting 'adhesive free adhesion' when brought into contact in the presence of water and subsequently dried. The development of the lap shear adhesion strength depends upon the interdiffusion and entanglement of grafted chains. Figure 3.6 shows scheme of grafted chain swelling.

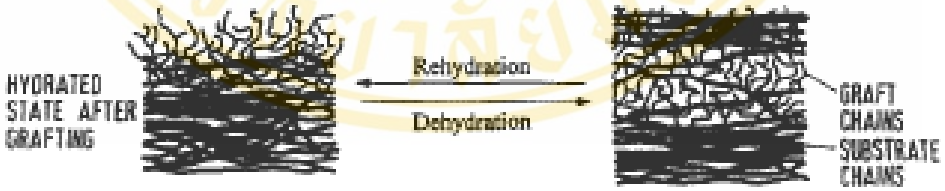

Figure 3.6 Scheme of grafted chain swelling

Effect of solvent for swelling on grafted chain mobility was also reported. Satyanarayana and Chatterji [41] studied swelling characteristics of amphiphilic polymer brushes in pure and mixed solvent systems. Amphiphilic polymer brushs are synthesized by the sequential graft copolymerization of crosslinked gelatin with methyl methacrylate (MMA) and acrylic acid (AA). They reported the swelling behavior of these systems in the mixture of ethanol and water. While PAA is soluble

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in both these solvents, PMMA is not soluble in either, but is soluble in a mixture of the two. After swelling in pure water or ethanol, the solvent could interact with the PAA chains alone, while the PMMA chains were in the contracted state. Thus, the swelling ratio was low. As in the mixture of water and methanol, both PAA and PMMA chains interacted equally well with the mixed solvent medium. PMMA chains expanded while PAA chains remain stretched. This resulted in high swelling ratio. Visualization of these swelling behaviors was schematically represented in Figure 3.7.

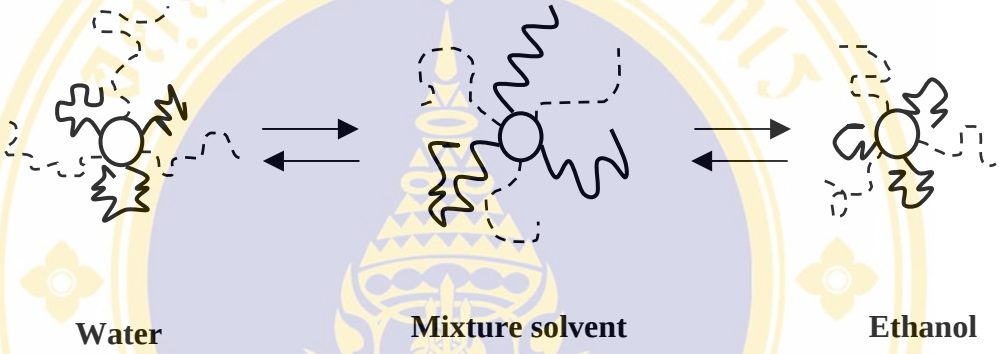

Figure 3.7 Visualizing the behavior of Gel-g-(PMMA, PAA) in ethanol/water mixed solvent system: (O) Gelx core; (--) PAA grafts; ( ) PMMA grafts

Tsuneda S. et al [42] studied local mobility of polymer chain grafted onto polyethylene monitored by fluorescence depolarization. Glycidyl methacrylate (GMA) was grafted onto porous polyethylene MF membrane by radiation-graft polymerization. It was found that GMA grafted chains stretched in water and shrank in benzene. This is because the grafted chain conformation is affected by solvent polarity. Moreover, the mobility of grafted chains was also changed by the degree of grafting. The expected conformation change of the grafted polymer chain in water and benzene as a function of degree of grafting is schematically illustrated in Figure 3.8.

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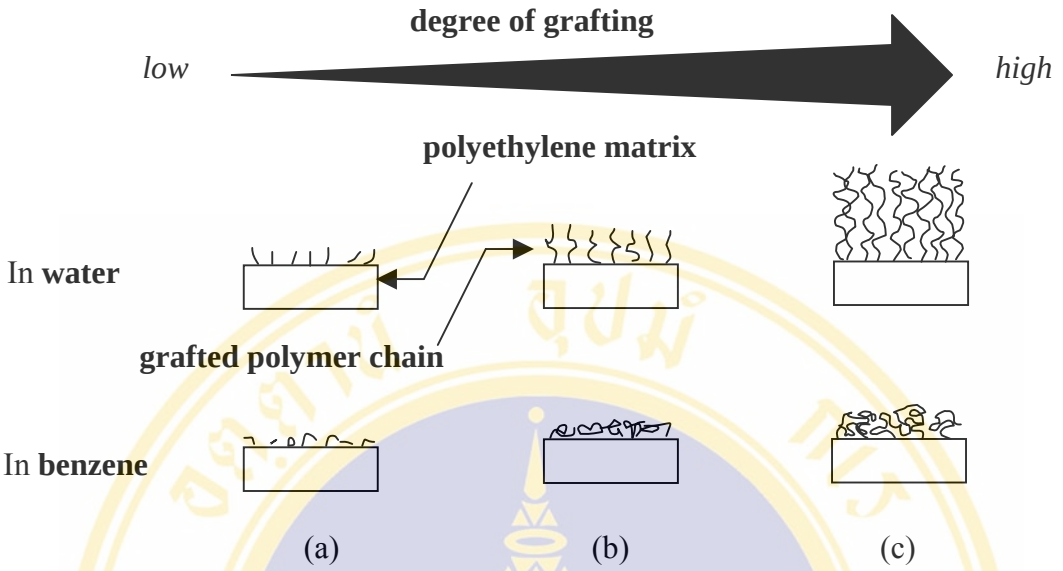

Figure 3.8 Schematic illustration of conformation of grafted polymer chain with different degrees of grafting (d.g.) in water and benzene. (a) d.g.= 0-20% (b) d.g.= 20-80% and (c) d.g.= 80-320%.

Iwata et al. [43] grafted PAA onto a porous nucleopore membrane to study the filtration rate of the grafted membrane as a function of graft density and pH. The PAA chains grafted on the membrane surface dynamically changed their configuration in response to the medium pH. In addition, AFM images demonstrated that the grafted chains shrank and precipitated on the surface of the membrane and wall of pores at acidic pH, thereby opening the pores of the membrane, whereas they hydrated and thus effectively closed the pores at neutral and alkaline pH. As shown in Figure 3.9, the PAA grafted chains dynamically opened and closed the pores in response to the medium pH.

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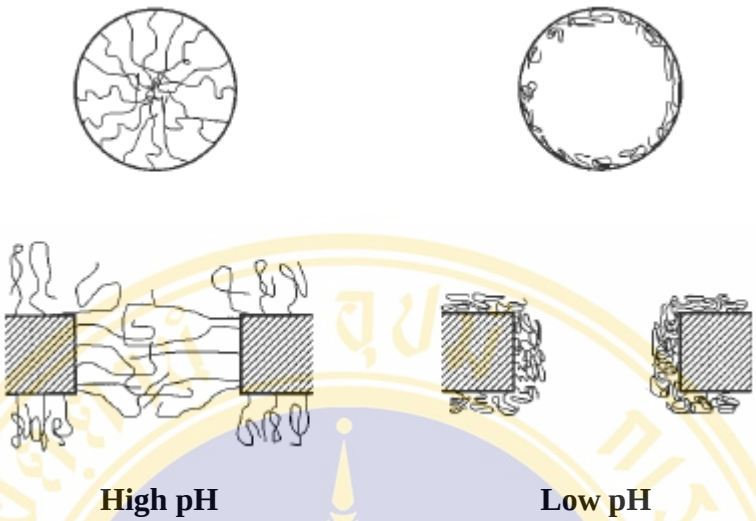

Figure 3.9 Schematic representation of the grafted polymer chains at low and high pHs onto a membrane.

Among the various types of monomer for surface grafting, AA and AAm grafted surface exhibits the great degree of swelling due to their hydrogel characteristic. Hydrogels are hydrophilic three-dimensional polymer networks capable of absorbing a large volume of water or other liquids [44, 45]. Thus, surface grafting with hydrogels could improve the hydrophilic of the substance surface. Hydrogels grafted chains exhibit mobile surfaces since the outermost surface layer contains large amounts of water, which acts as a plasticizer [24]. The grafted hydrogel showed advantageous degree of swelling in comparison with conventional monomer, owing to the high mobility of hydrogels grafted chains [44].

Considering on the degree of swelling, it is dependent upon several factors, e.g., the temperature responsive behaviors of grafted chain. Lee et al [45] studied the swelling behavior of surface grafted hydrogels that was affected by temperature change. It was found that the swelling ratio of PNIPAAm grafted surface was changed with different temperatures arising from the dissimilar structure of grafted chain.

Moreover, rate of swelling is also dependent upon mobility of grafted chain. Lee et al [44] studied pH/temperature-responsive behaviors of semi-IPN and comb-type graft hydrogels composed of alginate and PNIPAAm. It was found that comb type graft hydrogels which has mobile PNIAAm grafted chain exhibited fast swelling

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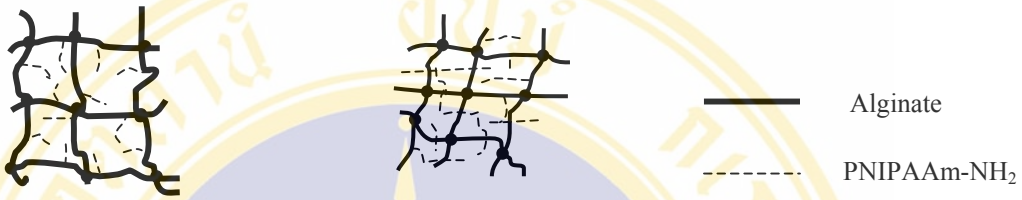
rate due to free and mobile grafted chains. By contrast, semi-interpenetrating polymer network (semi-IPN) which has compact structure of PNIAAm grafted chain showed slow swelling compared with comb-type graft hydrogel. Structures for comb-type graft hydrogel: (a) and semi-IPN hydrogel (b) are schematically illustrated in Figure 3.10.



a) Alginate/PNIPAAm Comb-Type graft hydrogel

b) Alginate/PNIPAAm Semi-IPN hydrogel

Figure 3.10 Schematic illustration of structure for: (a) alginate/PNIPAAm-NH_2 comb-type graft hydrogel and (b) semi-IPN hydrogel.

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CHAPTER 4
MATERIALS AND METHODS

4.1 Materials

In this study the materials used were:

1. Potassium persulfate (potassium peroxydisulfate) ($K_2S_2O_8$) was obtained from Fluka and used as received.
2. Ceric ammonium nitrate was obtained from Fluka and used as received.
3. Nitric acid (HNO_3) was obtained from Fluka and used as received.
4. Methanol (MeOH) was purified by distillation before used.
5. Acetone was distilled prior to use.
6. Monomers were reagent grade and obtained from Fluka.

   The monomers used were:

   - Acrylamide (AAm) was used as received without further purification.
   - Acrylic acid (AA) was purified by distillation under reduced pressure to remove the polymerization inhibitor.
7. High-density polyethylene (HDPE) fibre

   The fibre used in this work was 10× drawn high-density polyethylene (HDPE), namely Thai-Zex 6200B purchased from Bangkok Polyethylene Co., LTD.). It has a melt flow index of 0.30 and a density of 0.962 g/cm^3.
8. Linear low-density polyethylene (LLDPE) film

   The Linear low-density polyethylene (LLDPE) film used was kindly donated by Pacific Polymer Co., Ltd. The thickness of film was about 110 μm.
8. DER 331 resin (Standard liquid Bis-A epoxy resin)
9. Ancamine® 1618 curing agent (Cycloaliphatic amine)

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4.2 Instruments

Instruments used in this study were:

1. Tensile tester (Instron Model 5569)
2. Fourier Transform Infrared Spectrometer (Bruker Equinox 55)
3. Thermogravimetric Analyser (TGA2050)
4. Atomic Force Microscope (Nanocope III a model NS 3a/Digital Instrument, Inc.)
5. Vertex mixture (Scientific Industries, Inc.)

4.3 Preparation of Polyethylene Specimens

The samples of this study were prepared in 2 types:

4.3.1 High-density polyethylene (HDPE) fibre

Melt spinning was used to prepare isotropic PE fibre. PE pellet was melt in Randcastle microextruder. The processing was performed at screw speed of 5 rpm, temperature of 160, 180 and 190°C at three-barrel zones and 195°C at the spinneret. The molten PE was forced through spinneret and allowed to solidify in a current of water. Isotropic PE fibre was subsequently drawn at 212°F and at draw ratios (λ) of 9. The PE fiber had a diameter of about 200 μm. The drawn fibres have tensile strength of 0.8 GPa and modulus of 6 GPa.

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4.3.2 Linear low-density polyethelene (LLDPE) film

Linear low density polyethylene film was provided by Pacific Polymer Co., Ltd. The thickness of film was about 110 μm.

4.4 Surface Modification by 2-stage Method

In this study, the surface modification of PE was performed the two-stage method [10]. First, hydroxylation was performed to generate the hydroxyl groups on PE surfaces. The second stage is grafting of polar monomers onto functionalized polymer.

4.4.1 Hydroxylation or Functionalisation

In this work, PE samples were used in two forms; i.e., film and fiber. The PE film was cut into strip of 2x10 cm^2. For PE fiber, about 200 cm. long of fiber was wound onto glass frame. Before used, samples were cleaned with distilled acetone and dried at room temperature under atmospheric pressure. Samples were hydroxylated with an aqueous solution of 7% Potassium persulfate ($K_2S_2O_8$) in test tube and then purged with nitrogen gas to remove oxygen gas before starting the reaction. Hydroxylation was performed at 80° C for periods varying from 10 to 180 min. To expel the oxygen occurred in reaction at sample surface, test tubes were sharked in vertex mixture every 15 min. Samples were then removed, washed with hot water and dried at room temperature under atmospheric pressure.

4.4.2 Grafting by Ceric Ammonium Nitrate Technique

After hydroxylation, sample was submitted to grafting reaction. The grafting of the functionalized samples was done in aqueous solution of $3x10^{-3}$ M ceric ammonium nitrate and 0.05 N HNO_3. The solution was deaerated by passing N_2 for 30 sec. The reaction was carried out at 50°C for several periods of time (10-120 min). Grafted PE samples were extracted for 12 h with water to remove homopolymer.

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4.5 Homopolymer preparation

PAAm and PAA homopolymer were prepared by redox polymerization. The procedure for the homopolymer preparation can be described as follow: 10% of AAm and AA monomer and 1.5x 10^{-3} M ceric ammonium nitrate were dissolved in 0.05 N HNO_3. The solution was purged with nitrogen gas to remove oxygen gas and the reaction was performed at 50°C until the solution became gel. Then, the homopolymer gel was poured off to plate and dried in oven at 80°C for 2 days. Homopolymer had a thickness of about 0.237 mm. TGA and ATR-FTIR were measured to determine the homopolymer behaviour.

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4.6 Characterisation of Grafted Samples

4.6.1 Degree of Grafting

The degree of grafting on PE surface was determined by gravimetric method. Extent of grafting was expressed base on weight change of sample after grafting associated with the amount of grafted chains per surface area of sample, or defined as follow:

$$\text{Extent of grafting} = \frac{(W_1 - W_0)}{A} \quad (1)$$

where:

W_0 is the weight of sample before the grafting reaction
W_1 is the weight of sample after the grafting reaction
A is the area of sample

4.6.2 Atomic Force Microscope (AFM)

Atomic force microscope (AFM) image and force measurement were conducted using a Nanoscope III a model NS 3a/Digital Instrument Inc. In this study, two types of AFM were used; i.e. tapping mode and contact mode.

- Tapping mode

Images of surface morphology were recorded in taping mode using standard silicon nitride (Si_3N_4) integral tips, mounted on cantilevers with its scanning rate 0.5003 Hz.

- Contact mode

Hardness of AA and AAm homopolymer were investigated in contact mode using calculation on slope of extended line from force curves. The extended line was obtained from the corresponding downward deflection when the cantilever tip was

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contacted with the surface. Force curve and schematic of tip-interaction are shown in Figure 4.1. Scanning rate was 4.650 Hz and deflection set point at 0 V was used. In this study, rigidity of AA and AAm homopolymer were measured using the cantilever with spring constant 0.38 N/m, fitted to softer surface and 0.58 N/m, fitted to hard surface, respectively. For each value of slope of force curve, at least eight measurements at the same position were measured and averaged to reduce error from surface variation. In order to normalize the data from force curves obtained with different spring constant of cantilever, we have considered the following ratio:

$$\text{Hardness of AA and AAm homopolymer} \quad \alpha \quad \frac{\text{Slope}_{\text{AA, AAm}}}{\text{Slope}_{\text{Si}}}$$

Where:

$\text{Slope}_{\text{AA, AAm}}$ is the slope of AA or AAm homopolymer obtained from extended line of force curve (curve C in Figure 4.1)

Slope_{Si} is the slope of silicon obtained from extended line of force curve (curve C in Figure 4.1)

The silicon, a rigid reference sample, was used to scale the deflection sensitivity of force curve by dividing the slope value of sample surface.

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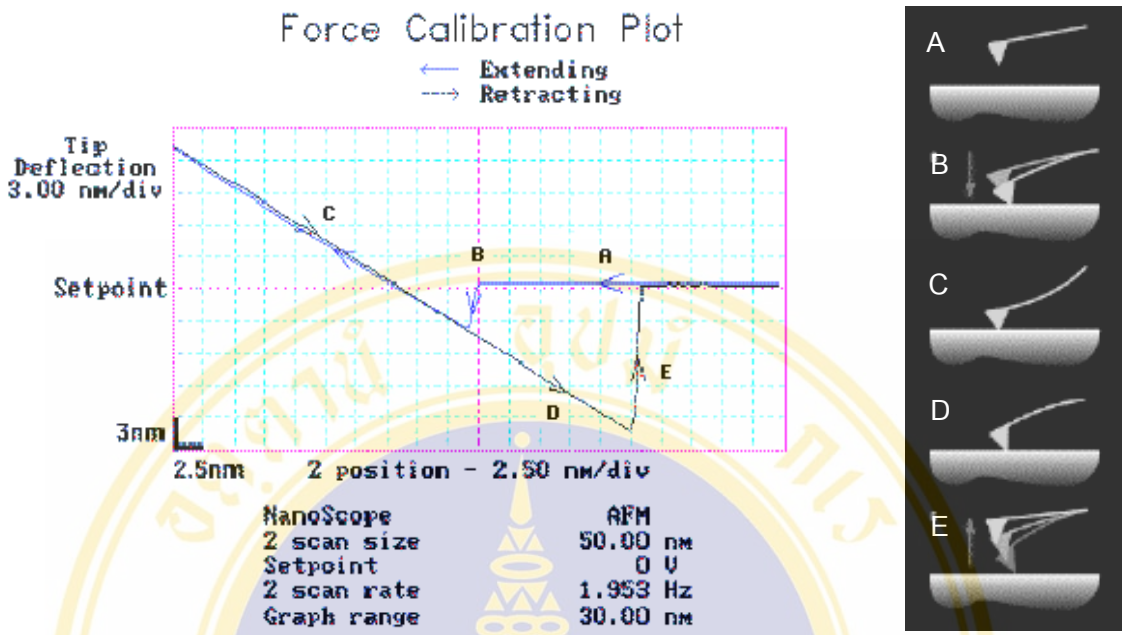

Figure 4.1. Force curve and tip-surface interaction

4.6.3 Thermogravimetric Analysis

The weight change of the homopolymer was analyzed by thermogravimetric analysis using TGA 2050. The moisture absorption of dried grafted films and water evaporation of swelled homopolymers was determined using weighing at 25°C under nitrogen atmosphere. Furthermore, characterization of moisture content was performed at 120°C under nitrogen atmosphere.

4.6.4 Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to characterize the chemical composition of treated PE surface and epoxy resin in two types.

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❖ ***Multi mode***

ATR-FTIR in multi mode was performed using Bruker Equinox 55 spectrometer. The sample was attached on a face of A ZnSe crytal and clamped after inserting silicone rubber on the sample. 64 scans at a resolution of 4 cm^{-1} over range of 4000-600 cm^{-1} was used for surface analysis.

❖ ***Single mode***

The measurement was operated with 64 scans at a resolution of 4 cm^{-1} over range of 4000-600 cm^{-1} and incident angle of 45°. A Ge crystal in a single reflection HATR type was used in this study.

The relative intensity of C=O stretching (1715 cm^{-1}) and CH_2 bending of PE (1450 cm^{-1}) were used as a measure of the amount of grafted poly(acrylic acid) and the relative intensity of $CONH_2$ **(**1660 cm^{-1}) and CH_2 bending of PE were used as a measure of the amount of grafted poly(acrylamide) onto the PE films.

4.6.5 Pull out Test

Pull out test was performed to measure the fiber-matrix adhesion. A single fiber was embedded into a silicone rubber mould as shown in Figure 4.2 Epoxy resin (DER 331 resin) and amine hardener (Ancamine® 1618 curing agent) were mixed in the ratio 2/1 wt/wt and then poured off into silicone rubber mould. The epoxy matrix was cured and kept in silicone mould at room temperature at least 5 days before testing was performed. Tests were run on an Instron tensile testing machine (Model 5569) at crosshead speed of 20 mm min^{-1}.

Pull out strength was defined as the failure load divided by the interface areas or calculated using this equation:

$$\text{Pull out strength} = \frac{F}{\pi dl} \qquad (2)$$

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where:

F is the maximum failure load that obtained from the fibre pull out load (N)

d is the fibre diameter (mm)

l is the immersion length that obtained from the thickness of the disc of resin (mm)

At least eight measurements were made for each value of adhesion strength and average values were taken.

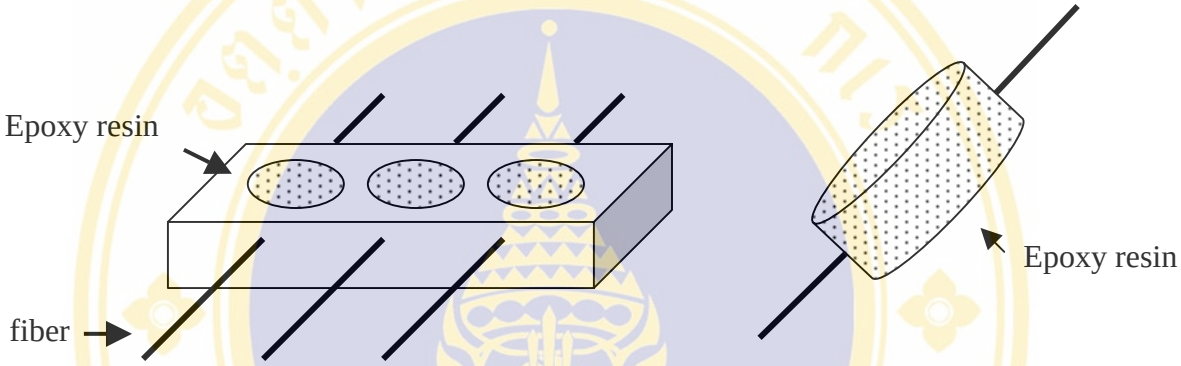

Figure 4.2 Scheme of the preparation of single fiber composite for pull out test

4.6.6 T-Peel Test

The adhesion strength between two PE films and epoxy resin was determined by T –peel test. The unmodified and modified PE films were cut into strips of about 2 x 3 cm^2. The two pieces of films were joined together with epoxy resin produced from the mixture of DER 31 resin and Ancamine® 1618 curing agent with 2:1 proportion. The assembly was pressed under light pressure and cured at room temperature for at least 5 days. The assembly was then subjected to T-peel test in an Instron model 5569 materials tester. All measurements were carried out at crosshead speed 20 mm min^{-1}. For each T-type peel strengths reported, at least 4 sample measurements were averaged.

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The peel strength was defined as follows:

$$\text{Peel strength} = \frac{2F}{W} \quad (3)$$

where:

F is the maximum failure load that obtained from the peel load (N)

W is the width of PE film (m)

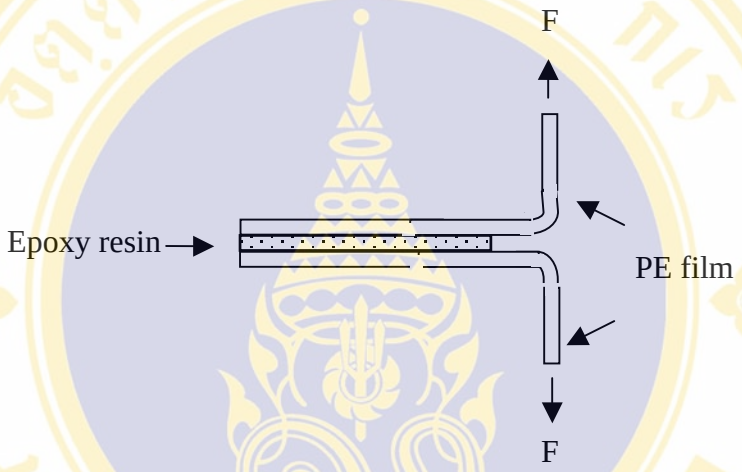

Figure 4.3 Scheme of the preparation for peel test

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CHAPTER 5
RESULTS AND DISCUSSION

Improving adhesion between PE and epoxy resin was the aim of this thesis. PE was modified by surface grafting of polar monomers that were AA and AAm monomers and was studied for changes in surface properties after grafting. Grafting was performed via 2-stage method proposed by Bamford et al [10]. It was intended to compare adhesion strength between PE grafted with AA and AAm and to propose various factors influencing their adhesion in order to understand their adhesion nature. Moreover, the study of the adhesion nature led to a method to improve adhesion between surface grafted PE and epoxy resin. This work investigated the surface modification in two form of PE, i.e. film and fiber. Since the limit of amount of grafting on fiber resulting in little adhesion changes, this thesis therefore mainly focused on film.

5.1 Effect of Type of Grafted Chains

In analysis of adhesion of AA and AAm grafted PE surface and epoxy resin, effect of type of grafted chains on surface adhesion was discussed and compared. Following previous study by Doaddara [46], adhesion strength could be improved by the presence of AA and AAm grafted chains. Nevertheless, adhesion strength between AA and AAm grafted film and epoxy resin are different. This could be due to the different nature of grafted chains resulting in different reaction to epoxy resin. Therefore, nature of adhesion of AA and AAm to epoxy resin and factors influencing the adhesion will be discussed in this first section.

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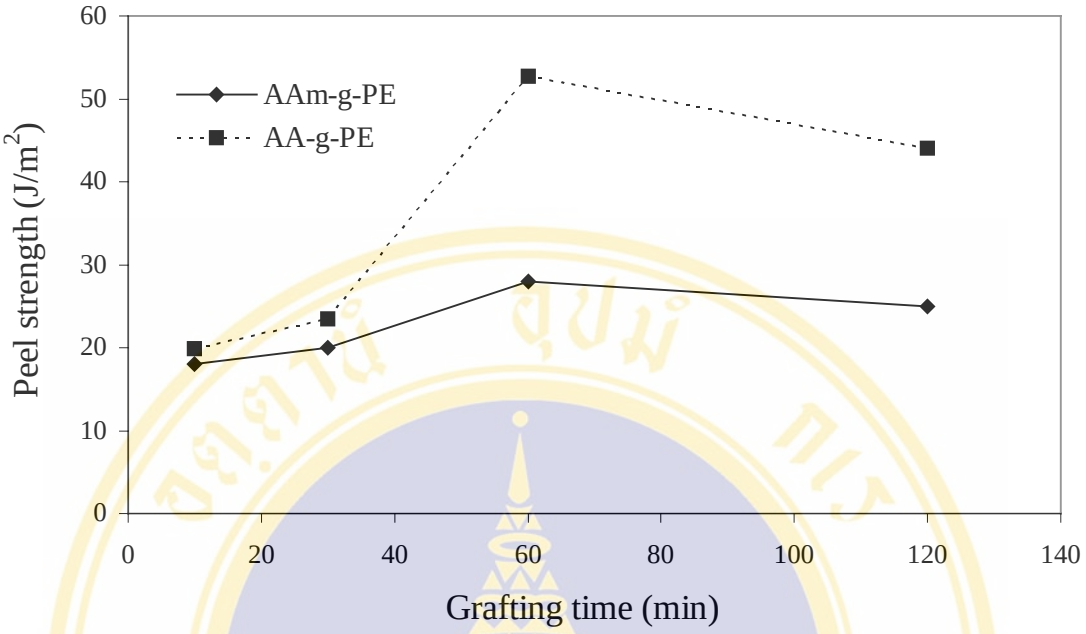

Figure 5.1 The relationship between peel strength of films grafted with AA and AAm and grafting time (Ht 30 min, HT 80°C, GT 50°C)

Peel strength of films grafted with AA and AAm are shown in Figure 5.1. It can be seen that peel strength increased with increasing grafting time for both AA and AAm grafting. When hydroxylation time was fixed at 30 min, maximum peel strength of AA and AAm grafted film was about 55 and 28 J/m^2, respectively. However, maximum peel strength of AA grafted films was about twice that of AAm grafted films after Gt 60 min. This result suggests that type of grafting chain strongly affected the adhesion strength. It had been suggested to be due to different amount of grafting and different adhesion nature of grafted chains for both types of monomer, which affects to reaction with epoxy resin [46].

To verify the above proposal, grafting level of both monomers was studied and compared by two methods. First, grafting level was determined by gravimetric method which corresponds to weight change of sample after grafting. Second, The existence of C=O on surface of AA and AAm grafted films can also be used to confirm grafting level by using ATR-FTIR.

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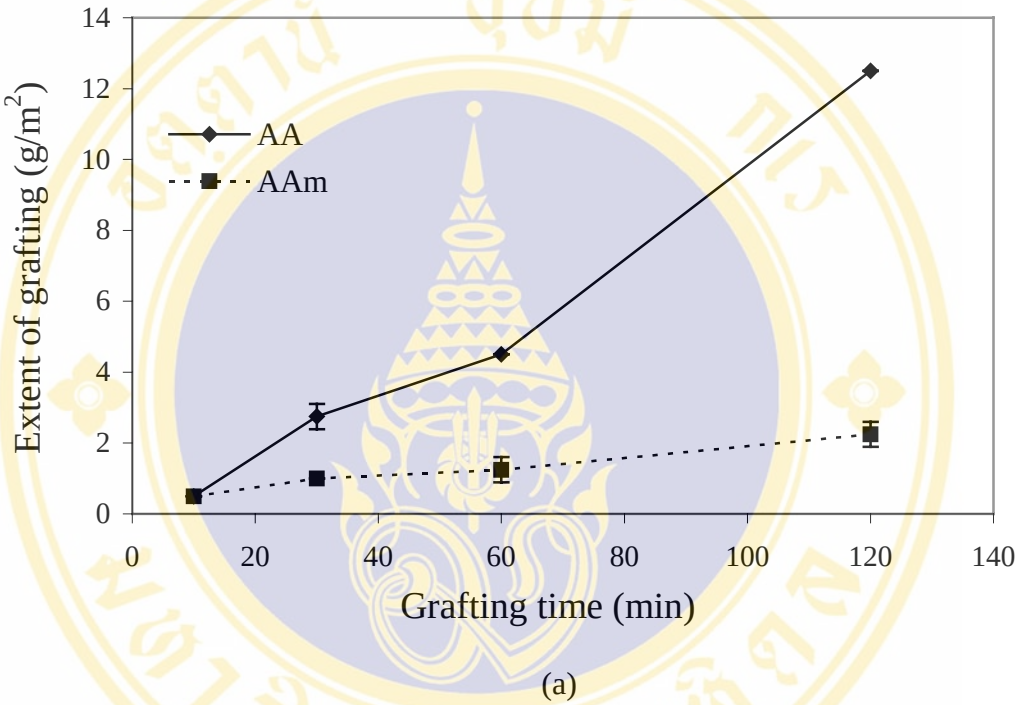
5.1.1 Extent of Grafting

The extent of grafting calculated from weight gain is relevant to amount of grafted polymer chains. Figure 5.2 (a) and 5.2 (b) display extent of grafting as a function of grafting time and peel strength, respectively.



(a)

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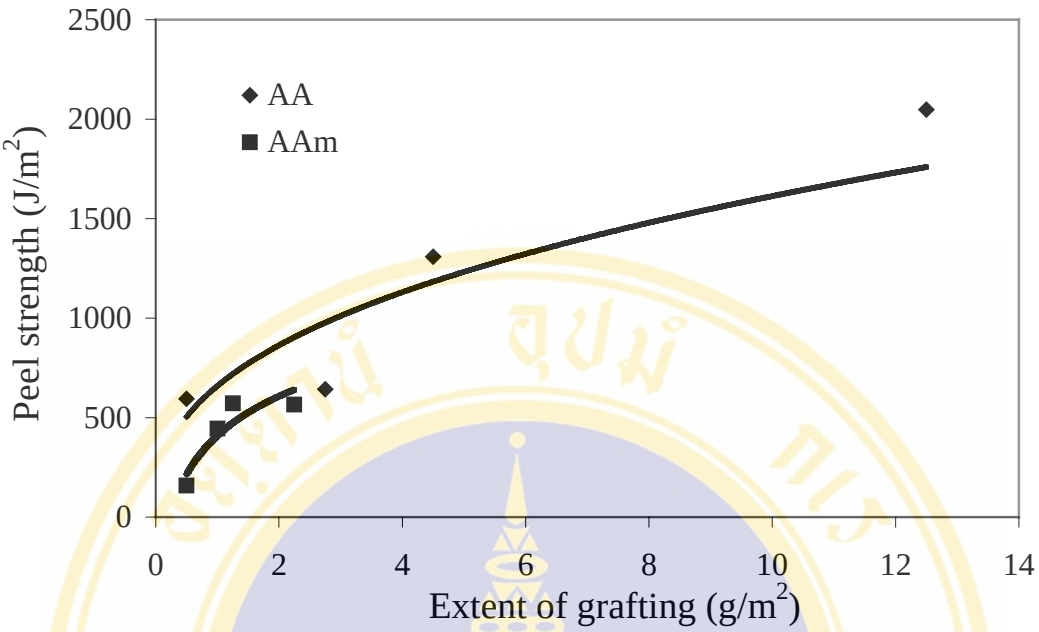

(b)

Figure 5.2 The relationship between (a) extent of grafting (AA and AAm) per surface area and grafting time; (b) peel strength of AA and AAm grafted film and extent of grafting (Ht 120 min, HT 80°C, GT 50°C)

From Figure 5.2 (a), it can be seen that extent of grafting of AAm grafted film slightly increased with grafting time and then level off at extent of grafting of 1 g/m^2, while that of AA grafted film increased significantly. Moreover, in comparison at the same grafting time, AA illustrated higher extent of grafting than AAm for all grafting time and could up to 6 folds at Gt 120 min. Owning to this result, it could be concluded that AA exhibited greater efficiency of grafting than AAm. This is similar to Doaddara's result [46].

In addition, relationship between peel strength and extent of grafting of AA and AAm was shown in Figure 5.2 (b). It was found that at the same extent of grafting AA displays higher peel strength than AAm. This is to say that type of grafted polymer was an important factor influencing to greater peel strength.

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5.1.2 Infrared Spectroscopy (ATR-FTIR)

To support the previous result of amount of grafting which effects from type of grafted chain, grafted level was also investigated by using ATR-FTIR. The relative intensity of C=O stretching (1715 cm^{-1}) and the relative intensity of $CONH_2$ (1660 cm^{-1}) on grafted PE film surface referring to amount of AA and AAm grafted chains was measured [46]. Figure 5.3 illustrated relationship between relative intensity (absorbance) (RI) of C=O strength to CH_2 bending of PE and grafting time. It can be seen that relative intensity of both AA and AAm increased with increasing grafting time. Furthermore, AA exhibits greater relative intensity than AAm about 2 folds.

This above result showed the same tendency to measurement of extent of grafting by gravimetric method. It could be confirmed that the effect of type of grafted chain had an influence on amount of grafting, resulting in adhesion strength as previously discussed.

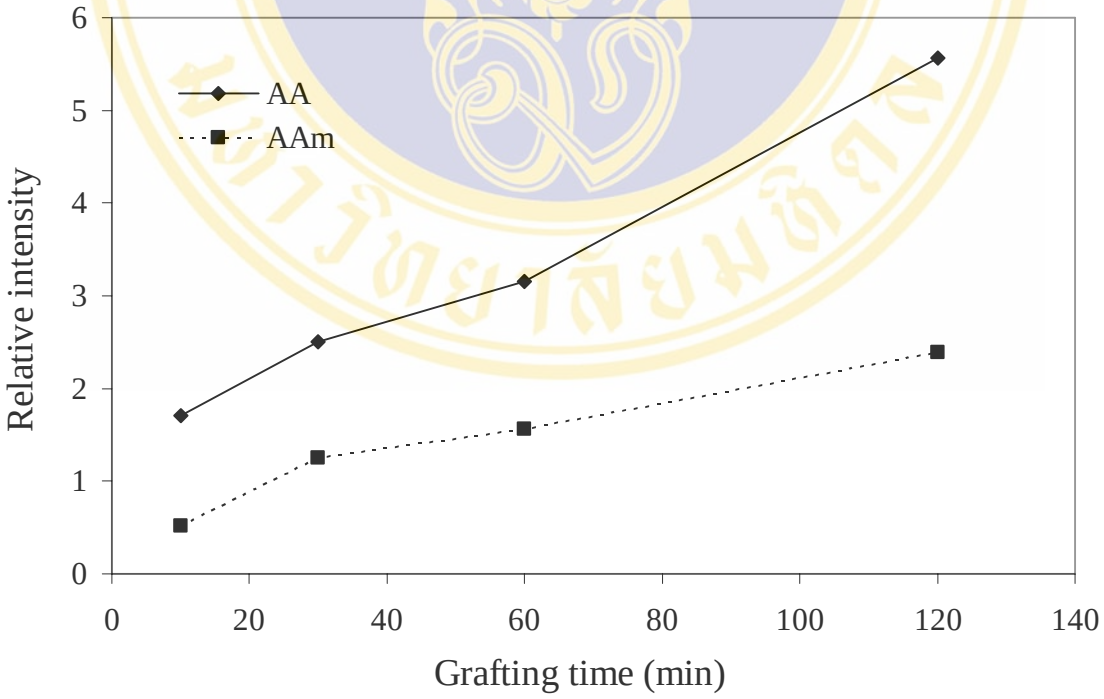

Figure 5.3 The relationship between relative intensity and grafting time (Ht 120 min, HT 80°C, GT 50°C)

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5.1.3 Nature of Adhesion

Besides the different amount of grafting between AA and AAm, different reaction to epoxy could be another possibility affecting to dissimilar adhesion strength. There are many researchers which propose reaction of matrix epoxy resin with AA and AAm grafted chains. Yu Z.J. et al [19] studied surface passivation of epoxy resin with a covalently adhered poly(tetrafluoroethylene) layer. Surface modification of the PTFE film was carried out by argon plasma pre-treatment, followed by UV-induced graft copolymerization with acrylic acid and acrylamide. They proposed that the carboxyl groups on the AA grafted PTFE film surface can react with both the epoxide group of the epoxy resin and the amine group of hardener. This resulted in strong adhesion of AA grafted PTFE film to epoxy resin matrix. On the other hand, AAm grafted PTFE surfaces displayed low adhesion to epoxy resin matrix. They suggested that the amide group of AAm grafted chains had low reactivity to the functional groups of the epoxy matrix.

On the contrary, Ranby [20] studied surface photografting onto polymers. They reported that at the same IR-values of O_{1s}/C_{1s} and N_{1s}/C_{1s}, the adhesion to epoxy resin of high strength PE fibers grafted with AAm was higher than AA. They proposed that the amide groups in the grafted AAm chains formed valence bond to epoxy groups. This would give a strong increase in adhesion. For AA, the carboxyl groups of grafted AA are not expected to react with epoxy groups. Therefore, the smaller increase in adhesion after AA grafting is interpreted as due to increased hydrogen bonding with no new valence bond formed. Furthermore, reaction possibility of carboxylic group and epoxy resin was also proposed by Norton et al [47] who studied effect of end-anchored chains on the adhesion at a thermoset-thermoplastic interface. They proposed that carboxylic groups at chain end of thermoplastic interface can react with epoxide groups of thermoset resin. From this point, there were the discrepancies between the possibility of reaction of surface grafted with AA and AAm with epoxy resin matrix. Therefore, it was necessary to prove these possibilities in this part.

The reaction of AA and AAm grafted chains with epoxy resin matrix was invertigated by determining functional groups of epoxy resin matrix, which reacts with functional groups of grafted chains. Epoxy resin matrix composes of 2 compositions,

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which are epoxy resin and amine hardener. In order to study possibilities of covalent bonding of functional groups in matrix epoxy resin with functional groups in AA and AAm grafted films, these grafted films were immersed in epoxy resin or amine hardener and then investigated their functional groups which reacts with functional groups of grafted chains by ATR-FTIR technique [48].

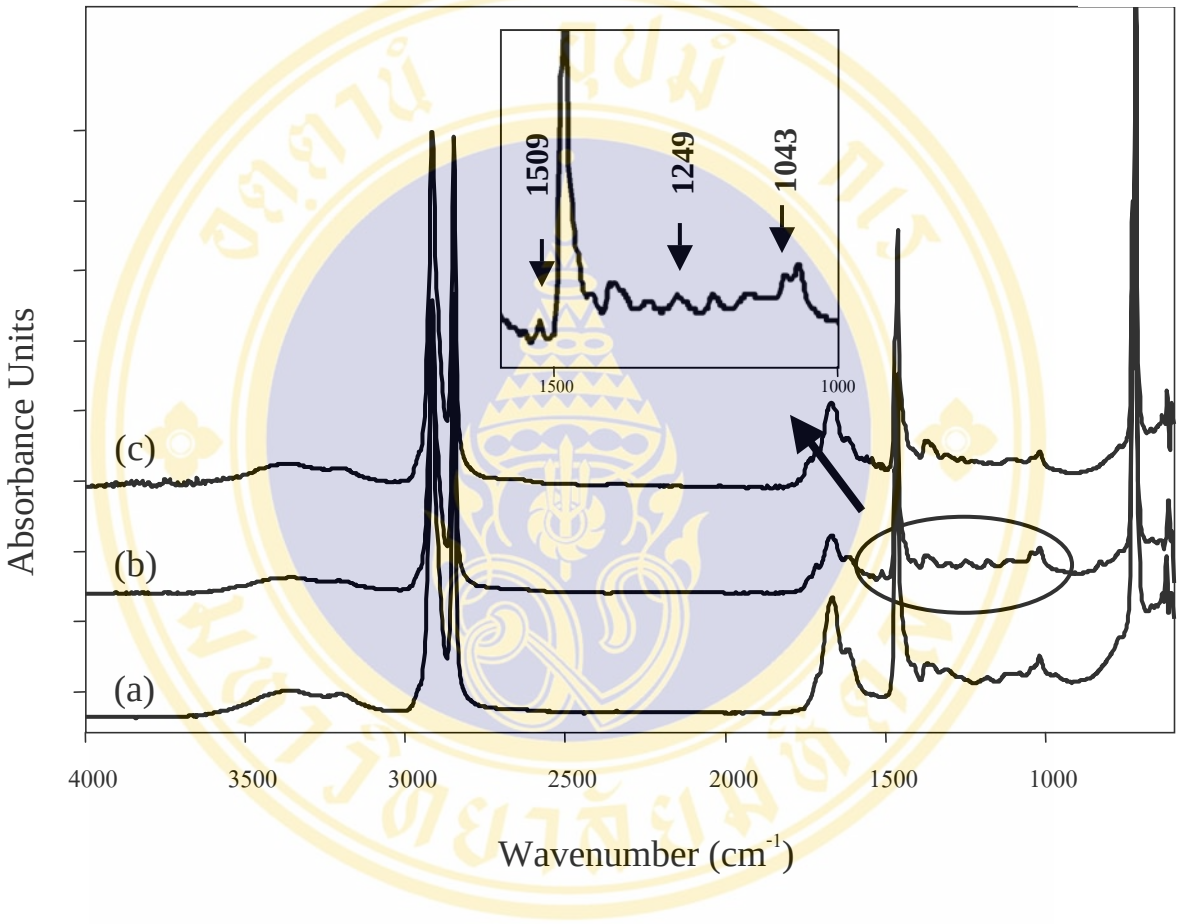

Figure 5.4 ATR-FTIR spectra of (a) AAm-g-PE film (b) AAm-PE film after immersing in epoxy resin and (c) AAm-PE film after immersing amine hardener.

ATR-FTIR spectra of AAm grafted PE film, AAm grafted PE film after immersing in epoxy resin and AAm grafted PE film after immersing in amine hardener are shown in Figure 5.4. This result referred to reaction of AAm grafted chain with epoxy resin or amine hardener. From spectrum of AAm grafted PE film after immersing in epoxy resin, new peaks in at wavenumber 1509, 1249 and 1043 cm^{-1} can be observed. These were attributable to C=C stretching (skeletal) of aromatic ring, C-O-C stretching of epoxide groups and C-H deformation (in plane) of aromatic

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ring from epoxy resin, respectively [48, 49]. Therefore, it confirmed the formation of covalent bonding between amide groups of AAm grafted chain and epoxide groups of epoxy resin. For spectrum of AAm grafted PE film after immersing in amine hardener, no difference from spectrum of AAm grafted PE film can be found. This may be deduced from the low reactivity between the functional groups of AAm grafted chain and the functional groups of amine hardener. It may be summarized that adhesion strength between AAm grafted film and epoxy resin matrix was mainly due to the covalent bonding of amine groups of AAm grafted chain and epoxide groups of epoxy resin.

Reaction of PAAm and epoxy resin was also reported in study of Plasma-graft polymerization of vinyl monomers with reactive groups onto a surface of poly(*p*-phenylene terephthalamide) fiber by Yamada et al [48]. It was reported the formation of covalent bonding of amino group of polycrylamide and epoxide group of epoxy resin, leading to an increment of pull out force.

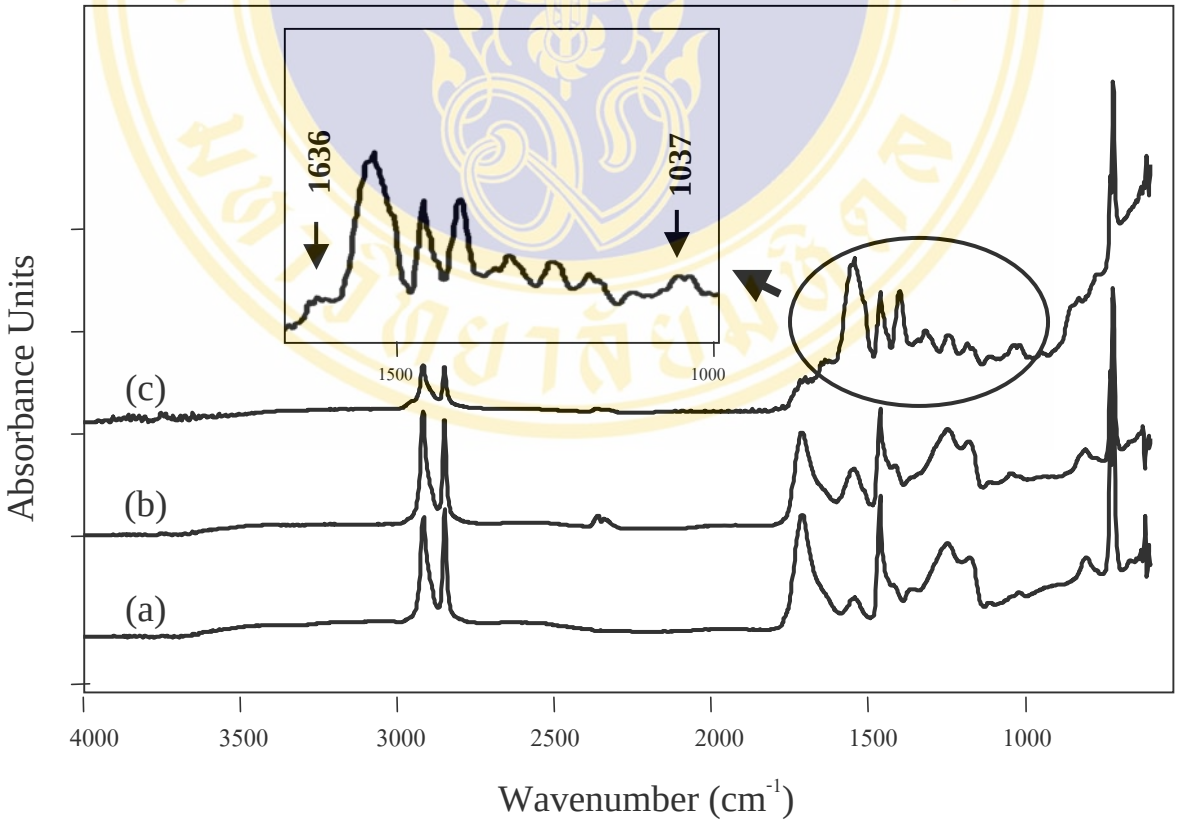

Figure 5.5 ATR-FTIR spectra of (a) AA-g-PE film (b) AA-g-PE film after immersing in epoxy resin and (c) AA-g-PE film after immersing amine hardener.

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ATR-FTIR spectrum of AA grafted PE film, AA grafted PE film after immersing in epoxy resin and AA grafted PE film after immersing in amine hardener are shown in Figure 5.5. It was found that new peak was not observed in spectrum of AA-g-PE film after immersing in epoxy resin. It was probable that the reactivity of the carboxylic groups and the epoxide groups of epoxy resin was too low, leading to low concentration of reacted component. Therefore, IR could not detect this new component. However, from the spectrum of AA-g-PE film after immersing amine hardener, N-H deformation and C-N stretching adsorption of amine hardener appeared at 1636 and 1037 cm^{-1}, respectively [49]. This is reasonable to assume that the formation of covalent bonds between carboxylic group of AA grafted chain and amine group of hardener was the main factor for adhesion improvement between AA-g-PE and the resin matrix.

As the above results of possible reactions of epoxy resin matrix with AAm and AA grafted chain, the major reactions are shown in Figure 5.6 (a) and (b), respectively. It was similar to Doddara's result [46].

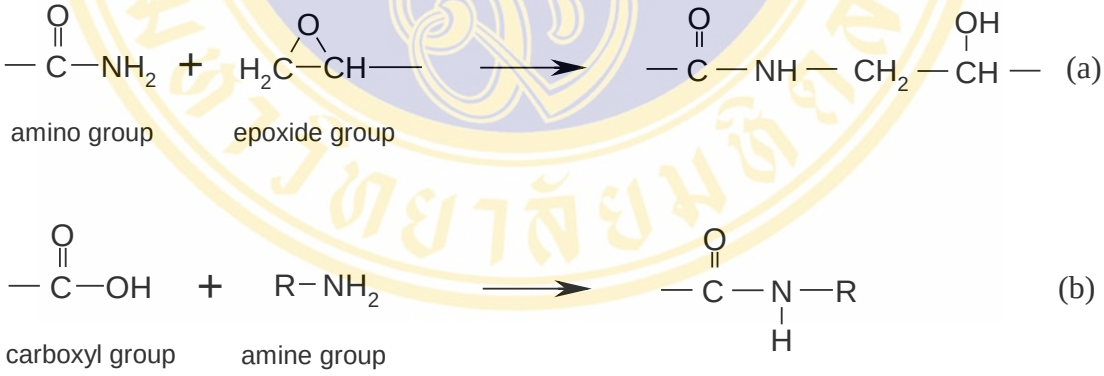

Figure 5.6 Possible reactions (a) amino group of polyacrylamide and epoxide group of epoxy resin; (b) carboxyl group of polyacrylic acid and amine group of hardener.

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5.1.4 Nature of Grafted Chain

Further insights into the adhesion of AA and AAm grafted PE with epoxy resin matrix can be gained by study of grafted polymer nature, which probably was another important factor influencing to adhesion strength. In fact, amide groups of AAm grafted chain can create strong H-bonding between neighboring chains [46]. This may results in high rigidity of AAm grafted chains and low adhesion to epoxy resin matrix because epoxide groups from epoxy resin matrix can not react with amide groups of AAm grafted chain. A contrasting result from AA grafted film, the carboxyl groups from AA grafted chain can absorb moisture in the air; hence AA grafted chain should have higher mobility than AAm grafted chain. Therefore, epoxide groups from epoxy resin matrix could easily find its way to react with carboxyl groups of AA grafted chain and led to the high adhesion strength of AA grafted chain with epoxy resin matrix. Thus, we proposed that the moisture content in grafted layer was major factor controlling grafted chain mobility. To check this proposal, the influence of moisture content in grafted layer was studied. Since the low grafting amount of grafted layer on grafted surface, moisture content was investigated in homopolymer by measuring %weight loss of AA and AAm homopolymer via TG analysis.

Table 5.1 %Weight loss of AA and AAm homopolymer at 120°C from TG analysis

	Polyacrylamide	Polyacrylic acid
%Weight loss	2.2	4.0

From Table 5.1, it can be seen that weight loss (at 120°C) of AA homopolymer was greater than that of AAm homopolymer about 2 folds. This result suggests that AAm homopolymer has lower moisture content than AA homopolymer. This provides the supporting evidence for the previous proposal.

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5.2 Effect of Decreasing Moisture Content of Grafted Layer

Since the prior results, we proposed that mobility of grafted chain was important factor affecting the grafted chain properties. Indeed, there exists only a few techniques, such as NMR [50-52] and fluorescence depolarization method [42, 53, 54], which can directly probe the movement of grafted chain. Since the study of segmental motion of grafted chain by direct method was complicated process, behavior of grafted chain mobility was investigated by indirect method. In this study, we considered grafted chain mobility through its effect on adhesion with epoxy resin.

5.2.1 Effect of Decreasing Moisture Content in Homopolymer

In our previous experiment, it was proposed that moisture content in grafted layer influence to grafted chain mobility resulting on the improvement of adhesion to epoxy resin. AA-g-PE film which had higher moisture content displayed greater adhesion with epoxy than AAm-g-PE film. It was interesting to study insights into the effect of grafted chain mobility for solving this suggestion. In this part, the effect of decreasing moisture content of grafted layer was performed to prove their influence on adhesion with epoxy resin.

Table 5.2 %Weight loss of AA and AAm homopolymer (before and after drying in vacuum oven at 60°C for 4 days) at 120°C from TG analysis

	Polyacrylamide	Polyacrylic acid
Before drying	2.2	4.0
After drying	0.6	0.9

Table 5.2 shows %weight loss of AA and AAm homopolymer (before and after drying in vacuum oven at 60°C for 4 days) at 120°C from TG analysis. It was found that moisture content of both AA and AAm homopolymer decreased after

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drying in vacuum oven. Moisture content decreased from 4.0% to 0.9% for AA homopolymer and from 2.2% to 0.6% for AAm homopolymer. This reflected that moisture content of AA and AAm homopolymer could be decreased by drying in vacuum oven at 60°C for 4 days. This indicated that drying in vacuum oven should be able to decrease moisture content in grafted layer of grafted film.

5.2.2 Effect of Decreasing Moisture Content on Adhesion

From the above suggestion that moisture content in grafted layer could be decerased by drying in vacuum oven. The adhesion of epoxy resin with AA and AAm grafted film dried in vacuum oven was further studied for confirming the absence of moisture content in grafted layer. In order to prepare the dried sample, the grafted PE film was cut into strip of 1x4 cm^2 and then placed in vacuum oven at 60°C for 4 days to reduce the moisture content in the grafted layer. After that, the sample was left under atmospheric temperature for different period of time, and then assembled with epoxy resin at light pressure for T-peel test. The T-peel test was employed to determine the adhesion changes after reducing moisture content in grafted layer.

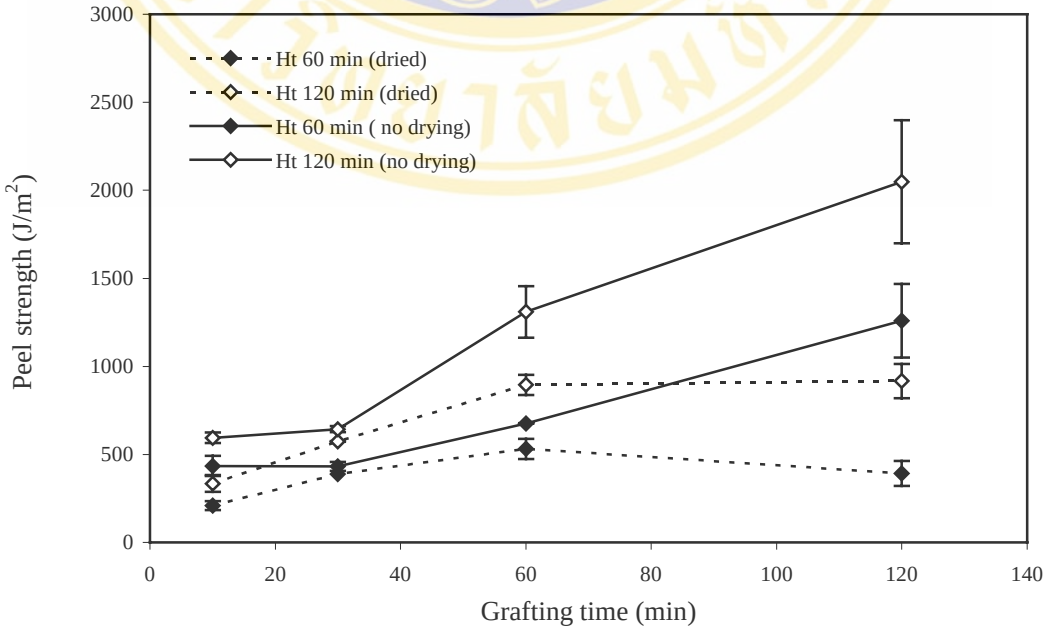

Figure 5.7 Effect of decreasing mobility of grafted chain on peel strength of AA-g-PE film (HT 80°C, GT 50°C)

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Peel strengths of epoxy resin and AA grafted film before and after drying in vacuum oven as a function of grafting time are shown in Figure 5.7. In both cases of hydroxylation time of 60 and 120 min, the peel strengths decreased distinctly after drying for all grafting times. It could be due to the lower moisture content in AA grafted layer after drying that affects to more constraint grafted chain movement. Thus, epoxy resin can react less with carboxyl groups from AA grafted chain. This can be displayed in Figure 5.8. From this result, it could be suggested that reducing grafted chain mobility by drying in vacuum oven had effect on decreasing adhesion strength of AA grafted film. This provides the supporting evidence for the proposal that great adhesion of AA grafted film was attributed to its high mobility of grafted chain, resulting in more reaction with epoxy resin.

Figure 5.8 Scheme of grafted chains after drying.

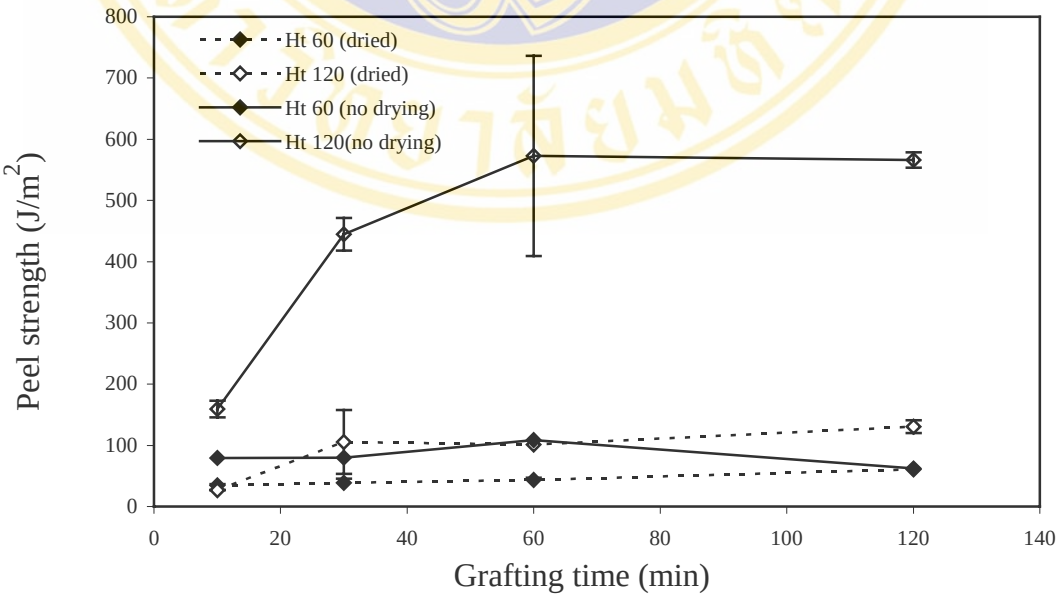

Figure 5.9 Effect of decreasing mobility of grafted chain on peel strength of AAm-g-PE film (HT 80°C, GT 50°C)

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The similar result can be observed in the case of AAm. Figure 5.9 displays peel strengths of epoxy resin and AAm grafted film before and after drying in vacuum oven as function of grafting time. After drying peel strength of AAm grafted film was greatly reduced in case of hydroxylation time 120 min and slightly reduced for 60 min hydroxylation. This result reflects that, even in case of AAm grafted film which had high rigidity of grafted chain and low moisture content in grafted layer, drying in vacuum oven also influenced in decreasing adhesion strength from reducing mobility of grafted chain. The above results could strongly confirm our proposal that moisture content in grafted layer was important factor influencing grafted chain mobility.

5.2.3 Surface Rigidity

Surface properties of AA and AAm homopolymer before and after drying were also investigated by AFM technique in contact mode. Force curves of force measurements of AFM can provide adhesion and rigidity properties of sample surface. Knowing the slope of force curve from retracting force can deduce the surface rigidity. Thus, in this experiment, the slope of force curve was used to characterize surface rigidity of AAm and AA homopolymer. Force curves of AA and AAm homopolymer were measured using the cantilever with spring constant 0.38 N/m, fitted to softer surface and 0.58 N/m, fitted to hard surface, respectively. In order to normalize the data from force curve at different spring constants of cantilever, slope of each homopolymer was divided with slope of silicon.

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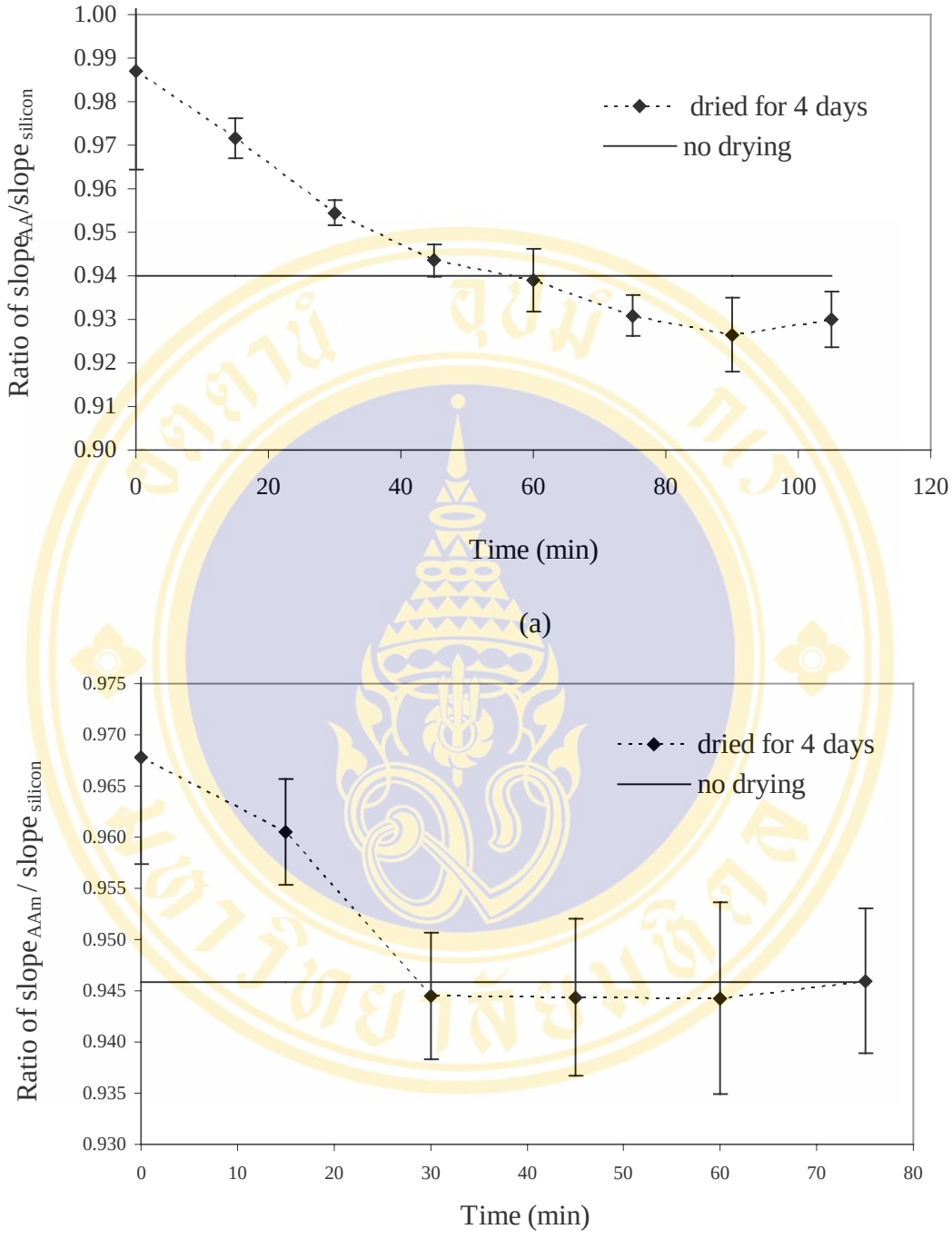

Figure 5.10 Relationship between the ratio of homopolymer and silicon slope and allowed time under atmospheric room temperature (a) AA (spring constant 0.38 N/m) and (b) AAm (spring constant 0.58 N/m)

From Figure 5.10 (a), it was found that after drying, the ratio of slope $_{AA}$ / slope $_{silicon}$ was higher than that of no drying. And the ratio decreased to the value of no

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drying with increasing standing time under atmospheric room temperature. This indicated that drying in vacuum oven provided the enhanced rigidity of the homopolymer surface. And rigidity decreased with increasing standing time due to moisture absorption of dried homopolymer. In case of AAm homopolymer shown in Figure 5.10 (b), a similar trend as AA homopolymer was observed. With increasing rigidity of homopolymer after drying, it assisted with the previous suggestion that adhesion strength of AA and AAm grafted films decreased after drying in vacuum oven due to the increasing rigidity of grafted layer and reducing grafted chain mobility, resulting in low adhesion with epoxy resin.

The comparison between data of no drying AA and AAm homopolymer showed that ratio of slope $_{AAm}$ / slope $_{silicon}$ (0.945) was little higher than ratio of slope $_{AA}$ / slope $_{silicon}$ (0.940). This indicated that surface rigidity of AAm homopolymer was close to that of AA homopolmer. This disagreed with the previous proposal that AAm grafted layer of AAm-g-PE film had higher surface rigidity than that of AA, resulted to lower interfacial adhesion of AAm-g-PE film. However, these results were obtained by using two types of cantilevers for different spring constants which fits to different surface rigidity and normalized the obtained data with surface rigidity of silicon. Thus, the error from the comparison of different spring constants could be occurred. Moreover, error from approximation of slope of force curve also affected to the obtained results.

5.2.3.1 Thermogravity Result

To determine moisture content that was adsorbed back to dried homopolymer after allowing under atmospheric temperature, weighing AA homopolymer that was dried in vacuum oven at 60°C for 4 days was performed with TG analysis at 25°C. As seen in Figure 5.11, it was found that weight of AA homopolymer did not increase with increasing allowed time. This may was because moisture was adsorbed only at outer layer of homopolymer. Nevertheless, surface rigidity of homopolymer could change because it mainly depended on property of surface layer.

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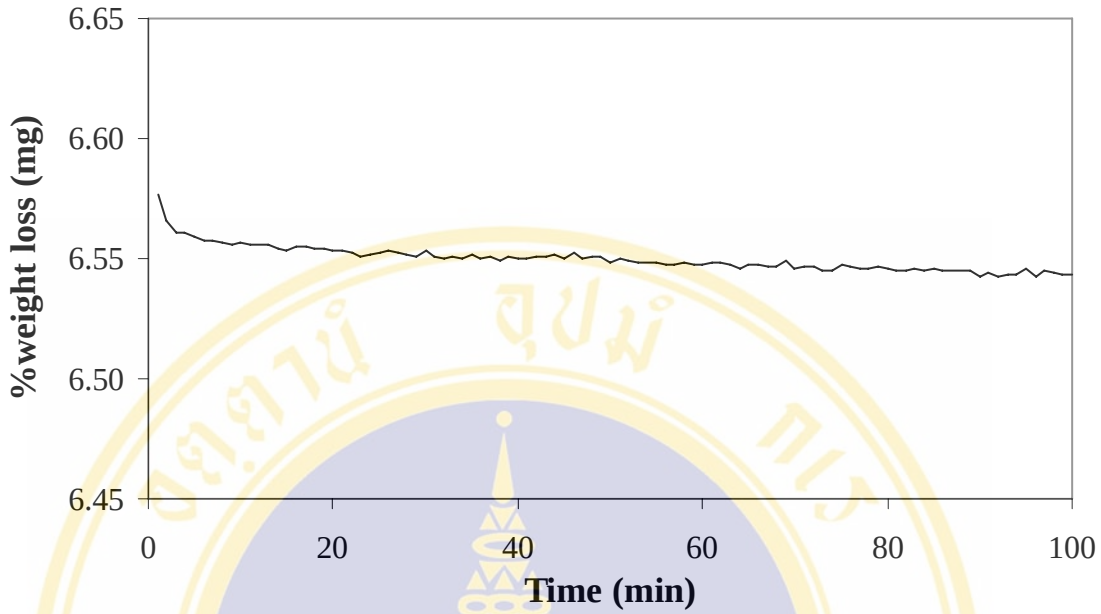

Figure 5.11 TG analysis curve of AA homopolymer after drying in vacuum oven at 60°C for 4 days (Analyze at room temperature)

5.2.3.2 Adhesion Result

Figure 5.12 illustrates the relationship of peel strength of epoxy / grafted film which was dried in vacuum oven at 60°C for 4 days and standing time under atmospheric temperature before assembling with epoxy resin. In case of AA grafted film, it was found that peel strength of dried film was lower than that of no drying, if the standing time was less than 1 hr. This could be due to the lower mobility of AA grafted chain after drying in vacuum oven. Subsequently, the peel strength of dried film at Gt 120 min increased gradually up to the value of no drying film. The reason was that the moisture content in grafted layer increased after standing at room temperature. On the other hand, the peel strength of dried film at Gt 30 min was not increased with increasing time. This may be due to its thin grafted layer resulted from short grafted chain. So, enhancement of moisture content had less influence to adhesion of short grafted chain and epoxy resin. These results clearly revealed that moisture content in grafted layer has strongly influenced on adhesion to epoxy resin.

In case of AAm grafted film, after allowing standing under atmospheric temperature before assembling with epoxy resin, peel strength of dried film increased

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slightly in the initial stage and then decreased. Maximum peel strength of dried film which was left under atmospheric temperature was lower than that of no drying grafted film about 4 folds for Gt 30 min and 3 folds for Gt 120 min. Moreover, it was noticed that adhesion strength of dried film could not reach the value of no drying film within 4 hr of standing time. This could be attributed to nature of AAm grafted chain which has high rigidity. Hence, moisture in air probably requires more time to absorb back to grafted layer. This resulted in low mobility of AAm grafted chain that affects to low adhesion with epoxy resin.

These results also supported our previous suggestion that more rigidity at grafted layer effected on low mobility of grafted chain leading to low adhesion to epoxy resin. Similar influence of the rigidity on mobility was also found in the study of visco-elastic and adhesion properties of adsorbed polyelectrolyte multilayers by Notley et al [55]. The multilayer was constructed from layer-by-layer absorption of polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) on silica surfaces. They proposed that more rigid adsorbed layer structure resulted from low mobility of the polymer in the adsorbed layer.

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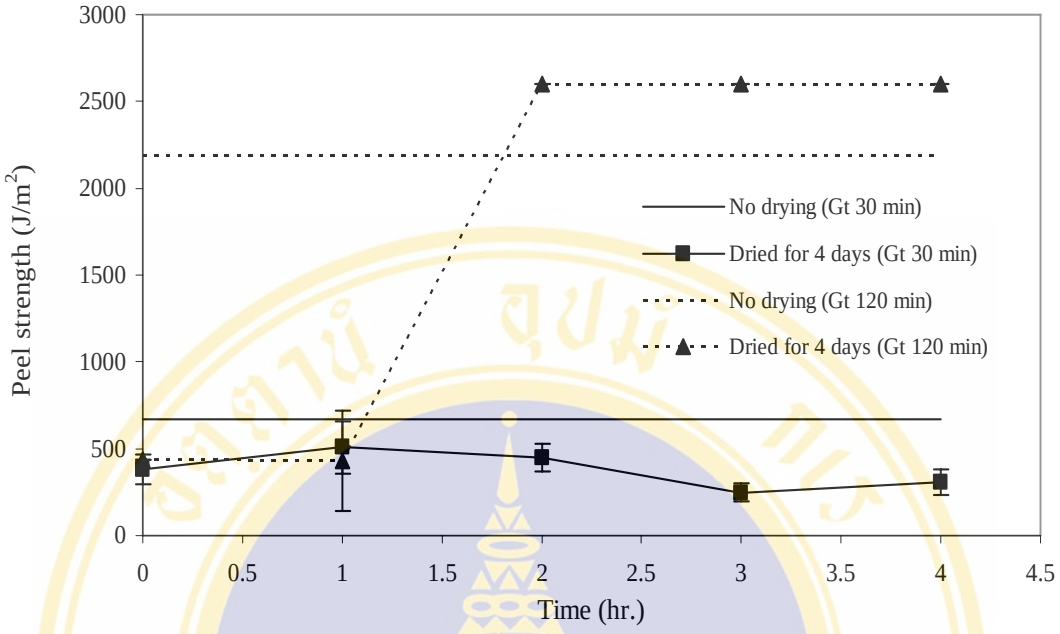

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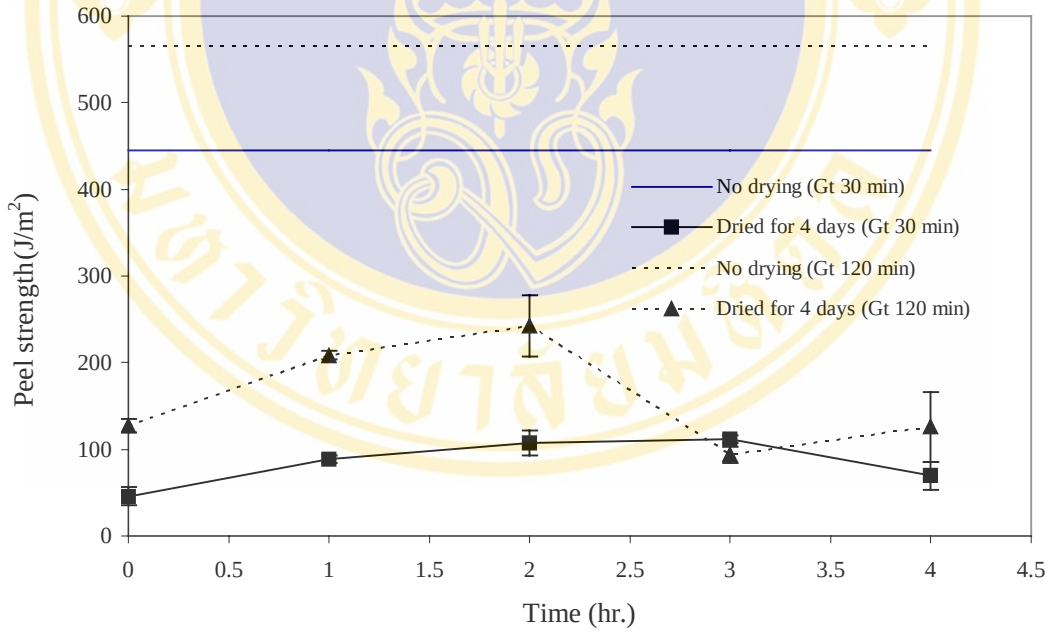

(b)

Figure 5.12 Relationship of peel strength of epoxy / grafted film which was dried in vacuum oven at 60°C for 4 days and allowed time under atmospheric temperature before assembly with epoxy resin (a) AA and (b) AAm (HT 80°C, Ht 120 min, GT 50°C)

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5.3 Effect of Increasing Mobility of Grafted Layer

From the previous results, it was shown that there was a limit of adhesion enhancement between AAm grafted film and epoxy resin due to the high rigidity of AAm chain. Similar result was reported in many literatures [21, 23, 46]. Zhang and Ranby [21] reported that enhanced adhesion of AAm grafted PP tape was also limited. They suggested that only a thin grafted layer can react with epoxy groups and contribute to adhesion. However, when compared with film that grafted with AA at same amount of grafting, film that grafted with AAm illustrated lower adhesion to epoxy resin. From our knowledge, besides the effect of moisture content in grafted layer, we assumed that AA grafted chain, which has lower Tg than AAm will have higher chain mobility, and flexibility than AAm grafted chins. Thus AA grafted chain can react more with epoxy resin because epoxy can easily permeate through AA grafted chain to react with carboxyl groups. For AAm, AAm grafted chain has higher Tg than AA grafted chain, so they may display higher adhesion to epoxy in some conditions due to their greater strength of chain entanglement as observed by Ranby [20].

In this part, experimental design was carried out to provide methods to improve adhesion of AAm with epoxy resin. In order to enhance adhesion, increasing opportunistic reaction of grafted chain and epoxy by increasing grafted chain mobility was proposed.

5.3.1 Effect of Swelling on grafted PE Film

It is known that increasing grafted chain mobility can be achieved by swelling in aqueous medium [16, 24]. Kang et al [16] reported that swelling of grafted chains in the presence of water resulted in enhancement adhesion strength of grafted PE film. They found that two surface grafted films are capable of exhibiting ‘adhesive free adhesion’ when brought into contact in the presence of water and subsequently dried. The development of the lap shear adhesion strength depends upon the interdiffusion and entanglement of grafted chains. Moreover, PAA and PAAm is hydrogels polymer which is able to swell in the aqueous solution. In fact, hydrogels grafted chains exhibit

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mobile surfaces since the outermost surface layer contains large amounts of water [24]. Hence swelling is an interesting way that can increase mobility of grafted chain. Thus, swelling behaviors of grafted PE film in various solvents and conditions were studied.

5.3.1.1 Effect of Type of Solvent on Adhesion

For study effect of increasing grafted chain mobility, swelling procedure was carried out in aqueous solution of water and methanol. Water and methanol were selected as swelling solvents due to their good properties such as simple, cheap and non-toxic. To prepare the swollen grafted samples, the sample was immersed in solvent for various times and various temperatures. The sample was blotted with tissue paper for removing the excess solvent at the surface. After that, the sample was immediately assembled with epoxy resin for adhesion testing. Unswollen and swollen films were determined for the effect of swelling by T-peel test according to the method reported earlier.

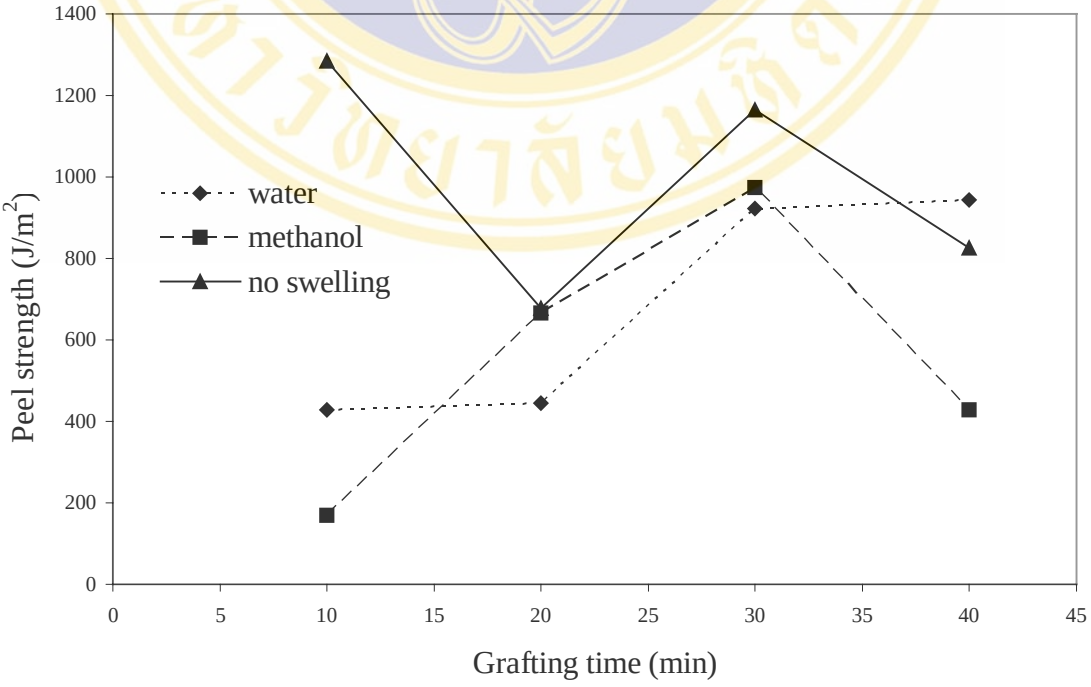

Figure 5.13 Effect of type of solvent on peel strength of AA-g-PE film with epoxy resin (HT 80°C, Ht 120 min, GT 50°C)

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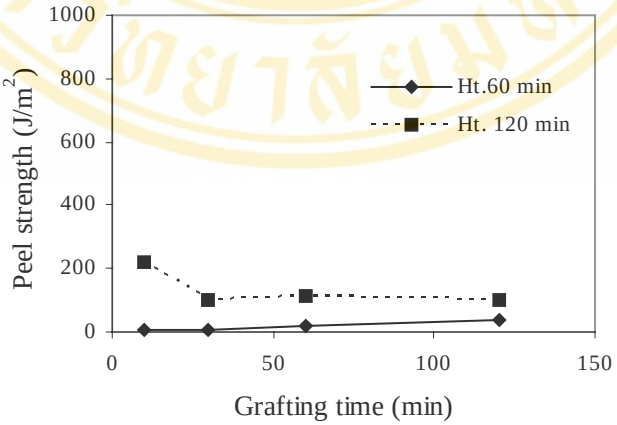
The effect of type of solvent on peel strength of AA-g-PE film with epoxy resin is shown in Figure 5.13. It was seen that after swelling with either water or methanol, peel strength of AA-g-PE film decreased. This could be due to the nature of PAA grafted chains, which have great liquid retention capacity [56]. This may led to high degree of swelling in grafted layer and high grafted chain mobility. Nevertheless, adhesion of AA could not be improved by increasing mobility through swelling since AA grafted chain has already high flexibility. Moreover, PAA chain, which has hydroxyl groups at the end of its side chain, can form strong H-bonding with both water and methanol. This resulted in existing of excess amount of water and methanol in grafted layer, which could compete with AA grafted chain for bonding with epoxy resin. It led to poor adhesion of AA-g-PE film and epoxy resin.

From the above result, it might be proposed that the presence of water or methanol in AA grafted layer could decrease interfacial adhesion of AA grafted film and epoxy resin. This observation was similar to the results obtained by Pattarachindanuwong [57]. The pull out strength of AA grafted fiber and acrylic resin significantly decreased after immersing in water for 30 days. It was reported to be due to softening of swollen AA grafted layer.



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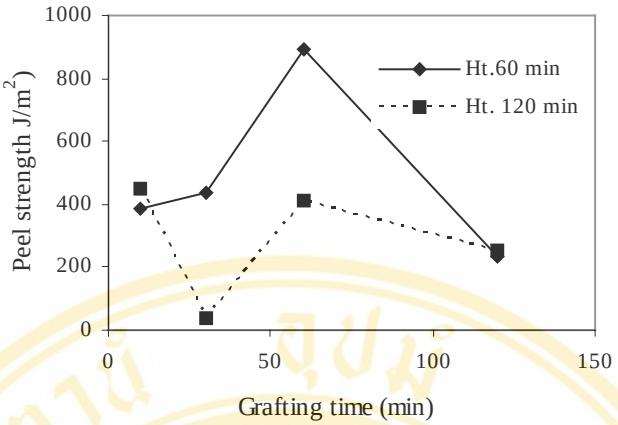

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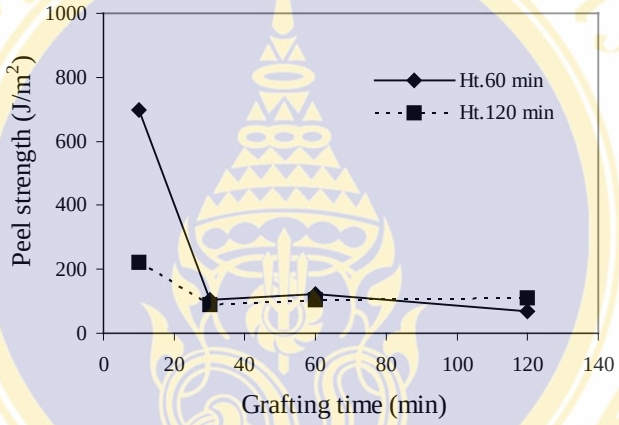

(c)

Figure 5.14 Effect of type of solvent on peel strength of AAm-g-PE film with epoxy resin (a) no swelling (b) swelled with water and (c) swelled with methanol (HT 80°C, GT 50°C)

Peel strengths of film grafted with AAm before and after swelling in water and methanol are shown in Figure 5.14 (a), (b) and (c), respectively. It could be seen that the peel strength of AAm-g-PE films swelled with water increased greatly. The highest value of 900 J/m^2 or 10 folds from that of no swelling was observed. In the case of AAm-g-PE films that swelled with methanol, peel strength increased only slightly. This suggested that water could efficiently enhance the mobility of PAAm chains and promote more reaction with epoxy resin due to higher probability between the reactive groups of epoxy and PAAm chains. This may be because swelling raised switching side of amide groups of AAm grafted chain to react with epoxide groups of epoxy resin.

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Among different hydroxylation time (Ht), adhesion of AAm-g-PE film at shorter Ht was greatly increased after swelling. This exhibited that the effect of swelling had more significant at low Ht. At low Ht, AAm-g-PE film had small amount of PAAm chains, so solvent could easy permeate through PAAm chains to increase mobility, leading to large accessible area for reaction with epoxy resin. On the contrary, at high Ht the surface of grafted film had high amount of PAAm chains. Thus solvent permeation became quite difficult. This caused small accessible area for react with epoxy resin. This resulted in the slight enhancement of peel strength.

In addition, effect of swelling at different grafting time was further considered. As seen in Figure 5.14, the effect of swelling seemed to have the more influence on improving adhesion at range of low Gt (10-60 min). This may be because at low Gt, AAm-g-PE film should have low density and short length of grafted chains [57]. Thus, mobility of AAm grafted chains has been sufficiently increased by swelling, leading to forming open structure of grafted chain. This provided a large accessible area for react with epoxy resin. On the other hand, high Gt had high density and long length of grafted chains [57]. Their mobility was highly restricted from more chain entanglement and strong H-bonding between neighboring chains, as discussed earlier in section 5.1. Consequently, solvent did not have enough power to increase their grafted chain mobility. Compact grafted chains were obtained, leading to low adhesion with epoxy resin. Grafted chain structures at different Ht and Gt after swelling are shown schematically in Figure 5.15.

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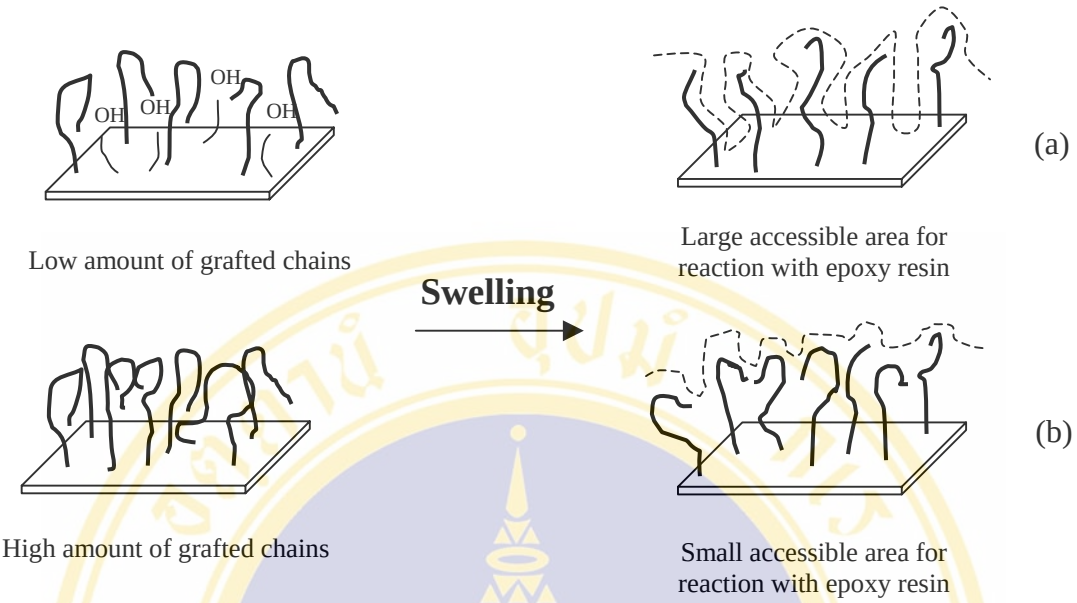

Figure 5.15 Schematic descriptions of grafted chain structures at different time of hydroxylation after swelling, including the accessibility of epoxy resin for react with grafted chain (a) short Ht or short Gt (b) long Ht or long Gt

Moreover, it was observed that AAm grafted film swelled with water had a much higher value of peel strength than that swelled with methanol. This result illustrated that water had more effect on enhancement of peel strength than methanol. It may be due to the greater polarity of water which can be better compatible with PAAm chains.

To check this suggestion, the effect of type of solvent on adhesion was further studied by swelling the samples with various portions of water and methanol and is given in Figure 5.16. As seen in this Figure, peel strength increased with enhanced water percentage. And 100% methanol gave the lowest peel strength. This could confirm that the effect of solvent polarity influenced strongly the adhesion. On account of high polarity of PAAm chains, water that had higher polarity than methanol was better in diffusion through PAAm chains. This would result in greater swelling and through higher mobility of PAAm chains.

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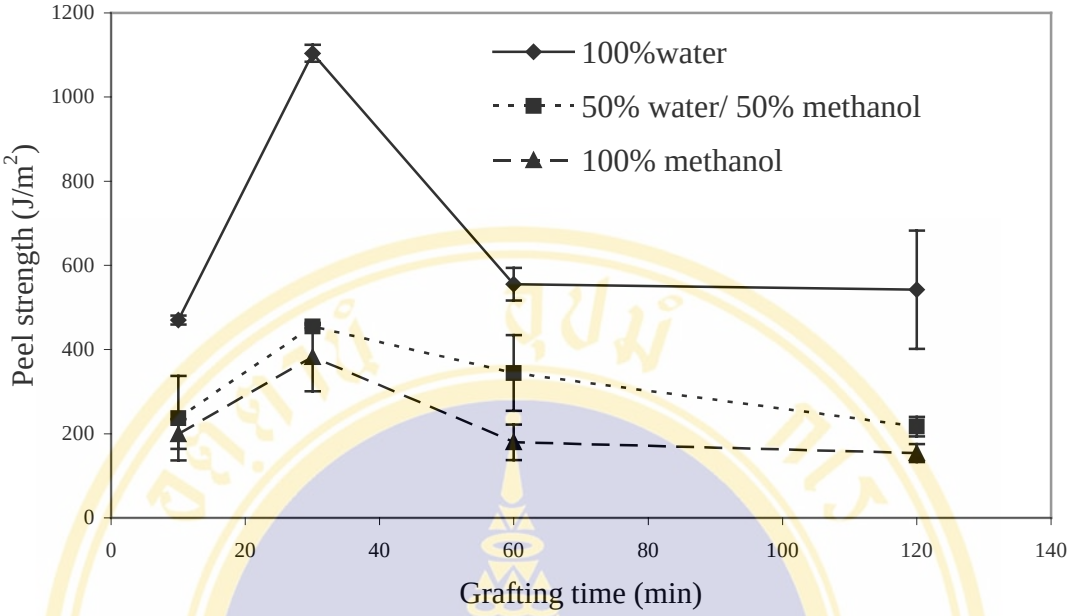

Figure 5.16 Effect of solvent polarity on peel strength of AAm-g-PE film with epoxy resin (HT 80°C, Ht 120 min, GT 50°C)

A similar result was reported earlier by Tsuneda et al [42] for the effect of degree of grafting and solvent polarity on grafted chain mobility. They studied local mobility of polymer chain grafted onto polyethylene monitored by fluorescence depolarization. Glycidyl methacrylate (GMA) grafted PE membranes exhibited shrinkage of grafted chain in benzene (nonpolar solvent). In water (polar solvent), grafted chain with stretching conformation displayed the increasing mobility at low degree of grafting, and then grafted chain mobility decreased with an increase in degree of grafting due to the tightness of stretching graft chain.

Zhao and co worker [58] studied surface morphology of tethered polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) bushes on flat silicate substrates. They reported that swelling in CH_2Cl_2 resulted in increasing mobility of PMMA chains, leading to smooth surface, while swelling in cyclohexane caused rough surface, attributable to collapse and aggregation of PMMA chains. This could be due to high restricted mobility of PMMA in cyclohexane.

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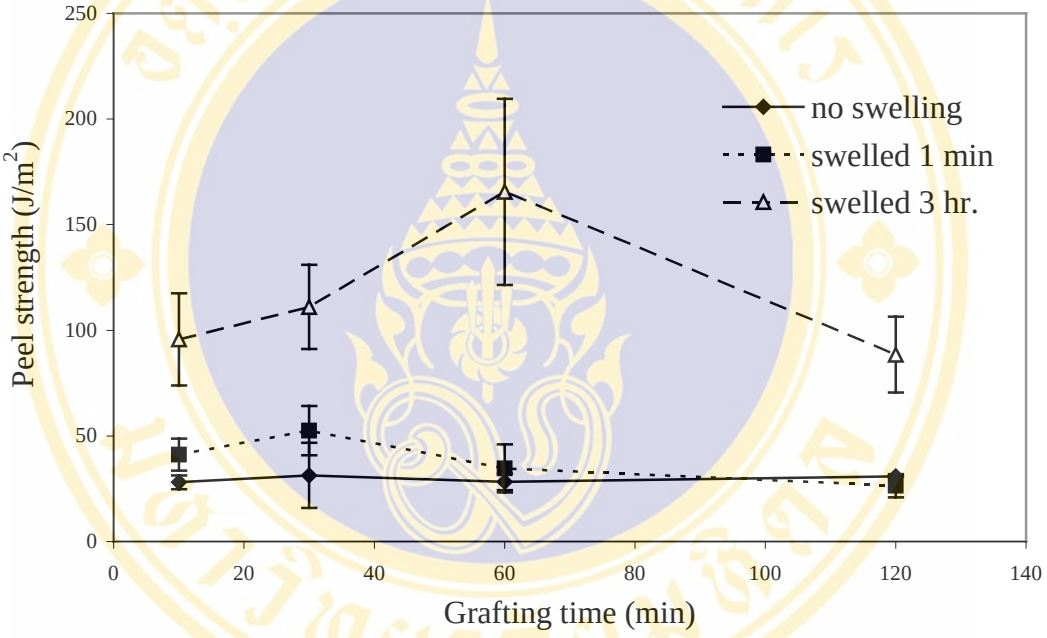
5.3.1.2 Effect of Swelling Time and Solvent Temperature on Adhesion

From the previous experiment, it was found that increasing AAm grafted chain mobility by swelling with water could significantly improve adhesion only at low Ht. and low Gt., leading to short and low amount of PAAm chains. Due to these results, raising adhesion of AAm grafted film at long Ht and long Gt becomes attractive. And the two possible ways were increasing swelling time and increasing swelling power through swelling with hot water.



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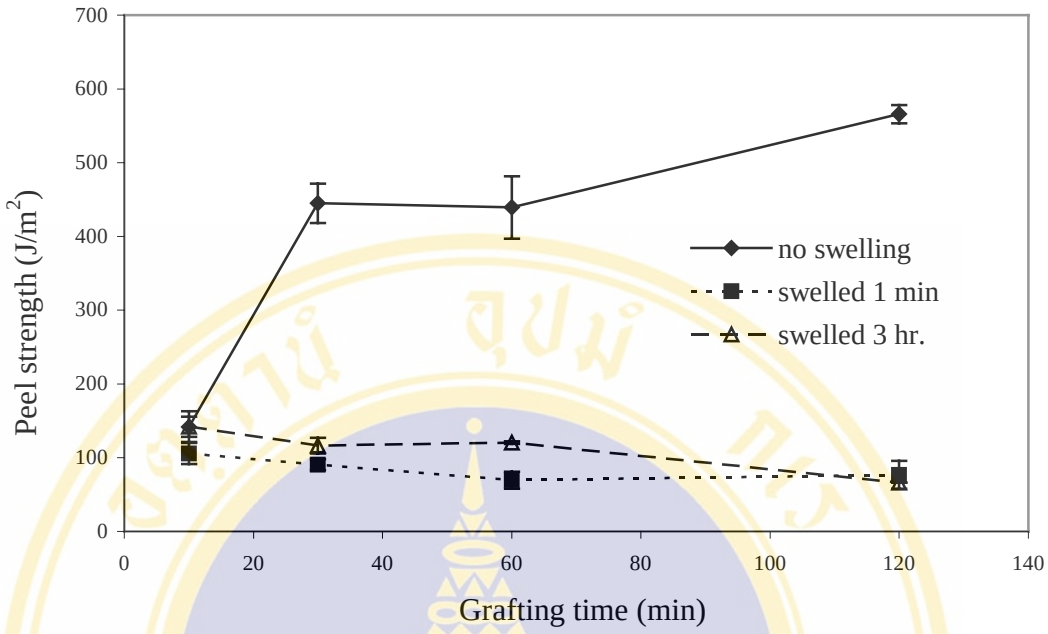

(b)

Figure 5.17 Relationship of peel strength of epoxy resin and AAm-g-PE film swelled with room temperature water for various time versus grafting time (a) Ht.60 min (b) Ht.120 min (HT 80°C, GT 50°C)

Effect of swelling time on adhesion of epoxy resin and AAm-g-PE film at Ht 60 min is shown in Figure 5.17 (a). It can be seen that peel strength of AAm grafted film at Ht 60 min, which has low amount of grafted chain, was greatly increased in the case of swelling time 3 hr while peel strength at swelling time 1 min was increased slightly. This could be concluded that at low amount of grafted chains, swelling with room temperature water could increase mobility of PAAm grafted chains. Moreover, peel strengths at swelling time 3 hr had more improvement than that at swelling time 1 min in all grafting time. This indicated that enhancement of swelling time also increased peel strength. This result may be explained by the increasing flexible time of grafted chain which results in more grafted chain mobility from the increasing swelling time.

On the other hand, peel strength of AAm-g-PE films hydroxylated for 120 min decreased in both swelled time 1 min and 3 hr, as seen in Figure 5.17 (b). This was because at high amount of grafted chains (long Ht) water at room temperature which had low swelling power could not increase mobility of PAAm grafted chains which

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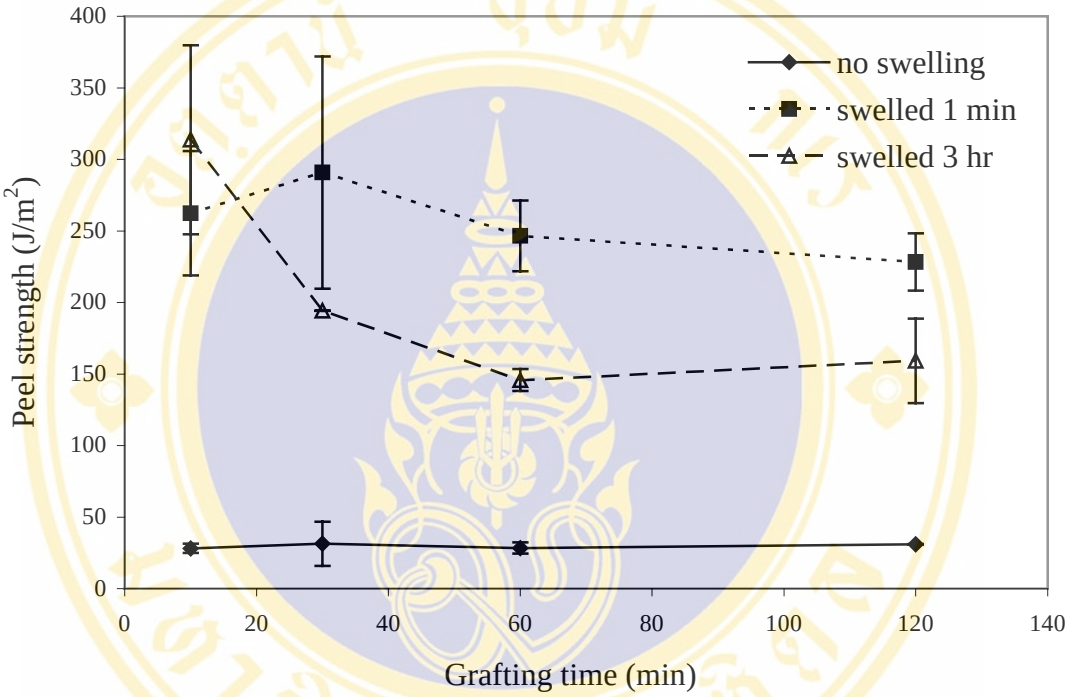
have high entanglement in spite of long swelling time. It resulted in no increase of peel strength. Moreover, decrease of peel strength after swelling may be due to competing of the excess water on grafted surface to react with epoxy resin.

From the above results, it was found that increase only swelling time could not increase mobility at high amount of grafted chain. Therefore raising swelling power by swelling with hot water was other way chosen for increasing chain mobility.



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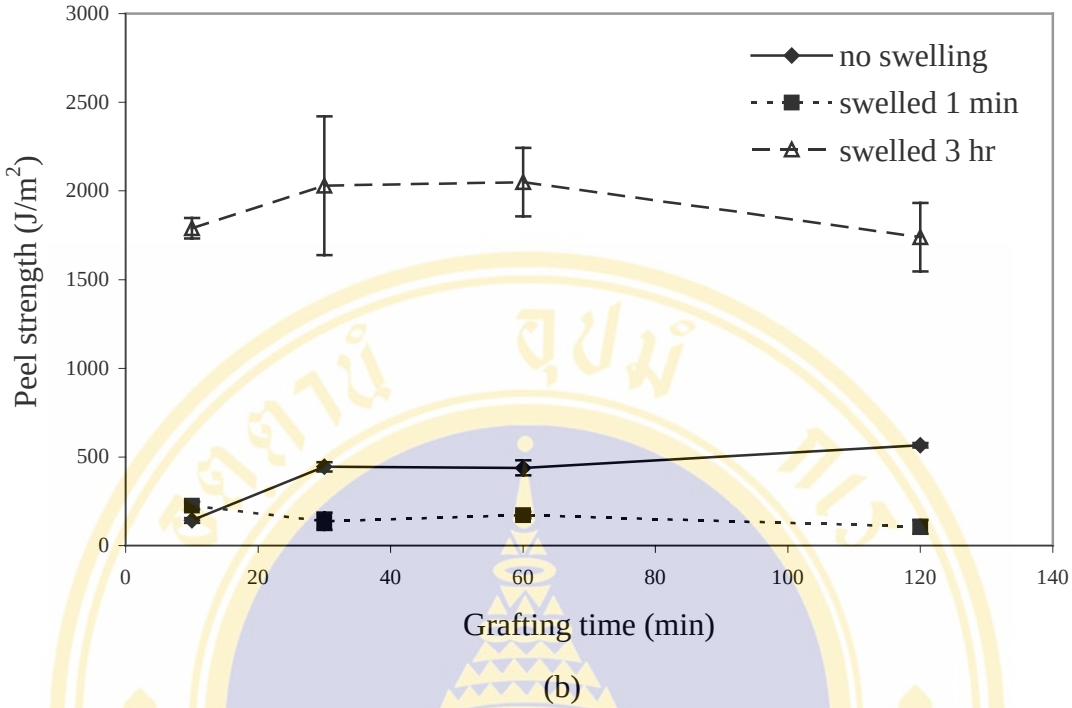

(b)

Figure 5.18 Relationship of peel strength of epoxy resin and AAm-g-PE film swelled with 80°C water for various time versus grafting time (a) Ht 60 min (b) Ht 120 min (HT 80°C, GT 50°C)

The effect of swelling in the 80°C water for various times on adhesion is shown in Figure 5.18. As seen in this Figure 5.18 (a), at low Ht which had low amount of grafted chain, peel strength of all grafting time increased after swelling in 80°C water for swelling time both 1 min and 3 hr and was higher than that swelled in room temperature water (see Figure 5.17(a)). This provided that peel strength could be greatly increased using swelling in high temperature water. Especially, in this case, swelling in 80°C water could raise grafted chain mobility despite low swelling time while swelling in room temperature water could not. The reason for this is the greater swelling power of 80°C water causing higher chain mobility.

In the case of Ht 120 min, as seen in Figure 5.18 (b), it was found that after swelling with 80°C water peel strength increased dramatically at swelling time for 3 hr in all grafting time whereas peel strength at swelling time 1 min decreased. This was because increasing swelling power by swelling in 80°C water could tremendously swell grafted chains although at high amount and long grafted chains (high Ht and long Gt). But in the case of swelling time 1 min, adhesion could not be improved

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because it did not have enough swelling time for swelling high entanglement of grafted chains at high amount and/or long grafted chains.

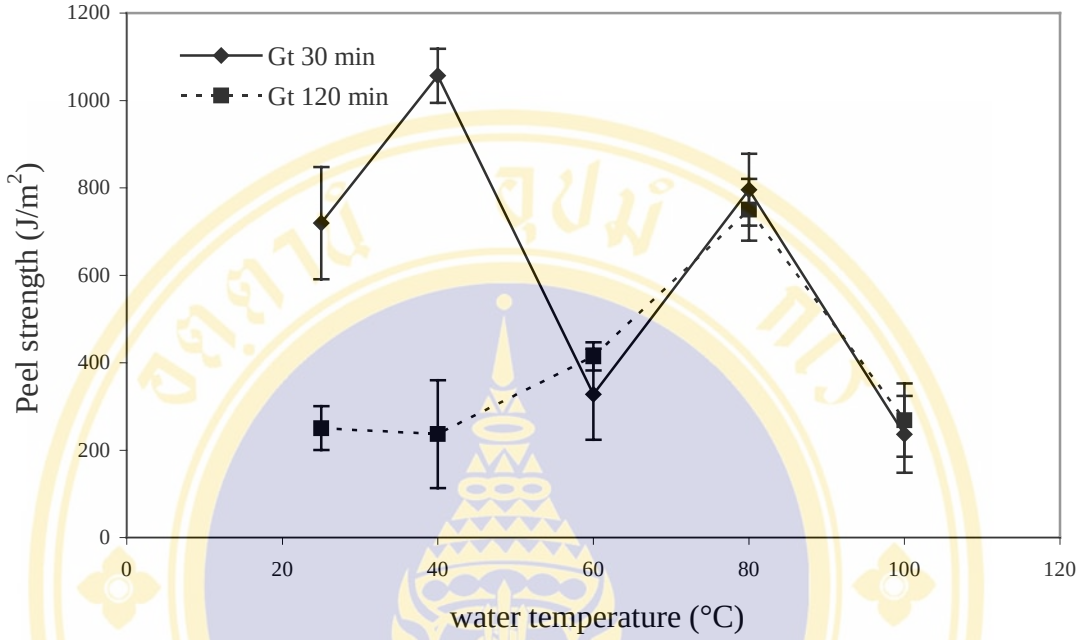

Figure 5.19 Relationship of peel strength of epoxy resin and AAm-g-PE film swelled with water at various temperatures for 3 hr. (HT 80°C, Ht 120 min, GT 50°C)

The influence of solvent temperature on adhesion was further studied by varying water temperature for swelling AAm grafted films, as seen in Figure 5.19. For Gt. 30 min, peel strength increased significantly at initial stage. Subsequently, peel strength had trend to decrease greatly. When the water temperature at 40°C, peel strength was optimum at about 1056 J/m^2 or about 2.5 times over peel strength of unswelled film. In the case of Gt.120 min, it was observed that peel strength had the resemble tendency as Gt.30 min. Peel strength increased with increasing temperature up to 80°C, after that peel strength decreased. The maximum peel strength was 750 J/m^2 or about 1.3 times greater than the unswelled film.

As seen in the above result, it could be confirmed strongly the effect of solvent temperature leading to swelling power. The reason for this phenomenon was attributed to the higher swelling power that increases with water temperature. Moreover, at different grafted chain lengths, the appropriate swelling power for highest improvement of peel strength differed. In the case of short grafted chains (Gt. 30 min)

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the appropriate swelling power occurred at swelling in 40°C water and at swelling in 80°C water for long grafted chains (Gt 120 min). This was because short grafted chain, which had low chain entanglement, could swell easily. Thus water at low temperature could increase grafted chain mobility. At the excess water temperature (>40°C), swelling will cause the excess water content in grafted layer so that peel strength was decreased. In the case of long grafted chain, high entanglement of grafted chain required higher swelling power, so enhancement of peel strength at swelling in water at low temperature was not observed. But when water swelling temperature was increased, which was enhancement of swelling power, grafted chains could have more movement up to swelling in water at 80°C that gives the maximum peel strength. However, when at temperature higher than 80°C, peel strength decreased. This could attribute to the excess water content in grafted layer or deforming of grafted films from over heating.

Table 5.3 % moisture content of AAm homopolymer (before and after swelling with 80°C water for various times) at 120°C from TG analysis

Swelling time	% moisture content
Pristine homopolymer	2.2
1 min	83.7
30 min	97.2
1 hr	97.5
2 hr	97.4
3 hr	98.9

Since the amount of grafting on surface was too small which may lead to little increasing moisture content in grafted layer after swelling, change in % moisture content of grafted layer on surface of grafted film after swelling was not observed. Thus, the effect of swelling on % moisture content was studied in homopolymer using TG analysis. Table 5.3 shows % moisture content of AAm homopolymer before and

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after swelling with 80°C water for various times. It was clear that increasing swelling time could raise efficiently % moisture content of AAm homopolymer when compared with unswelled homopolymer. This could be related to the increase % moisture content in grafted layer of grafted film after raising swelling time which results in change of grafted chain mobility. Nevertheless, little change of % moisture content was observed in spite of increasing swelling time. This could be attributed to its hydrogels and the high thickness of homopolymer, leading to fast water absorption [58, 59]. Therefore, % moisture content had great enhancement although swelling time was 1 min.

Table 5.4 % moisture content of AAm homopolymer (before and after swelling in water at various temperatures for 3 hr) at 120°C from TG analysis

Water temperature	% moisture content
Pristine homopolymer	2.2
25°C	97.5
40°C	97.4
80°C	98.9

The effect of solvent temperature on % moisture content of AAm homopolymer was also determined. This result is shown in Table 5.4. It could be seen that swelling for 3 hr with water in all temperature could increase dramatically moisture content of homopolymer from unswelled homopolymer. However, little change in moisture content of homopolymer was observed despite increasing water temperature for swelling. This should be differed from moisture content in grafted layer of grafted film which changes with swelling temperature. Since homopolymer had higher thickness than grafted layer, it could absorb water more than grafted layer of grafted film. Then, moisture content of homopolymer at plateau value was obtained even in low temperature water.

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5.3.1.3 Effect of Drying Time after Swelling on Adhesion

In order to study more effect of swelling, the influence of drying time after swelling was analyzed. The relationship between peel strength of AAm-g-PE films and the drying time after swelled in 80ºC water was evaluated and are shown in Figure 5.20. It could be seen that trend of peel strength seem to be decreased with increasing drying time and then decreased to the value of no swelling film at drying time 120 min either in Gt 10 and 30 min. This could be attributed to the decrease remaining water in swollen layer with increase drying time. At lower amount of water in swollen layer, grafted chain mobility will have less movement, leading to poor adhesion with epoxy resin. Moreover, this result also indicated that in the range of 1 hr of drying, swelling in hot water still effected on adhesion of AAm grafted film and epoxy resin.

Furthermore, measurement of weight change of homopolymer which swelled with 80°C water after drying at room temperature was direct method allowing studying the remaining water in swollen homopolymer.

TG analysis curve of AAm homopolymer which swelled in 80°C water for 1 min is shown in Figure 5.21. It was found that weight of homopolymer decreased with standing time at 25°C, attributable to weight loss of water in swollen homopolymer. In other words, water still remained in swollen homopolymer for 2 hr. The presence of water in homopolymer within 2 hr supported the above suggestion of the remaining water in swollen grafted layer which had an influence on grafted chain mobility and adhesion.

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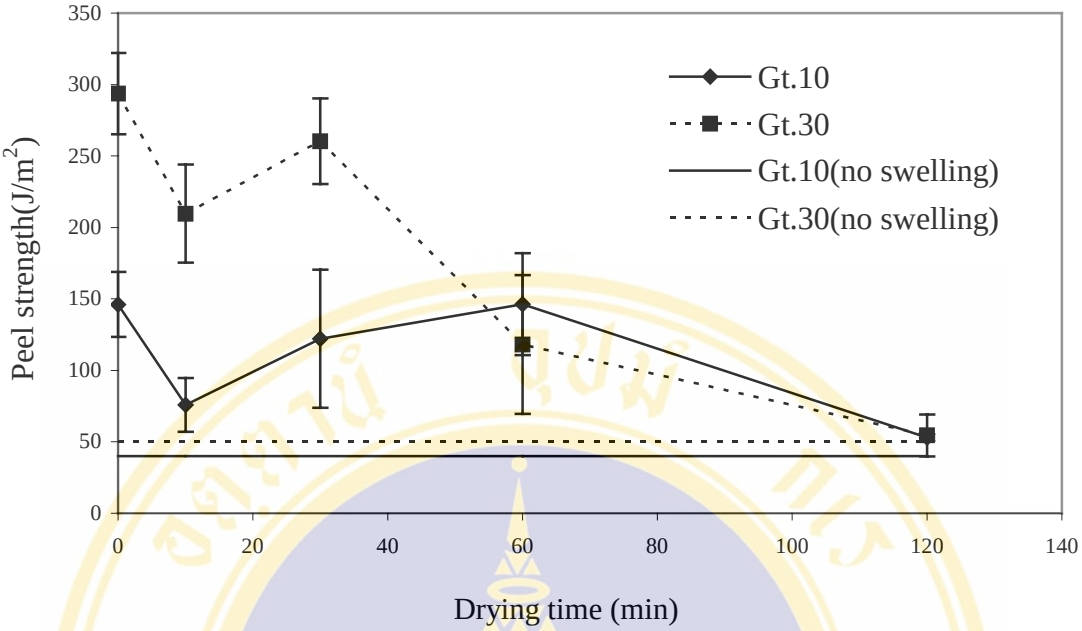

Figure 5.20 Relationship of peel strength AAm-g-PE film swelled with 80°C water for 3 hr. and then dried at room temperature for various times (HT 80°C, Ht 120 min, GT 50°C)

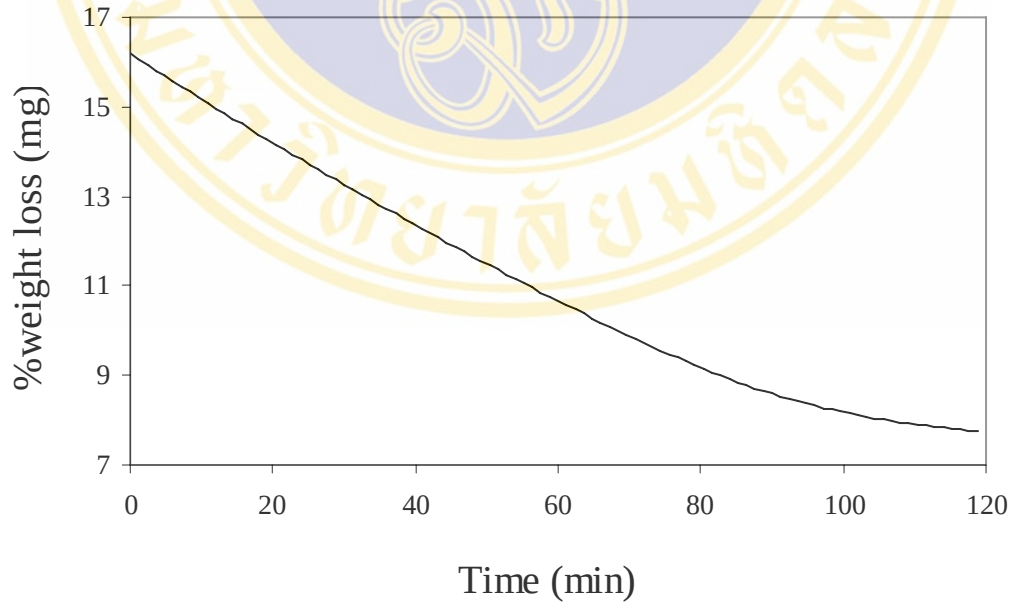

Figure 5.21 TG analysis curve of AAm homopolymer which swelled in 80°C water for 1 min. (Analyse at room temperature)

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5.3.2 Effect of Steaming on Adhesion

From the results of swelling by immersing PAAm grafted film in water, it was found that increasing moisture content in grafted layer influenced on adhesion improvement attributable to grafted chain mobility. Therefore, increase of moisture content in grafted layer by other method could also be expected to increase chain mobility, and promote improvement of adhesion. There are many ways to increase moisture content in grafted layer, and steaming with water is one of them. Hence, the moisture absorption of homopolymer which streamed with 100°C was studied in this part. To determine the effect of steaming on adhesion, two types of polymer were used in this experiment, i.e.; PAAm grafted film and PAAm homopolymer. For grafted film, it was cut into strip of 1x5 cm^2 and steamed with 100°C water. The swollen film was assembled immediately with epoxy resin for peel test after remove excess water at the surface by mildly blotting with tissue paper. For PAAm homopolymer, it was steamed with 100°C water and then was steady subjected to study weight change of steamed homopolymer by TGA.

Table 5.5 % moisture content of AAm and AA homopolymer (before and after steaming with water at 100°C for 3 hr) at 120°C from TG analysis

	Polyacrylamide	Polyacrylic acid
Pristine homopolymer	2.2	4.0
After steam	40.0	49.0

From Table 5.5, it can be seen that after steaming with 100°C water for 3 hr, moisture content of AAm and AA homopolymer was about 39% and 49%, respectively. In other words, it could be say that moisture content of AAm and AA homopolymer was about 18 and 12 times higher than that of unsteamed, respectively. This is associated with hydrogels nature of PAAm and PAA, which are able to absorb a large volume of water. It indicated that moisture content of homopolymer could be

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significantly increased by steaming. Therefore it could be expected that steaming could increase adhesion between AAm grafted film and epoxy resin. From this point, improvement of adhesion by steaming was anticipated.

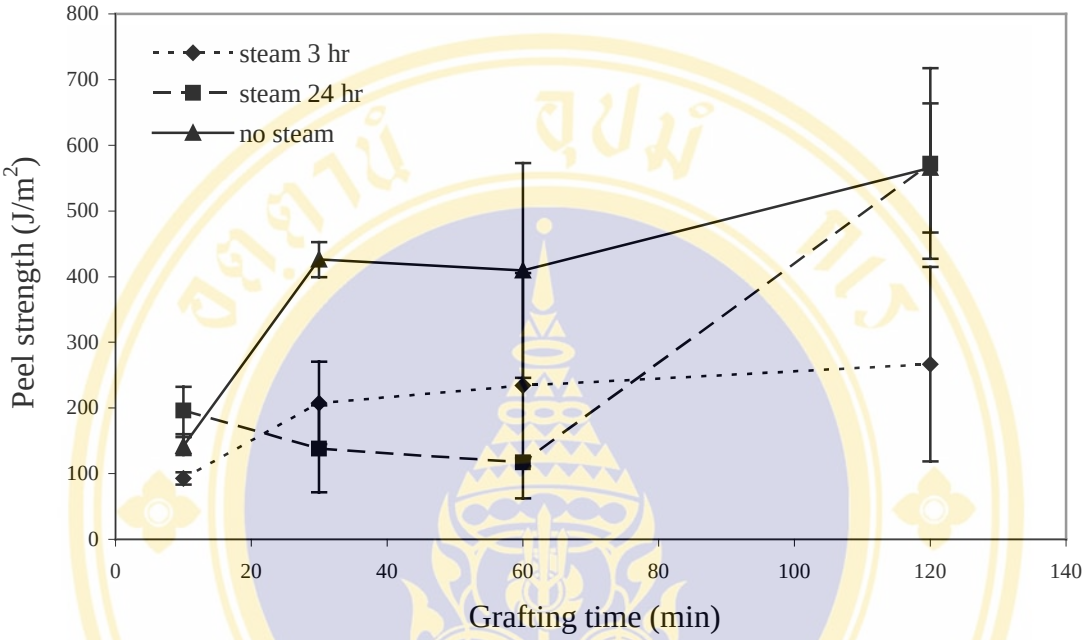

Figure 5.22 Peel strength of AAm-g-PE film steamed with 100°C water for various times (HT 80°C, Ht 120 min, GT 50°C)

Figure 5.22 shows the effect of steaming in 100°C water on peel strength of PE-g-AAm film with epoxy resin. It was found that after steaming, peel strength was decreased for both of steaming time 3 hr and 24 hr. This was because excess amount of water in grafted layer and deforming of grafted films from over heating (Figure 5.23), leading to poor adhesion of grafted film with epoxy resin.

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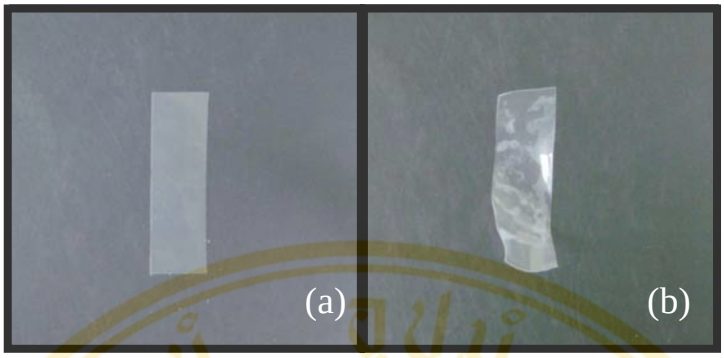

Figure 5.23 Photograph of AAm-g-PE film (a) before and (b) after steaming

5.3.3 Effect of Temperature on Adhesion

As seen in the results of effect of swelling in 80°C water which had significant improvement of adhesion, there are two postulations to explain this result. One is an increase in grafted chain mobility from high swelling power; another is an increase in temperature at grafted surface that may promote better reaction between epoxy resin and grafted chains. To consider these postulations, effect of temperature at grafted surface by warming on adhesion was studied.

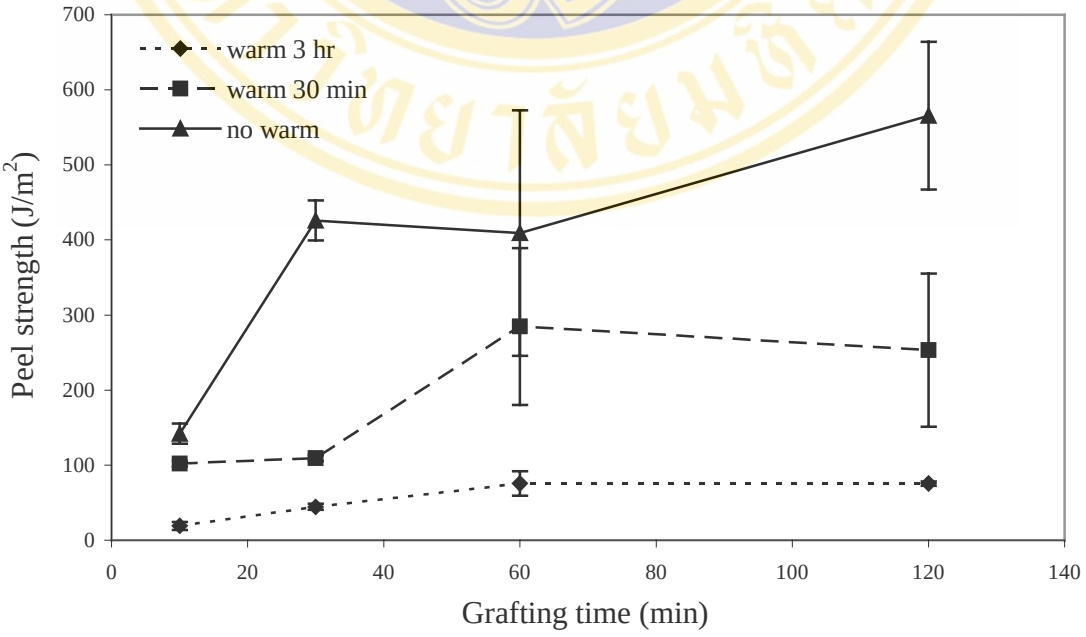

Figure 5.24 Peel strength of AAm-g-PE film warmed in oven at 80°C for various times (HT 80°C, Ht 120 min, GT 50°C)

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As seen in Figure 5.24, warming in an oven at 80°C affected on reducing of peel strength in both of warming time 30 min and 3 hr, especially in warming time 3 hr. peel strength decreased dramatically. This can be concluded that only increase of temperature at surface of grafted film was not enough to increase reaction between epoxy resin and grafted chain, while increasing mobility was an essential factor. Furthermore, warming caused evaporation of water in grafted layer so that grafted chains became more constraint. This affected on reducing ability of epoxy resin permeation to react with grafted chain and resulted in lower peel strength. According with this suggestion, it was reasonable to assume that high reduction of peel strength after warm for 3 hr affected from the high evaporation of water which depends on warming time.

5.3.4 Effect of Swelling of grafted PE Fiber on Adhesion

From previous results, it was clearly seen that swelling of grafted film provided significant improvement in adhesion. However, in some conditions which high adhesion between modified film and epoxy resin was obtained, modified films deformed during peel test due to low yield strength of film. The true value of adhesion strength from swelling could not be obtained. The study of adhesion improvement of grafted PE film was therefore limited. Thus, effect of swelling was moved to study in grafted PE fiber which has much higher yield strength than PE film. The single fiber pull out test was used to estimate the quality of interfacial bonding between differently treated and swelling conditioned PE fibers and epoxy matrix.

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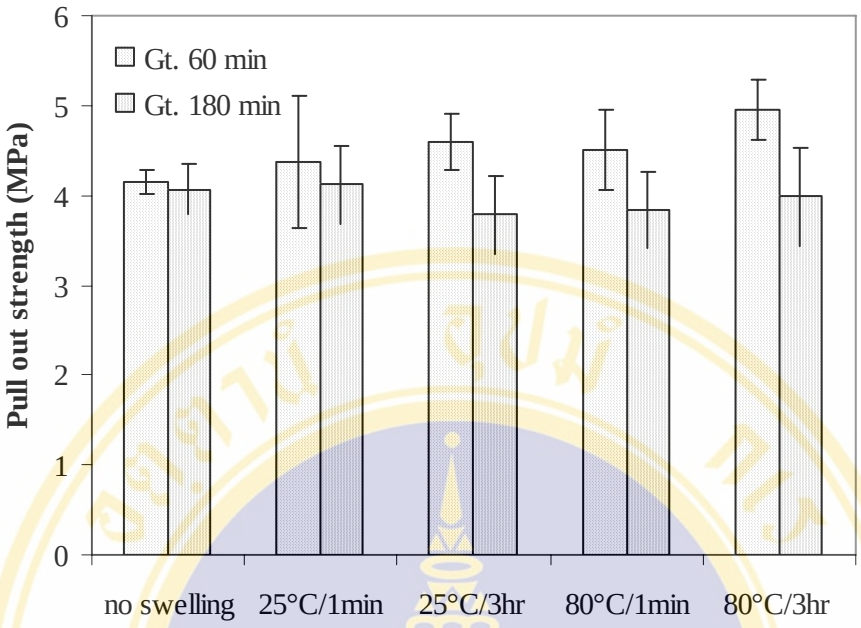

Figure 5.25 Effect of swelling on pull out strength of AA-g-PE fiber with epoxy resin (HT 80°C, Ht 180 min, GT 50°C)

Effect of swelling on pull out strength of AA-g-PE fiber with epoxy resin is shown in Figure 5.25. It could be seen that pull out strength of all swelling conditions are almost the same. This may be because swelling could not increase mobility of AA grafted chain which already has high flexibility. This is similar to the results of AA-g-PE film which have been discussed in the previous section.

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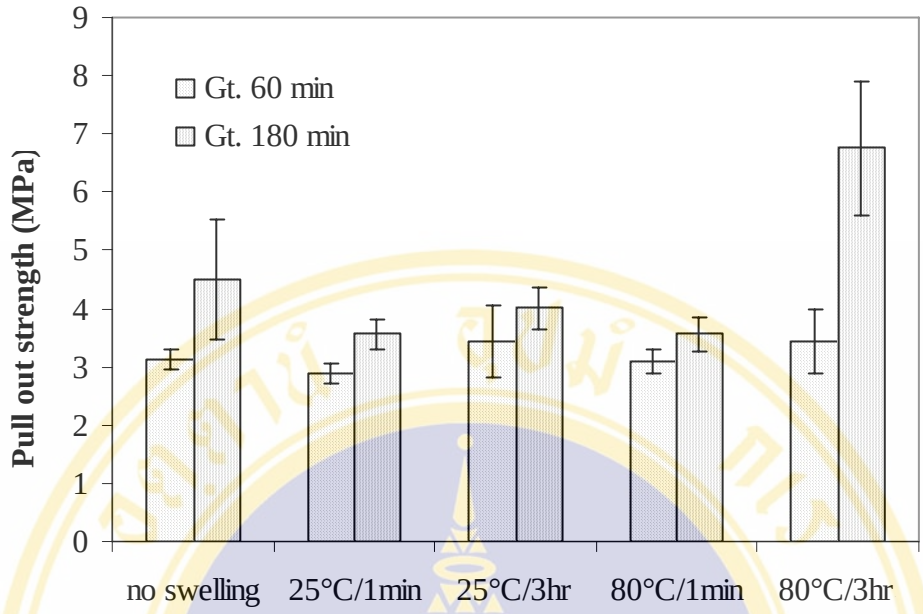

Figure 5.26 Effect of swelling on pull out strength of AAm-g-PE fiber with epoxy resin (HT 80°C, Ht 180 min, GT 50°C)

Figure 5.26 shows effect of swelling on pull out strength of AAm-g-PE fiber with epoxy resin. It was found that swelling in most conditions could not increase pull out strength. But in case of grafting time 180 min and swelling with 80°C water for 3 hr, pull out strength increased significantly about 2 folds. This suggested that swelling had little effects on the adhesion of AAm-g-PE fiber due to low grafting amount of PE fiber. Nevertheless, when amount of grafting and swelling power and time was high enough, adhesion could be improved.

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5.4 Surface Morphology Analysis

To evaluate surface morphology of interface between grafted surface before and after swelling and epoxy resin, atomic force microscopy (AFM) was used. The topography of samples was studied in tapping mode. It was expected to obtain more information to support results of swelling effect. The grafted films were swelled in water for a few minutes and then the excess water was removed. After that the grafted films were attached together by using epoxy resin as adhesive for 8-10 layers of grafted film. AFM examination was carried out on cross-section area of interface between grafted film and epoxy resin which was prepared by microtoming. Scheme of sample preparation is shown in Figure 5.27.

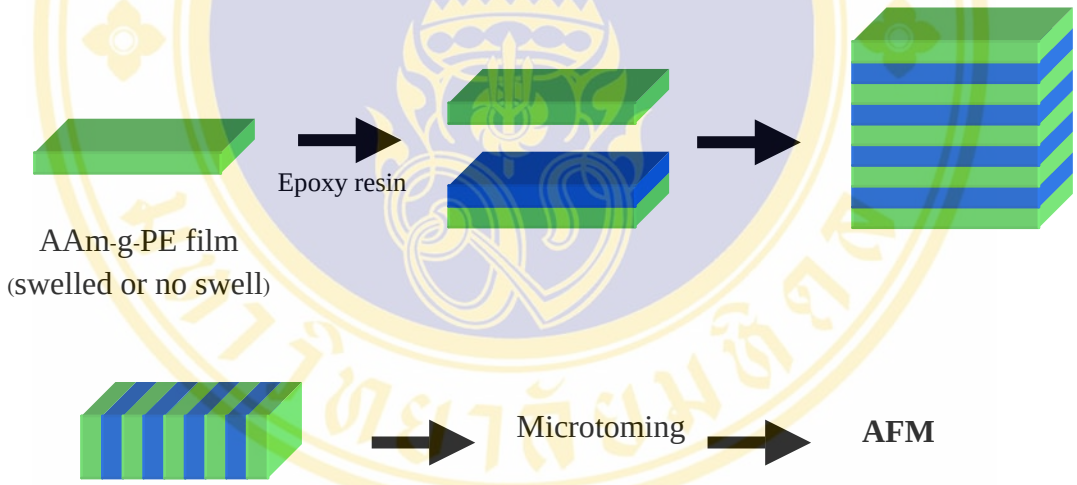

Figure 5.27 Scheme of sample preparation for AFM analysis

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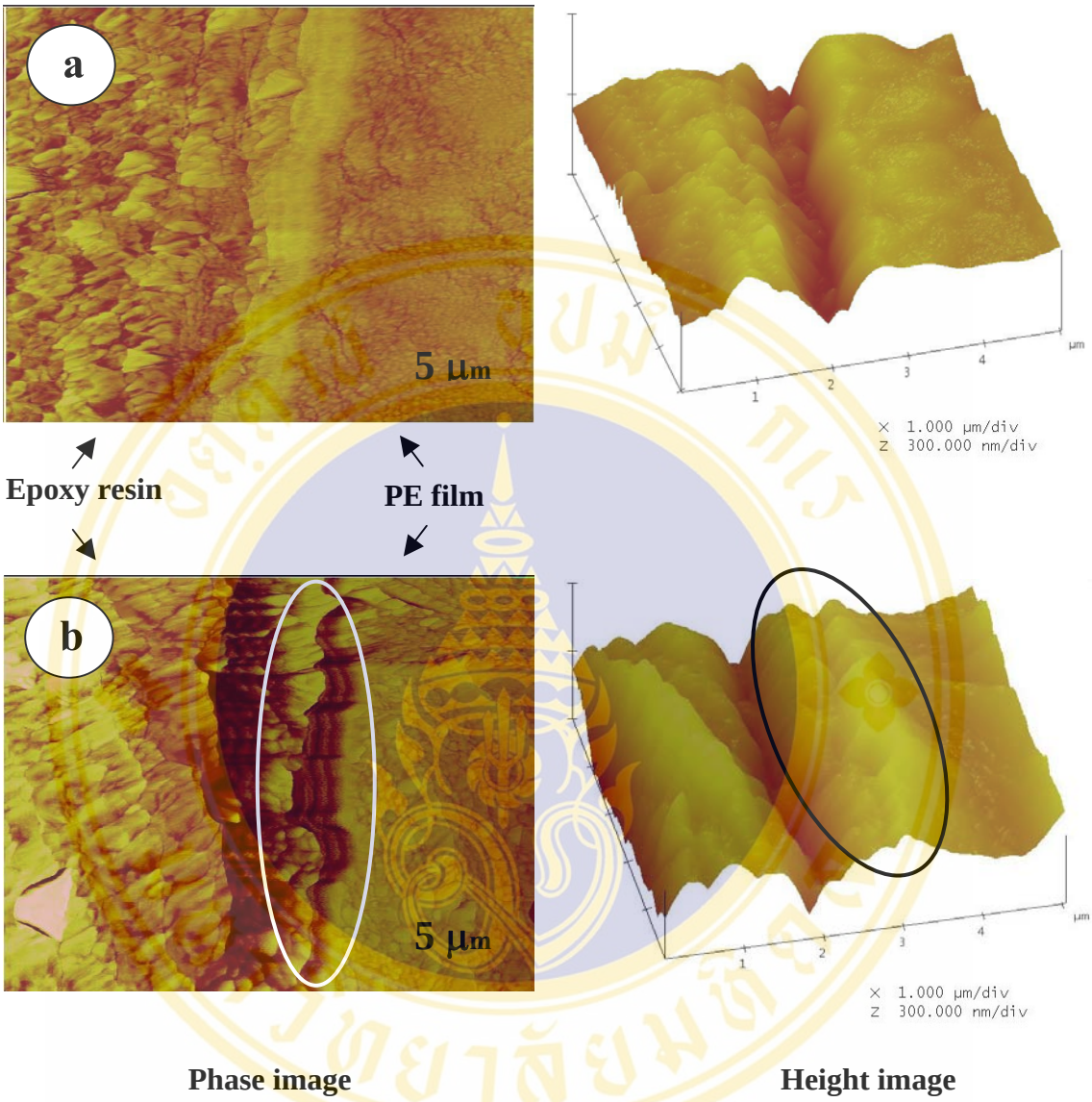

Figure 5.28 AFM images of interface of (a) no swelling (b) swelled AAm-g-PE film and epoxy matrix (scan size = 5 ×5 μm^2)

Figure 5.28 displays AFM images of interface of no swelling and swelled AAm-g-PE film and epoxy matrix. It can be noticed that there was a region between PE film and epoxy resin both in swelled and no swelling film. The height images reveal the presence of longitude hole with the depth corresponding to 300 nm. It can be said that there was the existence of grafted layer between grafted PE film and epoxy resin. A similar observation was also found by Zhang et al [60]. The difference in height of interface could be due to the dissimilar shrinkage of each layer after

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freezing dressing microtorming. After freezing, PE film and epoxy resin had higher shrinkage than grafted layer which had more compact network structure. When sample temperature came back to room temperature, PE film and epoxy resin therefore expanded more, leading to higher height when compared with grafted layer. Furthermore, by comparing between interface of swelled and no swelling grafted film, different feature of grafted layer was found. In phase image, the interface between PE film and swollen grafted layer (see white circles) was rougher than that of no swelling grafter layer. As in height image, it was also found rough structure of swollen grafted layer in parallel with PE film (see black circles). As a conclusion, it can be said that swelling of AAm grafted film caused rougher structure at interfacial of swollen grafted layer and epoxy resin, leading to an increased adhesion between grafted film and epoxy resin.

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5.5 Possibility of Increased Extent of Reaction with Epoxy Resin

From the previous results, it was found that swelling of AAm grafted chain had significant effect on adhesion improvement. We assumed that increasing grafted chain mobility was an important factor influencing on adhesion of grafted chains and epoxy matrix, owing to the presence of either physical or chemical interaction. However, mechanism which swelling affected on increased adhesion was not clearly understood. For better understanding of effect of swelling, the possibility of reaction of epoxy and PAAm was investigated by study of reaction possibility between no swelling and swelled AAm homopolymer and epoxy matrix. Evaluation of the content of reacted AAm on epoxy resin surface was carried out by the following procedure. Dried PAAm homopolymer was swelled with water in various conditions. After repelling excess water at surface, swollen PAAm homopolymer was attached with the mixture of epoxy resin and hardener, so that the existence of reaction between amide groups of PAAm homopolymer and epoxide groups of epoxy resin would be expected. The epoxy matrix was then cured at room temperature for 5 days. To remove the unreacted AAm homopolymer on the surface of epoxy matrix, the assembly was then extracted with hot water in ultrasonic bath. We expected that there were reacted functional groups of PAAm which still stained on epoxy matrix surface. The remaining functional groups of PAAm on epoxy matrix surface were analyzed by ATR-FTIR technique.

Figure 5.29 shows the ATR-FTIR spectra of the epoxy matrix and epoxy matrix which reacted with no swelling and swollen PAAm homopolymer. It can be seen that the spectra of epoxy matrix attached with no swelling and swollen PAAm homopolymer were not different from that of epoxy matrix. This suggested that new peak, attributable to the bonding formation between PAAm homopolymer and epoxy resin can not be observed by ATR-FTIR technique. From this result, it was possible that the content of chemical bonding of PAAm homopolymer and epoxy resin on epoxy matrix was too small to be detected with ATR-FTIR technique.

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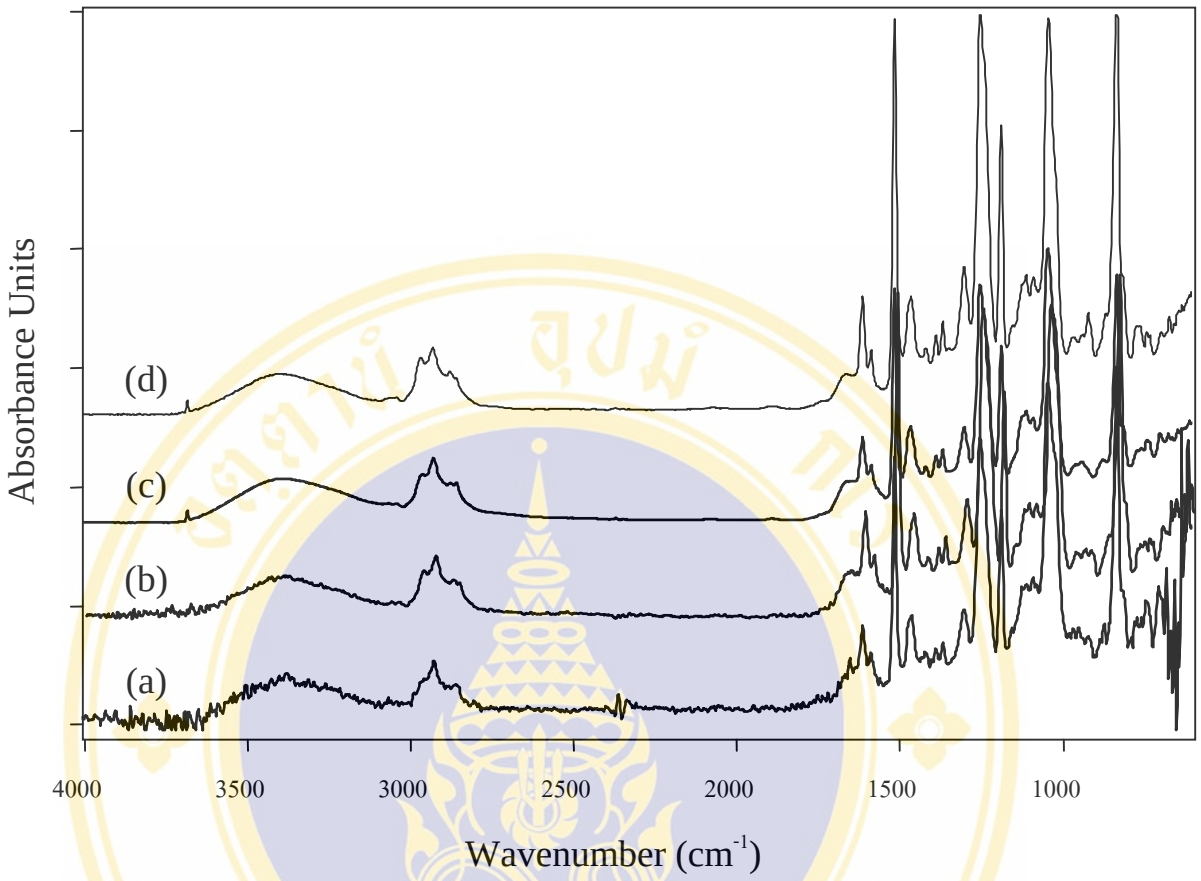

Figure 5.29 ATR-FTIR spectra of (a) epoxy matrix; (b) epoxy matrix attached with no swelled PAAm homopolymer; (c) epoxy matrix attached with PAAm homopolymer which swelled with room temperature water for 3 hr and (d) epoxy matrix attached with PAAm homopolymer which swelled with 80°C water for 3 hr

The study of reaction extent between swollen grafted chain in various conditions and epoxy resin matrix was further required for investigating the amount of the reacted component. In the previous section 5.1 (Figure 5.4), it was found that the formation of covalent bonds between amide groups of AAm grafted chain and epoxide groups of epoxy resin was major factor affecting adhesion strength between AAm grafted chain and epoxy resin matrix. This bonding formation was reflected from the presence of three component peaks at 1509, 1249 and 1043 cm^{-1}, attributable to C=C stretching (skeletal) of aromatic ring, C-O-C stretching of epoxide groups and C-H deformation (in plane) of aromatic ring from epoxy resin, respectively. Therefore, in this experiment, the extent of increased extent of reaction between swollen grafted

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chain and epoxy resin matrix was assessed from the concentration of the reacted component of swollen grafted chain and epoxy resin using ATR-FTIR technique.

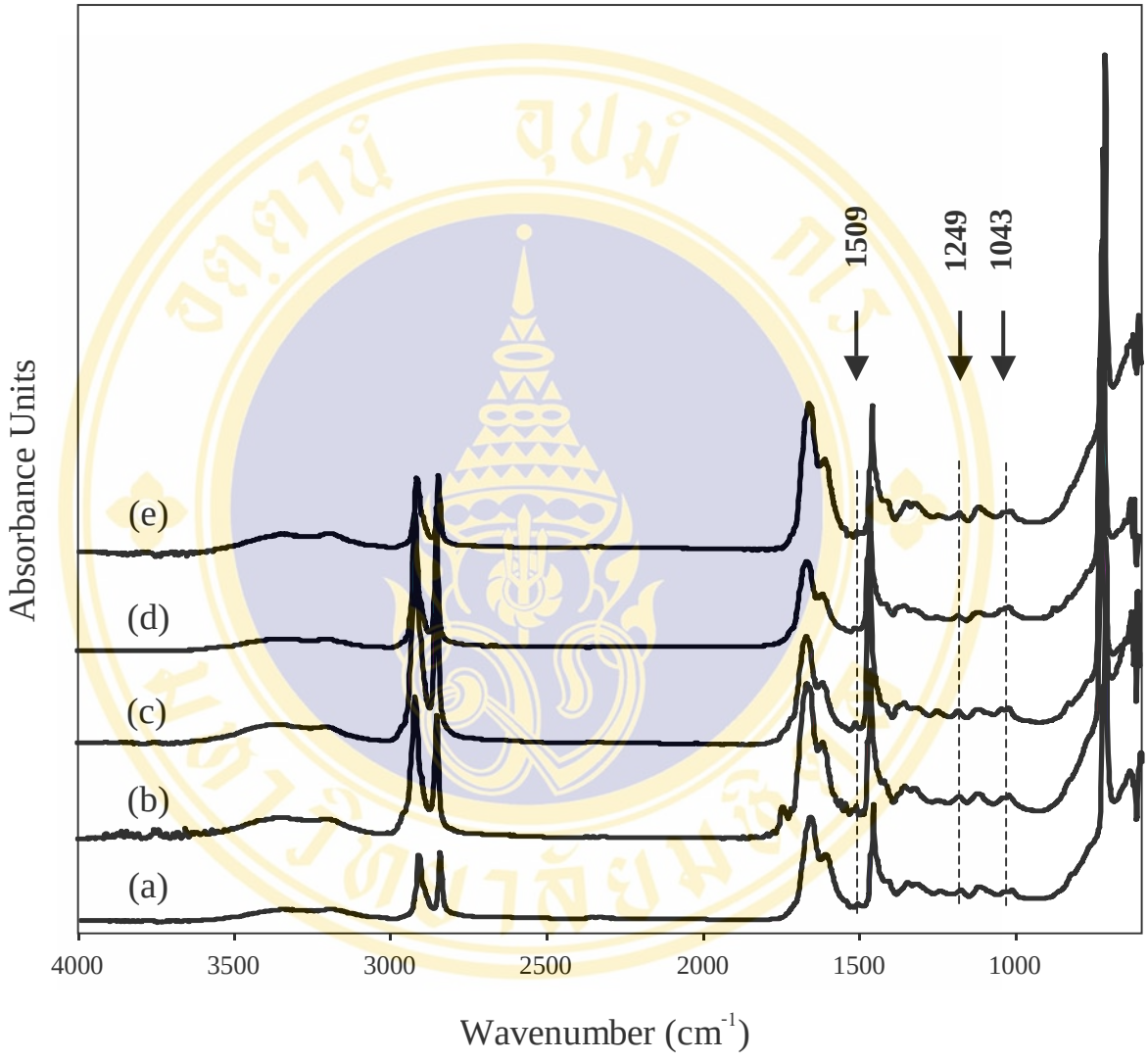

Figure 5.30 ATR-FTIR spectra of (a) AAm-g PE film; (b) swelled in 25ºC water for 1 min; (c) swelled in 25ºC water for 3 hr; (d) swelled in 80ºC water for 1 min and (e) swelled in 80ºC water for 3 hr after immersing in epoxy resin

Figure 5.30 illustrates ATR-FTIR spectrum of AAm-g-PE film which was swelled under various conditions and immersed in epoxy resin. It can be seen that the different contents of three component peaks at 1509, 1249 and 1043 cm^{-1} between no swelling AAm-g-PE film and swollen AAm-g-PE film in various conditions was not

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clearly observed. It was considered that swelling had less influence on increasing the number of chemical bonding between AAm grafted chains and epoxy resin. However, this result contrasted with the results of adhesion strength that significantly improved by swelling. This suggested that swelling improved adhesion by increasing physical interaction of grafted chain and epoxy resin such as interdiffusion of grafted chains, while number of chemical interaction was still the same. Moreover, increasing interaction between AAm grafted chains and amino groups of amine hardener was another possible reason for increasing adhesion, as are shown in Figure 5.31. As AAm-g-PE film was swelled in water, AAm grafted chains could form H-bonding between hydrogen of amino groups from AAm grafted chains and hydrogen of water, then hydroxyl groups of water enhanced the chemical reaction with amino groups of amine hardener, leading to increasing adhesion between AAm-g-PE film and epoxy resin matrix.

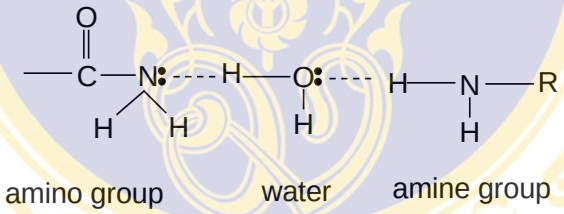

Figure 5.31 Possible reaction of amino group of polyacrylamide and amine group of hardener.

Similar effect of swelling which increases physical interaction on adhesion was also found in the study of tailoring the interface in polyethylene fiber/matrix composites by Cohen et al [61]. They studied a physical method for improvement of the interfacial adhesion between UHMWPE fibers and matrix based on surface swelling of UHMWPE fibers. It was found that strong interfacial adhesion was obtained by the formation of an interfacial layer that is physically entangled with the surface of the swollen fiber with the matrix material while chemical composition of swollen fiber was not different from original fiber.

In addition, correlation between physical interaction of polymer chain and adhesion has been reported. Norton et al [47] studied effect of end-anchored chains on

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the adhesion at a thermoset-thermoplastic interface. It was found that physical interaction which obtains from penetration of grafted chains into the epoxy was an important influence on adhesion improvement. Creton et al [62] reported entanglement of chain at interface can affect the achieved adhesion. Similar result was reported by Nardin et al [63] who studied the effect of the molecular length of n-alklysilanes on the adhesion at a rubber/glass interface.

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CHAPTER 6
CONCLUSIONS

This research focused on the methods for improving adhesion between surface grafted PE and epoxy resin matrix. The surface grafting of PE films and fibers was modified via 2-stage method. The PE surface was first functionalised by decomposition of potassium persulfate ($K_2S_2O_8$) and subsequently grafted with AAm and AA monomers by ceric ion technique. Since the low amount of grafting on fiber leads to little adhesion changes, this thesis therefore mainly studied on film. The adhesion change of grafted PE and epoxy resin matrix in various conditions was measured. The chemical structure and surface structure of interface between grafted PE and epoxy matrix were also investigated. The results are summarized as follow:

1. By comparison between surface grafting with AA and AAm, peel strength of AA grafted surface was higher than that of AAm. This was attributed to the difference in degree of grafting and bonding nature with epoxy resin matrix and mobility of grafted chain.

2. Reducing moisture content of grafted layer by drying in vacuum oven resulted in reducing adhesion strength of both AA and AAm. This related to the low mobility of grafted chains which reflected to high rigidity of grafted layer after drying.

3. Swelling of AAm grafted chain has a significant influence on the increasing interfacial adhesion with epoxy matrix, attributable to the increasing grafted chain mobility. On the other hand, swelling of AA grafted chain resulted in reducing interfacial adhesion with epoxy matrix. This is because AA grafted chain has already high flexibility, therefore adhesion of AA could not be improved by increasing mobility through swelling.

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4. Improved adhesion of AAm grafted film through swelling was affected by solvent polarity, swelling power and swelling time. Moreover, swelling had more effect on short and low amount of grafted chains.

5. Improved adhesion in swollen AAm grafted film/epoxy resin may be attributable to an increased physical interaction of grafted chains and epoxy matrix such as interdiffusion of polymer chains.

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APPENDIX

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Appendix A

Effect of type of grafted chains

Table A1 Peel strength of grafted PE film

Ht (min)	Gt (min)	Peel strength (J/m^2)	
		AA-g-PE film	AAm-g-PE film
30	10	20	18
30	30	24	20
30	60	53	28
30	120	44	25

Table A2 Extent of grafting of grafted PE film

Ht (min)	Gt (min)	Amount of Grafting (g/m^2)		Relative intensity		Peel strength (J/m^2)	
		AA	AAm	AA	AAm	AA	AAm
120	10	0.5	0.5	1.7	0.5	595	159
120	30	2.8	1.0	2.5	1.3	644	445
120	60	4.5	1.3	3.2	1.6	1309	573
120	120	12.5	2.3	5.6	2.4	2048	566

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Appendix B

Effect of decreasing moisture content of grafted layer

Table B1 Peel strength of grafted film before and after drying

Ht (min)	Gt (min)	Peel strength (J/m^2)			
		AA		AAm	
		No drying	Dried	No drying	Dried
60	10	435	208	28	34
60	30	432	388	43	39
60	60	676	532	34	43
60	120	1259	393	31	60
120	10	595	335	159	27
120	30	644	574	445	106
120	60	1309	895	573	101
120	120	2048	917	566	131

Table B2 Peel strength of epoxy resin / grafted film dried in vacuum oven at 60°C for 4 days and then allowed at room temperature for various time before assembly with epoxy

Ht	Gt	time at room T (hr.)	Peel strength (J/m^2)	
			AA	AAm
120	30	no vac	57.69	26.70
120	30	0	86.19	10.79
120	30	1	150.43	4.62
120	30	2	79.65	14.43
120	30	3	52.80	4.48
120	30	4	72.06	15.86
120	120	no vac	400.24	12.44
120	120	0	0.00	7.71
120	120	1	287.41	5.06
120	120	2	yield	35.74
120	120	3	yield	9.84
120	120	4	yield	40.59

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Appendix C

Effect of increasing mobility of grafted chains

Table C1 Peel strength of grafted film before and after swelling

Ht (min)	Gt (min)	Peel strength (J/m^2)					
		AA			AAm		
		no swelling	water	methanol	no swelling	water	methanol
60	10	—	—	—	8	385	698
60	30	—	—	—	8	435	105
60	60	—	—	—	21	891	122
60	120	—	—	—	36	233	70
120	10	1284	429	169	40	449	220
120	30	677	445	665	50	36	89
120	60	1166	922	973	40	411	106
120	120	826	944	429	100	252	109

Table C2 Peel strength of AAm grafted film after swelling with room temperature water or 80°C water

Ht (min)	Gt (min)	Peel strength (J/m^2)			
		room temp. water		80°C water	
		1 min	3 hr	1 min	3 hr
60	10	7.56	21.80	43.39	66.01
60	30	11.68	19.92	81.16	0.00
60	60	11.34	44.11	24.76	7.76
60	120	5.54	17.95	20.03	29.53
120	10	14.32	20.90	20.96	58.11
120	30	7.36	10.71	48.37	391.40
120	60	11.57	1.71	18.44	192.88
120	120	18.86	0.10	38.46	192.54

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Table C3 Peel strength of AAm grafted film after swelling with water at various temperatures

Ht (min)	Gt (min)	Peel strength (J/m^2)				
		25(°C)	40(°C)	60(°C)	80(°C)	120(°C)
120	30	719.39	1056.53	327.93	795.77	236.31
120	120	250.30	236.83	414.76	750.03	268.51

Table C4 Peel strength of AAm grafted film after swelling with 80°C water for 3 hr and then dried at room temperature for various time

Ht (min)	Gt (min)	Peel strength (J/m^2)				
		no drying	10 min	30 min	60 min	120 min
120	10	146.08	75.82	122.05	146.32	52.95
120	30	293.63	209.61	260.27	118.04	54.50

Table C5 Peel strength of AAm grafted film after steaming with 100°C or warming in oven at 80°C for various times

Ht (min)	Gt (min)	Peel strength(J/m^2)			
		Steaming		Warming	
		3 hr	24 hr	30 min	3 hr
120	10	92.76	196.23	19.01	102.00
120	30	207.67	137.91	44.56	109.36
120	60	234.14	117.39	75.78	284.695
120	120	266.75	572.23	75.56	253.32

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Table C6 Pull out strength of grafted fiber after swelling

Ht (min)	Gt (min)	Swelling		Pull out streangth (MPa)	
		temp.(°C)	time	AA	AAm
180	60	—	—	4.16	3.12
180	60	25	1 min	4.37	2.87
180	60	25	3 hr.	4.60	3.45
180	60	80	1 min	4.50	3.08
180	60	80	3 hr	4.96	3.43
180	180	—	—	4.07	4.50
180	180	25	1 min	4.12	3.56
180	180	25	3 hr	3.78	4.01
180	180	80	1 min	3.83	3.56
180	180	80	3 hr	3.99	6.75

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