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PRODUCTION DEVELOPMENT OF A PRESSURE SENSITIVE ADHESIVE FROM NATURAL RUBBER LATEX

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งานวิจัยนี้มีวัตถุประสงค์เพื่อพัฒนาการผลิตสารยึดติดที่ไวต่อความดัน(Pressure Sensitive Adhesives, PSAs) จากน้ำยางธรรมชาติ และ ศึกษาคุณสมบัติทางกายภาพของสารยึดติดที่ไวต่อความดันที่ผลิตได้ โดยจะทำการศึกษาผลกระทบของเวลาที่ใช้ในการย่อยโมเลกุลน้ำยาง ปริมาณ และชนิดของเรซิน (Resin)ซึ่งในงานวิจัยนี้ใช้ ยางสนน้ำ(Rosin ester aqueous), SE376A และ SE790G เป็นเรซินที่เติมลงไปในน้ำยาง ที่มีต่อค่าแรงดึงลอกที่ 180°(180°peel adhesion), การยึดติด(tack) และ เวลาแขวน(Holding time) น้ำยางที่นำมาใช้นี้จะเป็นน้ำยางที่ผลิตได้ในประเทศ โดยจะทำการย่อยน้ำยางด้วยสาร $K_2S_2O_8$ และ โพพานอล (propanol) แล้วน้ำยางที่ได้ย่อยโมเลกุลแล้วไปผสมกับเรซินตามอัตราส่วนที่กำหนดไว้ งานวิจัยนี้ได้ออกแบบการทดลองโดยประยุกต์ใช้หลักทางสถิติ เพื่อลดจำนวนการทดลอง แต่ยังได้ผลการวิเคราะห์ในเชิงสถิติในระดับที่เชื่อถือได้ การวิจัยนี้ได้ทำการออกแบบการทดลองปรับสูตรสารยึดติดที่ไวต่อความดัน โดยวิธีการออกแบบเซ็นทรัลคอมโพสิท (Central composite Design, CCD) และวิเคราะห์ผลการทดลอง โดยวิธีพื้นที่ผิวตอบสนอง (Response Surface Mothedology,RSM) เพื่อแสดงความสัมพันธ์ระหว่างตัวแปรอิสระต่างๆ กับคุณสมบัติของสารยึดติดที่ทำการศึกษา ผลจากการวิจัยพบว่า เวลาที่ใช้ในการย่อยโมเลกุลน้ำยางไม่มีผลต่อการเปลี่ยนแปลงแรงดึงลอก 180° และการยึดติด แต่จะมีผลต่อเวลาแขวน โดยเมื่อเวลาที่ใช้ในการย่อยโมเลกุลน้ำยางเพิ่มขึ้นจะทำให้เวลาแขวนลดลง ในขณะที่การเปลี่ยนแปลงปริมาณเรซินจะมีผลโดยตรงกับคุณสมบัติทั้งหมดสารยึดติด แรงดึงลอก 180° และการยึดติด จะเพิ่มขึ้นเมื่อเพิ่มปริมาณของเรซิน SE376A และ SE790G แต่เวลาแขวนจะลดลงเมื่อปริมาณของเรซินทั้งสองเพิ่มขึ้น แรงดึงลอก 180° และเวลาแขวนจะเพิ่มขึ้น แต่การยึดติดจะลดลง เมื่อปริมาณของยางสนน้ำเพิ่มขึ้น การเปลี่ยนแปลงไปของคุณสมบัติทางกายภาพของการยึดติดที่ไวต่อความดันนั้นขึ้นอยู่กับปริมาณและชนิดของเรซินที่เติมลงไป

ภาควิชา.................วิศวกรรมเคมี............................. ลายมือชื่อนิสิต.......................................

สาขาวิชา................วิศวกรรมเคมี............................. ลายมือชื่ออาจารย์ที่ปรึกษา.............................

ปีการศึกษา..............2542.. ลายมือชื่ออาจายย์ที่ปรึกษาร่วม.........................

4070231221 :MAJOR CHEMICAL ENGINEER
KEY WORD :PSAs/LATEX PRESSURE SENSITVE ADHESIVE/WATER-BASED/ADHESIVE

JITTRAPORN LAYANUN : PRODUCTION DEVELOPMENT OF A PRESSURE SENSITIVE ADHESIVE FROM NATURAL RUBBER LATEX. THESIS ADVISOR : ASSISTANCT PROFESSOR M.L. SUPAKANOK THONGYAI,Ph.D, THESIS COADVISOR : MS. PATRA KANTASILP, 134 PP. ISBN 974-334-062-9.

This research aims to develop a methodology of making Pressure Sensitive Adhesive (PSAs) from natural rubber latex and to study the physical properties of PSAs. The effects of depolymerisation time, contents and types of tackifier resin on 180°peel adhesion, tack and holding time have been investigated in the natural rubber, which was manufactured within Thailand. The natural rubber was depolymerized using $K_2S_2O_8$ and propanols mixed with tackifier resin at various conditions. The experimental design method namely the technique of Central Composite Design (CCD) had been employed in order to minimize the number of experiments. The technique of Response Surface methodology (RSM) was used to construct the empirical model, which can explain the relationship between each variable factor and their response. The depolymerization time was found to play an important role on holding but not on 180°peel adhesion and tack. The holding time decreases as the depolymerization time increases. Types and contents of tackifier resin have influence on adhesion properties. Tack and 180°peel adhesion increase with content of tackifier resin for SE376A and SE790G. However the holding time decreases with increasing the content of these tackifiers. For resin ester aqueous tackifier, 180°peel adhesion and the holding time increase with the content of tackifier, whereas tack decrease with increasing the tackifier content.

ภาควิชา..............วิศวกรรมเคมี...................... ลายมือชื่อนิสิต ....
สาขาวิชา..............วิศวกรรมเคมี...................... ลายมือชื่ออาจารย์ที่ปรึกษา..........................
ปีการศึกษา............ 2542.............................. ลายมือชื่ออาจารย์ที่ปรึกษาร่วม......................

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CHAPTER I

INTRODUCTION

The Pressure Sensitive Adhesives industries are founded upon the use of natural rubber which maintains the major importance as a basepolymer for solution adhesive. However, the trend of development is leading towards the solution adhesives, in the direction of more water-based dispersions or non-carrier systems such as hot-melt glues. Historically, PSAs have been based mainly on the solutions of polymers in organic solvent. Natural rubber is a particularly favored material. In recent years, the uncertain economics of oil-derived solvents have encouraged manufacturers to seek alternative solvent-free adhesive bases. This movement has been sustained and accelerated by the pressure of legislation to control the emission of solvents into the environment. Of these alternative adhesives, the main emphasis at the moment is placed on the hot-melt materials compounded from thermoplastic polymers and modified resins, and on the water-based polymer latexes. Currently, the PSA tape market is still dominated by solvent adhesive technology. However, during the last 3-4 years hot-melt and water-based adhesives have taken more stake in the market share. In 1996, the market share for the different adhesive systems was as follows:

Table 1.1 Market shared of PSA tapes in 1996.[Hullu,1997]

Solvent-based	60 %
Hot-melt	20 %
Water-based	20 %

In recent years, many technical efforts have been put into the development of alternative adhesive like hot-melt. Although the technical performance of hot-melt adhesives has improved significantly, the growth of hot-melt tapes have so far been less than predicted. At the same time, water-based acrylic adhesive has grown significantly in PSA tapes. It is expected that solvent-based adhesives consumption will remain constant in the near future but the growth of tape adhesives will move towards the water-based technology. This is because the water-based adhesive offers broad formulation options and good runability properties, so the water-based tape adhesives have the best chance to flourish.

The main advantages of a latex-based system over a solvent-based one are as follows:

1. Reduce pollution and toxic hazards
2. Reduce fire risk in the factory
3. Allow minor modifications to use the existing coating plant
4. Offer solids content at spreading viscosity. To some extent, this is countered by the lower evaporation rate of water

The three main critical factors in formulating a water-based adhesive are:

1. Adhesive performance
2. Coatability
3. Economic viability

Formulating the adhesive performance itself is the least difficult method since excellent adhesive raw materials are available for the formulation of PSAs for each application. However, it is difficult to get these raw materials in stable emulsion or dispersion form to be able to process under (high) shear conditions on coating machines. So the coatability, in particular, is the key issue.

Finally, the economic viability of the NR latex concept is an important factor because of the cost-driven nature of the adhesive market.

1.1 Project objectives

1.1.1 To produce Pressure Sensitive Adhesive, PSA from natural rubber latex.

1.1.2 To study the physical properties the abcve (1.1.1).

1.2 Scope of the project

1.2.1 Study the fundamental theory of natural rubber latex, pressure sensitive adhesive and other relevant additives in this work.

1.2.2 Depolymerize natural rubber latex.

1.2.3 Produce pressure sensitive adhesives from depolymerized natural rubber latex.

1.2.4 Establish the physical properties of pressure sensitive adhesive.

CHAPTER II

LITERATURE REVIEW

In this project, the production of pressure sensitive adhesives (PSAs) from natural rubber latex and the physical properties of the PSA products are studied. The followings are literature review on the relevant subject which done by many other experts.

In 1979, Bemmels C.W. found that a water-based rubber resin PSA could be produced by mixing highly solid resin solution with isoprene containing latex together with small amount of carboxylation (at least pH about 8). The tackifier resin was added to the rubber latex in highly solid resin solution in an organic solvent. Preferably, this solution contained a small amount of a polar solvent such as isopropyl alcohol. The resin solution was dispersed in the water system of the latex in a finely divided state. This was accomplished by adding the resin solution to the latex system slowly together with high shear agitation.

In 1981, Brosse J.C., Boccaccio G., and Pautrat R. reported the chemistry of liquid natural rubber. The depolymerization of natural rubber molecules was obtained by adding chemical additives, which cause degradation in the latex phase. All chemical modification studies in the paper were conducted on high molecular weight liquid rubber and could be applicable to liquid rubber using an easy to operate. It was suggested that understanding a number of applications for non-modified liquid rubber could result in prelude to obtain the compounds of highly added value and wide variety of usage.

In 1981, Gazeley K.F. investigated the relationship between the physical properties of PSA from natural rubber latex and the particle size of resin emulsion. It was found that the physical properties of small particle size of resin emulsion were better than large particle size of resin emulsion. The effects of surfactant on physical properties of PSA had been studied in this work. Parry and Ritchie[Gazeley,1981] used the probe technique to investigate the effects and obtain results showing the reductions in tack of latex adhesives approximately 30-60% compared with solvent adhesives of similar composition. Oldack[Gazeley,1981] found that it was no loss of probe tack after adding 4 phr or higher concentration of non-ionic surfactant to a latex tackifier with 300 phr of a water dispersible resin.

In 1985, Gazeley K.F. and Mente P.G. studied the properties of PSA from modified natural rubber latex. The depolymerized latex used in this paper was prepared by an oxidative method. The reaction was performed overnight at wide range of temperatures. It was found that the effect of molecular weight distribution, structural difference or difference in polarity contributed to the properties of the pressure sensitive adhesives. The peel strength was subjected to the molecular weight of rubber latex. Cohesive performance depends on the molecular weight As a result, the failure mode changed from cohesive to adhesive as the blend ratio of unmodified rubber rose above 25% approximately. The effect of adding two types of tackifier to latex was also investigated. The result showed that the aliphatic hydrocarbon resin gave higher peel strength than the rosin ester because it was softer than rosin ester. The mode of failure changed from adhesive to cohesive as resin content increased.

In 1986, Bristow G.M., Sears A.G. and Wheelans M.A. studied some possible new applications for liquid natural rubber, LNR. For valcanized plasticzier LNR, the retention of tensile strength after aging under relatively severe conditions was much better than that of aromatic oils. An LNR coating certainly reduced dusting, but accelerator efficiency was slightly reduced and there was little evidence for improved dispersion, even under adverse mixing conditions.

In 1986, Kendall F.F. and Chu S.G. studied the rheological properties of SBR, natural rubber, acrylic latex and their blends with tackifiers. It was found that high molecular weight natural rubber was insoluble in solvent base adhesive. The complete solubility in the solvent could be achieved by milling to low obtain molecular weight rubber. On the contrary, the natural rubber latex systems, which retained the high molecular weight portion, showed improved cohesive strength. Therefore, water based adhesives could yield superior shear performance compared with solvent base adhesives. The difference between modulus of the natural rubber latex and the milled smoked sheet rubber led to the conclusion that the storage modulus of NR latex was higher than milled smoked sheet rubbers. The degradation of the rubber did not change the $\tan\delta$ peak temperature, but it reduced the modulus at high temperature. This modulus reduction was proportional to the lower shear performance. A tackifier, which had a higher T_g than the latex rubber, can increase the glass transition temperature of the latex mixture. However, it decreased the room temperature modulus value of the blend at low loading of tackifier and then increased the modulus at high loading. The minimum G' was dependent on the resin-rubber solubility. The addition of tackifier to elastomer decreased the modulus of elasticity and increased T_g of the blend.

In 1990, the tackification of water based polymers for Pressure Sensitive Adhesives (PSAs) was studied by Yang H., Jacob L., and Heymans L. It was found that the viscoelastic properties of the adhesives depended on the quantity of tackifier. The storage modulus in the bonding region continuously decreased as more resin was blended into the polymer. The lower storage modulus favored bonding by increasing the efficiency of contact between the adhesive and the adherend. The loss modulus at the debonding region continuously increased as more resin was blended with the polymer. This occurred because the T_g of rosin was higher than the

T_g of the polymer and the peak of the loss modulus was proportional to T_g of the blend.

In 1992, Hercules Inc. had developed two resin dispersions, Tacolyn 1070 and 1085, which could increase the performance of water-based PSAs by adding tackifier system to form emulsion adhesive. The base resin was the modification of acrylic latex polymers. Since Tacolyn 1070 resin dispersion was not used in conventional rosin ester chemistry, it provided superior oxidative stability, aging and good UV stability. Tacolyn 1085 also was designed to have two attribute keys: the versatile modification of a wide range of polymer latexes, and the good moisture resistance for the usage in humid or wet environments. This was accomplished by using the base resin that had good compatibility with a number of different polymer types. Coupling with the usage of the efficient surfactant systems, it enables a good moisture resistance. Both products were manufactured using state-of-the-art technology to provide dispersion with high solids and small mean particle size of 0.25 μm and narrow particle size distribution to ensure stable condition under the high-speed coating operation.

In 1994, Dehnke M.K. compared the adhesive between hot-melt and water-based pressure sensitive adhesives. It was found that hot melt PSAs were the best in applications where high peel, tack, and shear bonds were desirable without the heat and sunlight aging. Water-based styrene-butadiene copolymers had good compounding and coating flexibility, but they must be confined to applications where the resistance to heat and UV were not required. Acrylic water-based PSAs provided an excellent balance of compounding and coating flexibility as well as an excellent heat and UV resistance.

In 1995, Charles, O.P. reported that various components constituted the disperse phase of the aqueous dispersion and had a combined weight from 30 to

70% of the total weight. The curing entity was the combinations of plurality of curing agent speeds. The adhesive entity was the combinations of plurality of adhesive elastomer having different molecular weights. High-temperature quality masking tapes made from the new PS adhesives avoided freeze-down and ghosting.

In 1996, Ferrandiz-Gomez T.P., Fernadez-Garcia J.C., A. Cersar Orgiles-Barcelo, and Jose Miguel Martin-Martinez compared the compatibility between polychlorprene and aromatic hydrocarbon resin. It was found that the compatibility depended on the resin content. The cohesion, tack, mechanical, thermodynamic, rheological, and adhesion properties of polychlorprene adhesives should improve if the resin content was lower than 50 phr. Furthermore, the resin content that was higher than 50 phr resulted in a decrease in the adhesion, tack, and mechanical properties of the adhesives. The failure was ascribed to a loss of compatibility between the hydrocarbon resin and the polychoroprene.

In 1997,Hulleu J.G. studied tackifier waterborne adhesives, new formulating opportunities for PSA tapes. It was that the consumption of solvent borne adhesive remained static for the near future and the demand for tape adhesives was higher in the consumption of hot-melt and/or water-based adhesive. Availability of suitable water-based technology, offered broad formulation options combined with good runability properties, was the key factor for the growth potential of water based tape adhesive. Experimental work in this study demonstrated that, next to the classic solvent-based and hot-melt technology, water-based technology was available and offers technically and economically interesting alternative opportunities to formulate high performance PSAs.

In 1998,Tangpakdee J., Mizokoshi M., Eno A., and Tanoka Y. suggested a novel method for preparation of low-molecular-weight natural rubber latex. Low-molecular-weight natural rubber (LNR) and LNR latex was prepared by oxidative degradation of deproteinized natural rubber (DPNR) latex in the presence of 1 phr of

$K_2S_2O_8$ and 15 phr of propanol, by shaking at 60°C. The intrinsic viscosity $[\eta]$ of DPNR with only $K_2S_2O_8$ decreased from 7.2 to 5.5 after 2 hours and increased to 6.5 after 3 hours. After adding propanol to latex, the intrinsic viscosity decreased significantly, i.e. $[\eta]$ was approximately 0.5 after 5 hours of the reaction. However, it appeared that for rubber from high-ammonia natural rubber (HANR) latex the intrinsic viscosity decreased slightly. The concentration of latex and the kind of surfactant used for stabilizing the latex had little effect on the degradation rate of DPNR latex. The LNR latex was stable as the latex formed and the dried rubber coagulated from latex was transparent and colorless.

In 1999,Tanaka Y. found that the deproteinization of fresh latex (FL-latex) or commercial high ammonia latex (HA-latex) was carried out by incubation with a specially made proteolytic enzyme and surfactant. The nitrogen content of rubber decreased from 0.30%(HA-latex) to less than 0.02% after double centrifugation. The mechanical stability of deproteinized latex (DPNR) was higher than 400 sec. The green strength (: strength of pure rubber) was almost the same before and after deproteinization. The film from DPNR showed a significant decrease in the water absorbability and electron conductivity. The film from HA-latex showed a network structure of non-rubber components by electron microscope, as DPNR, although DPNR showed slightly lower modulus and stress at break.

CHAPTHER III

THEORY

3.1 Nature of Adhesives

The total adhesive force holding two materials together is the sum of two factors, namely specific adhesion and mechanical adhesion. Specific adhesion represents the chemical bonding. Mechanical adhesion is the bonding force provided by interlocking action. The total force holding two materials together is proportional to the bonding area. It is a common misconception that only roughening the surface of a joint increases the strength of the bond because it provides more mechanical interlocking. The roughened surface may be more difficult to wet with the adhesive, and this may be the result in discontinuity adhesive film. Consequently, The best result is generally obtained with surfaces that are smooth but not polished.

3.2 Mechanism of Adhesives

Adhesives bind two substrates together by many forces. In this section, some of the forces will be explained and verified. The main forces are,

1. Mechanical interlocking force
2. Diffusion theory force
3. Electronic theory force
4. Adhesion theory force

These forces bind adhesi ve with substrate 1, adhesive to adhesive and adhesive with substrate 2. These forces link two substrates together.

3.2.1 Mechanical Interlocking Force

The principle of the mechanical interlocking force is very simple. The adhesive fails to interlocks keyholes that distribute all around the surface. However, these situations can not occur well if adhesives fall down capillary holes (Figure 3.2.1)

The equation of the optimum point strength of the mechanical interlocking is

(Constant) x (Mechanical interlocking) x (Interfacial chemical component)

From Wake's experiment [Kinloch,1987], the values of the various for the present experiment were

Constant	0.23
Mechanical interlocking	2.9
Interfacial chemical component	5.9

The interfacial chemical component appears twice as important as the mechanical effect. However, as commented by Wake [Kinloch,1987], in the experiments of Perrin and Pettet they could remove the interfacial completely by selecting the appropriate surface treatment, but the mechanical component could only be minimized. Hence, the earlier remark was controlled by mechanical interlock.

There are two types of the mechanical interlocking substrates : mechanical and chemical interlocking substrates. The mechanical interlocking substrate comes from rubbing or scratching the interface to get rid of unwanted material such as oil and releasing agents.

The rest of the treated surface of the mechanical interlocking is called chemical interlocking substrates. There are many ways to treat the surface such as etching, electroform etching, and chemical etching. There are papers about treating the surface of electroformed copper. The form of the surface will effect the strength of the joint. The strength of the joint will increase when the rugosity increases. The rugosity will distribute the force and introduce the plastic deformation at the joint. That is why the strength of the joint is markedly better.

3.2.2 Diffusion Theory Force

This is the force that binds the adhesives together. It comprises Van der Waal force, which is very weak by itself but, because of the high molecular weight, when united it is able to holding the polymers. This comes from the word "like dissolves like" theory. The molecules that are similar will dissolve one another. However, this rule depends on the thermodynamic theory. The indicator, which relates the possibility to dissolve, is called Solubility factor (δ). If the solubility factors of the two substances are equal, these two substances may mix together thermodynamically. If the two different, those two substances cannot be mixed together thermodynamically.

3.2.3 The Electronic Theory force

The electronic force that happened between surfaces have different electronic chager. The magnitude depends significantly on the gap between the surface. Though, there are some theories and experiments in this field, they have not yet drive at conclusion. However, if the surface dose not crack, no electronic bond occurs.

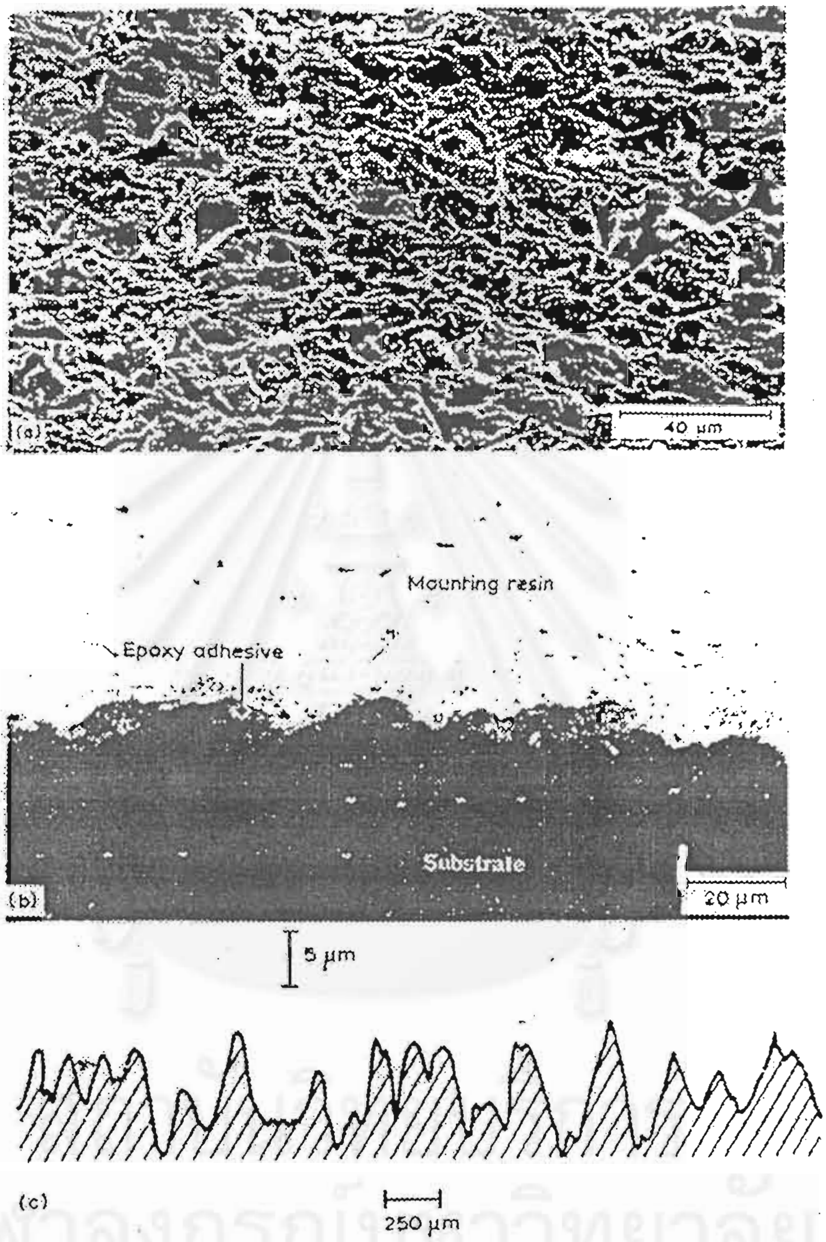


Figure 3.2.1 (a) Scanning electron micrograph of an abraded mild steel surface. (b) Optical micrograph of a normal section cut of an epoxy/abraded steel interface. (c) Talysurf profilometer trace for an abraded steel surface. [Kinloch,1987]

3.2.4 Adsorption Theory Force

Adsorption is the important theory that explains the significance of the secondary bond. Primary bond is the bond that adhesive binds with adhesive. Have the bonding is done between adhesive and the substrate with this makes the strength of the joint incredibly increase.

The strength of the joint depends on both primary and secondary forces. If the joint is free from air trap and other contamination, the strength of the joint will be high.

3.3 Theory of Pressure Sensitive Adhesive.

Pressure Sensitive Adhesives (PSAs) are materials which, in dry form are aggressively and permanently tacky at room temperature and firmly adhered to a variety of dissimilar surfaces upon contact with little need of force; even mere finger or hand pressure will do. They do not require activation by water, solvent, or heat to exert a strong adhesive holding force toward such materials as paper, plastic, glass, wood, cement, and metals. They have a sufficiently cohesive holding and elastic nature so that, despite their aggressive tackiness, they can be handled with fingers and removed without leaving a residue.[PSTC,1997]

For general adhesive working through adhesion phenomena, the adhesive fluid is transformed after bonding into a solid. In the case of PSAs, the adhesive still conserves its fluid state during the bond building. Thus, its resistance to debunking is moderate and the joint may be delaminated without destroying the laminate components in most cases. PSAs are characterized by a built-in capacity to achieve instantaneous adhesion to a surface without activation like a treatment with solvent or heat, and also by having internal strength, so the adhesive material will not break up before the bond between the adhesive material and the surface ruptures. PSAs must possess viscous properties in order to flow and to be able to dissipate energy during the applications. The adhesive must be elastic and in addition, store rupture energy in order to provide good peel and tack performance.

PSAs used in self-adhesive laminates are adhesives through their viscoelastic fluid state, can build up the joint without the need to change this flow state during or after application. On the other hand, their fluid state allows controlled debonding, giving a temporary character of bonded adhesive.

PSAs are composed of a rubbery type elastomer combined with liquid or solid resin tackifier component. A mixture of resin may be used to provide a balance of properties, which cannot be obtained with either resin above. Other fillers are added to change the rheological properties of the adhesive or to add colors. Antioxidants are used to stabilize the adhesive against oxidation, heat degradation and light degradation. Quantity of tackifier is necessary to build good tack in the adhesive which increases quite rapidly with the amount of resin added until it reaches maximum. After this point, the tack diminishes quite suddenly. The maximum amount of resin to be used depends on the type of resin chosen, and possibly the solubility of the particular resin in the rubber phase.

The properties, which are essential in characterizing the nature of PSAs, comprise tack, peel adhesion and holding. The first measures the adhesive's ability to adhere quickly, the second ability to resist removal through peeling and the third to hold in position when shear forces are applied.

Pressure sensitive adhesive coated materials are functionally divided into two broad classes, permanent and removable. The first of these is represented by the permanent materials in which the properties of PSAs are selected so as to form an adhesive bond with the target substrate which is strong and, apart from degradation, does not weaken significantly with time. The second broad class consists of removable or peelable PSA-coated materials in which the PSAs form an adhesive bond, of functionally adequate strength with the target, and then an extended period of adhesion can be peeled from the substrate, without damaging it, without leaving any residue of PSA on the target substrate without the adhesive coated material tearing itself apart.

3.3.1 Adhesion/Cohesion Balance

A balance of cohesive strength and viscoelastic properties is required to allow the PSA to spread over a surface with application of minimum pressure and so that it is removable from that surface without leaving any adhesive residue. The characteristics of these adhesives are based on three parameters;

1. Tack, or the wettability of surfaces;
2. Adhesion, or peel;
3. Cohesive strength, sometime called shear resistance, or ability to resist flow or creep under an applied load, or holding time.

A proper balance between tack, peel/adhesion and cohesion is necessary in most cases. It should be mentioned that formulating high tack and peel using viscous formulating agent decreases the shear resistance. A high cohesion level is given by the rubber-like component of the adhesive or by partial crosslinking.

3.3.2 Tack

Pressure sensitive adhesive tack is the property related to bond formation. It is the property which enables the adhesive to form a bond with the surface of another material upon brief contact under light pressure. Each individual's impression of tack is the sensation experienced in bringing the thumb finger lightly into contact for a short time with a pressure sensitive adhesive and quickly withdrawing it. The concept of tack remains difficult to define. It has been known as one of the following : tack, wet tack, quick stick, initial adhesion, finger tack, thumb tack, quick grab, quick adhesion and wettability. The Pressure Sensitive Tape

Council prefers "quick stick" and defines it as " that which allows a PSA to adhere to surface under a very slight pressure"[PSTC, 1997]. The American Society for Testing and Materials defines "tack" as "the force required to separate an adherent and an adhesive at interface shortly after they were brought rapidly into contact under a light pressure of short duration" [ASTM,1998]. Tack and bond formation, in general, involves molecular interactions at the adhesive and adherend interface.

Tackifier, plastizers, solvents, and temperature all of these impart tack to soften elastomers by their increasing the ease of deformation of the adhesive in short time spans. Tackifiers and plasticizer are not similar. Tackifier increases the modulus at low temperature in short time and high frequencies, but decreases the modulus at high temperature in longer time and low frequencies. A plasticizer decreases the modulus at all temperatures, times, and frequencies. High tack is associated with adhesives that would have high elongation to break in simple tensile strength test. High molecular weight and flexible backbone polymers provide this stress distribution property. The rate of increasing tack depends on the chemical type and melting point of the resin.

Besides tack, in terms of the bonding process, the adhesives must also have the ability to wet and spread on the adherend. The requirement that the surface be wetted by adhesive implies that the surface energies or surface tensions of the adhesive and adherend are favorable for spreading of the adhesive. Low viscosity and short relaxation time of elastic deformation is required for good bonding. Tack increases with an increase in contact time because a longer contact time affords time for the adhesive to flow.

The mechanism of tackification is more easily explained when the viscoelastic basis of tack is understood. The dispersed phases, which presumably consists of a solution of low molecular weight polymer in the resin, are responsible for the tack of the adhesive. The continuous phase of high molecular weight polymer saturated with resin is presumed to make no contribution the tack but provide cohesive strength.

Factors influencing tack

1. Influence of the nature of the adhesive: Tack may differ according to the chemical composition on the state of the adhesive. PSAs that have different chemical bases exhibit a different tack levels. On the other hand, PSAs within the same class of monomers may display a different tack, depending on the specific monomer characteristics, chain structures, and molecular weight. However, most PSAs are formulated and the formulating additives change the tack.

2. Influence of molecular weight: The tack properties are the functions of the molecular weight. The upper limit of molecular weight will cause adhesive failure because a lowered ability of the adhesive to adsorb energy before the interfacial bond is broken, or cause poor wetting because of the lowered flow of the adhesive. Thus tack decreases when the adhesive molecular weight increases. Relatively low molecular weight base elastomers and relatively high molecular weight tackifier resins should be used to improve the tack properties.

3. Effect of crosslinking: Crosslinking of adhesive yields higher shear and lower tack properties. Generally, crosslinking reduces the chain mobility with increasing T_g, so the tack is decreasing. Tack increases continuously upon adding soft, viscous components.

4. Influence of the coating weight: The thickness of the adhesive layer influences the flow conditions. Therefore the coating weight will influence the tack. Proper coating weight is required. Too much or too little coating weight will be detrimental to tack or other properties.

3.3.3 Peel Adhesion

Resistance of peel or peel force is one of the important characteristics of pressure sensitive adhesives. It denotes the tensional force required for separating the adherend and the adhesive film during peel test. Not only the peel force might be dependent on the adhesion, it also depends on many other factors such as viscoelastic properties of adhesive, stiffness of the adherend, rate of separation temperature, etc. Pressure Sensitive Tape Council defines peel adhesion as the force per unit width required to break the bond between a tape and the surface when peeled back, usually at 180^0 at standard rate and condition [PSTC,1997]. A standard peel tests is carried out at a constant peel rate and it is expected that a pressure sensitive tape will strip off cleanly from the adherend, without leaving visually noticeable residue. This type of failure is called adhesive failure and it occurs at ,or near, the adhesive-adherend interface. In case of crosslinked, or very high molecular weight, adhesive, this transition might not be observed. High peel adhesion requires a certain tack level for bonding and certain cohesion for debonding.

Factors influencing peel adhesion

1. Influence of adhesive's nature on peel: Similar to tack, peel resistance is a function of the chemical nature and molecular characteristics of the base polymer. In contrast to tack, peel adhesion increases while the cohesion increases to a limit only.

2. Influence of the chemical composition of the formulated adhesive peel. It should be mentioned that for removability no tackifier or low level of tackifier should be used. More than 50% of tackifier will make the adhesive nonpeelable. Fillers also influence the peel adhesion, by improving the modulus but decrease the contact

area and diffusion rate. Therefore, over 10-15% fillers concentration decrease the peel.

3. Effect of crosslinking on peel adhesion. Generally, crosslinking exerts a more complex influence on the peel. A low degree of crosslinking improves the cohesion and the peel, whereas a high crosslinking degree lowers the tack and the peel.

4. Influence of the molecular weight of the adhesive on the peel: The rheologies of the adhesive influence its adhesive characteristics. Therefore, the peel is also a reverse function of molecular weight: Increasing the chain mobility and diffusion rate will decrease the peel.

3.3.4 Cohesion

Cohesive, shear resistance, or holding time is considered as a force required to pull the pressure sensitive material parallel to the surface, which was affixed with a definite pressure. Pressure Sensitive Tape Council defines "cohesive" as "the ability of the adhesive to resist splitting". Good cohesion is necessary for clean removal [PSTC,1997]. Cohesion is measured in terms of the time required to pull(shear) a standard area of tape from a test panel under standard load. Commonly used tackifier levels cause a decrease in shear strength.

Factors influencing shear resistance.

1. Influence of nature of the adhesive: Special built-in function groups, crosslinking, and high molecular weight can ensure a high shear and a low tack properties. Permanent adhesives provide a higher level of cohesive shear strength than PSAs. Rubber-resin adhesives provide a compromise between high cohesive strength and good quick stick required in automatic labeling.

2. Shear resistance depends on molecular weight: Cohesives increase with molecular weight. However, at the decrease of viscosity and holding power the molecular weight decreases. The shear resistance is improved by the increase of melting point of the resin.

3. Influence of crosslinking on the shear: Crosslinking affects polymer properties in a manner similar to the size of molecular weight but in a more pronounced way. Crosslinking imparts high shear(high cohesion) and lower tack.

3.3.5 Tackifier

The properties of a pressure sensitive adhesive depend on the viscoelastic nature of the adhesive mass. In formulating a pressure sensitive adhesive, a rubbery polymer provides the elastic component while a low molecular weight tackifier constitutes the viscous component. Thus, it is the tackifier which ultimately determines the viscoelastic behavior and the final properties of the finished adhesive.

All rubber-based adhesives require resin tackifier as a main component. These materials impart tack. The tackifier content of rubber-base adhesive is usually 60-110 phr elastomer [Benedek,1996].

Tackifiers are low in molecular weight, ranging from 300-3000 [Bikerman,1996]. Tackifiers with softening point between 60 and 115°C are used most widely for blending with latexes, rubber or acrylic [Benedek,1996]. Tackifiers are available in aqueous dispersion. Tackifiers should have close solubility as the elastomers with which they are blended.

For using with latex adhesives, tackifiers are produced on aqueous dispersions. It is important here that the dispersants used be compatible with the surfactant in the polymer emulsions. A quantity of tackifier is necessary to build good tack in the adhesive and that the tack increases quite rapidly with the amount of resin added until it reaches a maximum. After this point the tack diminishes quite suddenly. The maximum amount of resin to be used depends on the type of resin chosen and possibly the solubility of the particular resin in the rubber phase.

Generally, in order to obtain an improved tack, and easy way is to added some tackifier. A tackifier level of 10-20% is enough for tack improvement of acrylic-based PSAs[Benedek,1996]. A higher tackifier level is imposed mainly for the improvement of the peel adhesion, not for tack. The loss of the shear resistance due to the tackification process is a function of the elastomer and tackifier nature and their ratio.

3.4 Theory of natural rubber latex

Latex is defined as a stable dispersion of a polymeric substance in an essentially aqueous medium. From the definition given above, it shows that latex is an essentially two-phase system, consisting of a disperse phases and a dispersion medium. The disperse phases consist of small particles, normally less than 5μ in diameter. The serum is also used rather loosely tc connote the dispersion medium [Blackley, 1966].

As a class, polymer latexes form a special type of hydrosol, the differentiating feature of which is the polymeric character of the disperse phase. They are intermediate in character between the extreme hydrophilic and hydrophobic types of classical colloid chemistry. Generally, the hydrophobic character predominates.

In the simple instances, the particles are either spherical or so nearly spherical (as to be regarded as such) for all practical purpose. In more complicated cases, the particles may have regular geometrical shapes of lower symmetry, such as ellipsoidal. In still more complicated instances the particles may be quite irregular in shape. The linear dimensions of colloidal particles may conveniently be expressed in angstrom units (A$^{\circ}$), microns (μ) or millimicrons (mμ). All latexes are polydisperse to a lesser or greater extent. The nature and extent of this polydispersity is characterized by a particle-size distribution.

3.4.1 The stability and destabilization of latexes

The latex stability has two quite distinct aspects. Firstly, it concerns the tendency of an individual particle to undergo changes by interactions with the aqueous phase. Such interactions are important in the case of natural latexes, but they are generally confined to the hydrolysis of non-rubber constituents, which are associated with the surfaces of the particles. Occasionally, however, there may be interactions between the aqueous phase and the polymers themselves. Secondly, the important aspect of latex stability concerns the interactions that may occur between the particles themselves. If more than one particle are presented in the system, the possibility now arises that two or more particles may first cohere to give a loose aggregate, and subsequently coalesce to give a single, larger particle.

The term "coacervation" will be applied quite generally to any process, which destabilizes latex to such an extent that the particles agglomerate and coalesce in large numbers. It is found that the resultant coacervate may assume to fall into one of the following three distinct forms. Firstly, they can become gel by gelation process. Secondly, they can become coagulum by coagulation process. Thirdly, they can become flocks by flocculation process.

In the gelation process, the latex gradually changes from a fluid system to a uniform, semi-rigid gel of the same shape and size as the original. Gelation is usually accompanied by the spontaneous contraction of the gel, that the serum is exuded, equaled to the contraction.

In coagulation process, few lumps of polymer rapidly separate from the latex and remain suspended in a medium, which is correspondingly depleted polymer.

The coagulum itself contains the network of coacervated polymer particles, together in the variable amount of entrapped serum.

In a flocculation process, the formation process of a large number of tiny agglomerates of polymer particles is the result of this process. The agglomerates are known as flocks. Flocculation is appropriately regarded as a kind of microcoagulation. Indeed, in some cases, the amount of the effect is particle size of the latex. In these events the flocculated latex will be like a cream or sediment more rapidly upon standing.

Chemical destabilizing agents

It is convenient to subdivide chemical coacervants in the three groups: direct coacervants, heat-sensitizing coacervants and delayed-action coacervants. The first group includes those substances which bring about an immediate and evident destabilization as soon as they are added to the latex. Attention will be confined here mainly to anionic latexes which owe their stability to the negative charges conferred by adsorbed carboxylate ions.

A large number of substances function as direct chemical coacervants for carboxylate-stabilised anionic latexes. It is convenient to classify them under five categories as follows;

- Strong acids,
Metallic ions,
Water-miscible organic solvents,
Polymer-miscible organic solvents,
Cationic surface-active substances.

For the heat-sensitizing coacervants, they include a number of substances which have relatively little effect upon the stability of latex at room temperature.

When latex, which contains one of these substances, is heated to exceed the threshold temperature, coacervation occurs rapidly. In these circumstances, coacervations usually occur as gelation, because when uniformly distributed the latex gradually coacervates. Heat-sensitizes are conveniently discussed under three sub-headings:

The zinc amine system,
Polyvinyl methyl ether,
Polypropylene glycols.

For the Delayed-action coacervants, the third group of chemical coacervants includes substances which make little effect when initially added to latex, but bring about a gradual coacervation after the lapse of a certain time. Delayed-action coacervants may be classified as: (I) salts of hydrofluorosilicic acid, (ii) salts of other fluoro acid, (iii) other delayed-action coacervants. According to Twiss and Amplett (1940), persulphates in the presence of reducing agents are able to cause a slow coacervation of natural rubber latex, due solely to the gradual liberation of hydrogen ions[Blackley,1966].

Physical destabilizing agents

The risen temperature should increase the collision frequency by only about 15%[Blackley, 1966]. Its stability enhances lowering the temperature of latex. The second physical agency which tends to destabilize latexes is mechanical agitation. The particles are thereby caused to collide more frequently and more violently by agitation.

3.5 Statistical Approaches for Experimental Analysis

3.5.1 Response Surface Methodology (RSM)

RSM is the collection of mathematical and statistical techniques which are useful for analyzing problems in which several independent variables influence a dependent variable or response. If the independent variables are denoted as x_1, x_2,..., x_k. these variables are continuous and controllable by the experimenter with minimal error. The response (y) are assumed to be random variables. The response (y) reveals levels of the independent variables as shown in Equation (3.5-1)

$$y = f(x_1, x_2, \ldots, x_k) + e \qquad \ldots(3.5\text{-}1)$$

where e is a random error component.

If the expected responses are represented by E(y) or η they can be called a *response surface* Then the surface is represented by a relationship shown in Equation (3.5-2).

$$\eta = f(x_1, x_2, \ldots, x_k) \qquad \ldots(3.5\text{-}2)$$

The equation (3.5-2) may be represent a two-dimensional response surface graphically by drawing the x_1 and x_2 axes and visualizing the E(y) axis perpendicular. Then plotting response surface curves and contours of constant expected response. The yields the response surface as in Figure 3.5.1 and 3.5.2

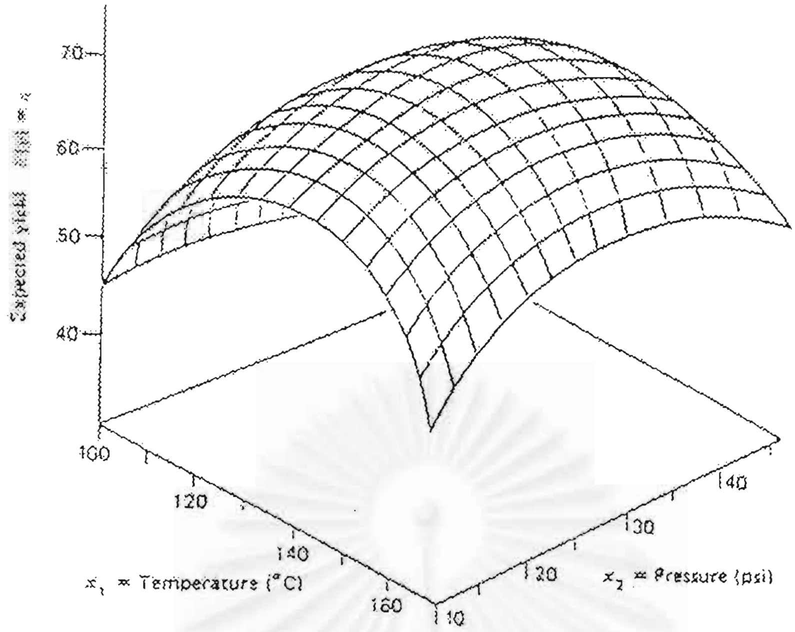


Figure 3.5.1 : Example of a response surface shows the relationship between the response (η) with independent variables x_1 and x_2. [Montogomy,1996]

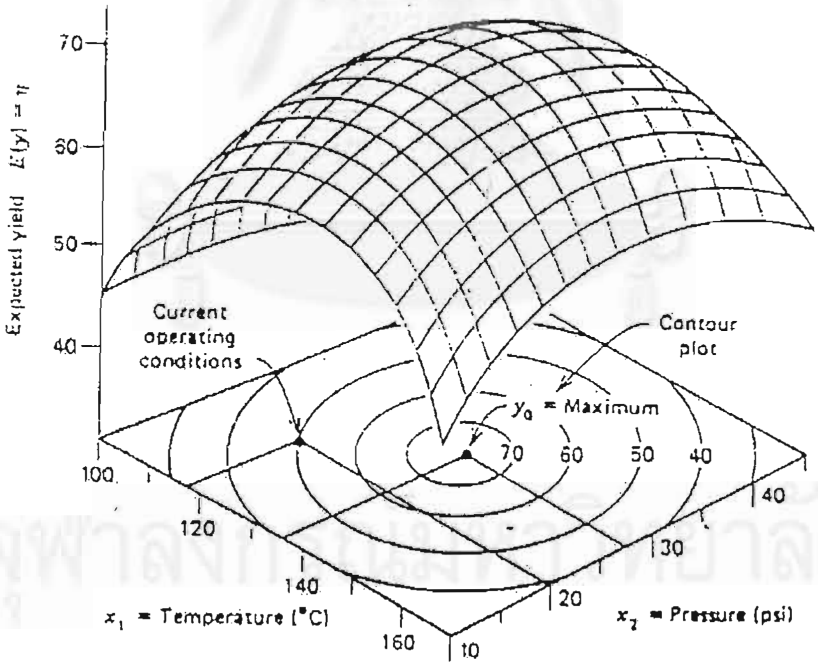


Figure 3.5.2 : Example of a contour curve show the relationship between the response (η) with independent variables x_1 and x_2. [Montogomy,1996]

In most RSM problems, the forms of the relationship between the response and the independent variables are unknown. Thus, the first step in RSM is to find a suitable approximation for the true functional relationship between y and the set of independent variables. Usually, a low-order polynomial in some region of the independent variables is employed. If the response is well-model by a linear function of the independent variables, then the approximating function is the first-order model as shown in Equation (3.5-3).

$$y = B_0 + B_1 x_1 + B_2 x_2 + \ldots + B_k x_k + e \qquad \ldots(3.5\text{-}3)$$

If there is the curvature in the system, then a polynomial of higher degree, such as the second-order model must be used.

$$y = B_0 + \sum_{i=1}^{k} B_i x_i + \sum_{i=1}^{k} B_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} B_{ij} x_i x_j + e \qquad \ldots(3.5\text{-}4)$$

The method of least squares is used to estimate the parameters (B) in the approximating polynomials [Montgomery, 1984]. Figure 3.5.3 illustrates how, by suitable choices of the coefficients, the second order surface in x_1 and x_2 can take on a variety of useful shapes. Both the contour plots and the associated surfaces are shown in Figure 3.5.3.

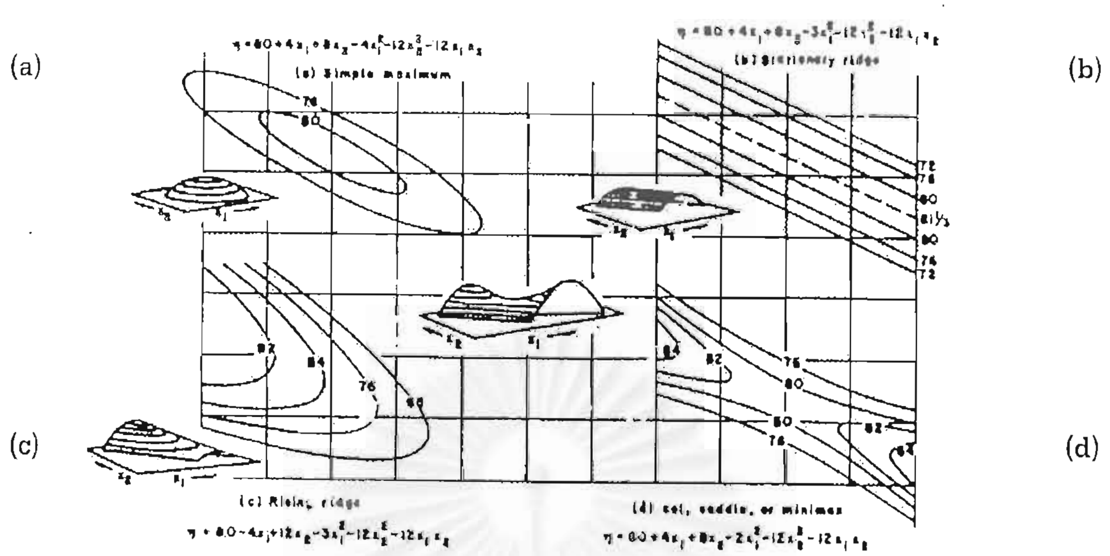


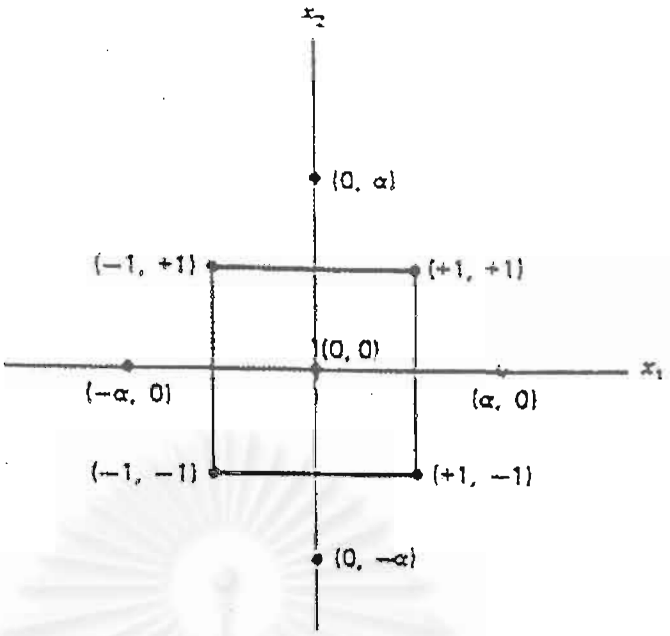
Figure 3.5.3 : Some examples for the types of surfaces defined by second-order polynomials in two predictor variables, x_1 and x_2. [Montogomy,1996]

A simple maximum is shown in Figure 3.5.3(a), and a stationary or flat ridge in Figure 3.5.3(b). Figure 3.5.3(c) shows a rising ridge, and Figure 3.5.3(d) shows what is variously called a col, saddle, or minimax [Box,1987].

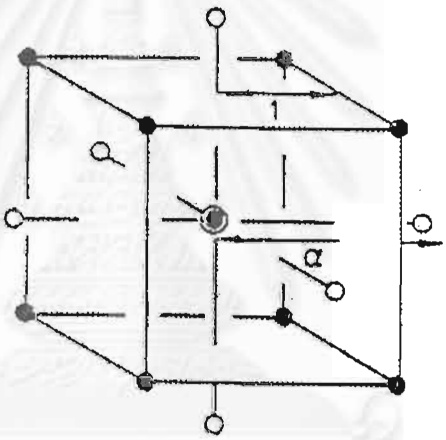
3.5.2 Experimental Designs for Fitting Response Surface

An experimental design or fitting a second-order model must have at least three levels of each factor so that the model parameters can be estimated. The preferred class of second-order response surface designs is the class of *rotatable* designs.

The most widely used design for fitting a second-order model is the central composite design. These designs consist of a 2^k factorial or fractional factorial (coded to the usual ±1 notation) augmented by 2k axial points $(\pm\alpha, 0, 0,..., 0)$, $(0, \pm\alpha, 0,... ,0)$, $(0, 0, \pm\alpha,..., 0)$,..., $(0, 0, 0,..., \pm\alpha)$ and n_0 center points $(0, 0,..., 0)$. Central composite rotatable designs for k = 2 and k = 3 are shown in Figure 3.5.4



(a) k = 2



● Factorial (or "cube") points, with coordinates (±1, ±1, ±1)

○ Axial (or "star") points, distance α from origin

◉ Center points.

If the design is blocked into cube and star portions, some center points would be in the cube block, some in the star block

(b) k = 3

Figure 3.5.4 : Central composite rotatable designs for k = 2 and k = 3. [Montgomery, 1984].

Rotatable designs for any number k of x-variables can be built up from these three components. The value of α must be $2^{k/4}$ in order to make the design rotatable. Table 3.5.1 shows the components of the design for k =2, 3, 4, 5 and 6. Note that with 5 and 6 x-variables, the size of the experiment is reduced by using a half-replicate of the 2^k factorial. With a half-replicate, The value of α becomes $2^{(k-1)/4}$. Tables 3.5.2 show example of the central composite rotatable design for 2 independent variables, x_1, x_2, respectively.

Table 3.5.1 : The comparison of number of experiments was designed by factorial design and by central composite rotatable design for k independent variables at 5 levels of variables. [Montogomy,1996]

Number of Independent Variables (k)	Number of experiments with 5 levels of variables					
	Factorial (5^k)	Central Composite Rotatable				
		Cube Point	Star Point	Center Point	Total	α value
2	5^2 = 25	4	4	5	13	1.414
3	5^3 = 125	8	6	6	30	1.682
4	5^4 = 625	16	8	7	31	2.000
5	5^5 = 3,125	16	10	6	32	2.000
6	5^6 = 15,625	32	12	9	53	2.378

It is convenient not to have to deal with the actual numerical measures of the variables X, but instead to work with coded or "standardized" variables x. For example, if at some stage of an investigation, the current region of interest for X are defined to be $X_0 \pm t$, where X_0 is the center of the region, then it would be convenient to define an equivalent working variable x [Box,1987] where.

$$x = \frac{X - X_0}{t} \qquad \text{...(2-32)}$$

Table 3.5.2 : Example of the central composite rotatable design for 2 Independent variables, x_1 and x_2.[Box,1987]

Experimental	**Coded variables of independent variables**		**Response**
	x_1	x_2	(y)
1	-1	-1	y_1
2	1	-1	y_2
3	-1	1	y_3
4	1	1	y_4
5	-1.414	0	y_5
6	1.414	0	y_6
7	0	-1.414	y_7
8	0	1.414	y_8
9	0	0	y_9
10	0	0	y_{10}
11	0	0	y_{11}
12	0	0	y_{12}
13	0	0	y_{13}

CHAPTER IV

EXPERIMENTAL WORK

The experimental procedures are divided into three parts: (i) Latex preparation (ii) Adhesive preparation (iii) Test of adhesive. The details of the experiments are described as follows.

4.1 Latex Preparation

4.1.1. Material

Depolymerized latex was prepared from normal commercial centrifuged high ammonia concentrate latex (High-Ammonia Latex (HA Latex) from PATTANI INDUSTRY (1997) Co., Ltd., Thailand) with HA latex content 61.5 % total solid content (TSC) and 60.0 solid Dry Rubber Content (DRC). The ammonia content was 0.7 % of total latex weight. pH of latex was 10.7. Radical initiator used was $K_2S_2O_8$. Propanol was used as reagent to reaction mixture. Both chemical reagents were of the analytical grades.

4.1.2. Depolymerization Procedure

HA latex 200 ml was prepared. Then initiator and reagent were added into the latex and stirred at 400 rpm by Heiddph RZR2050 electronic mixer. The reaction was carried out in a mixing machine by heat latex at 60°C with hot plate stirrer.

4.1.3. Molecular Weight Analyses

Intrinsic viscosity (η) of natural rubber latex in dry form was determined by using an Ubbelhode viscometer in 0.1-.02 g/dL of toluene solution at 25°C. Natural rubber latex was dried at 25°C for 17 hours. The viscosity-average molecular-weight (M_v) is estimated from Mark-Houwink relation, where the Mark-Houwink constants are $K = 33.1x10^{-5}$ and $a = 0.71$.[Billmeryer,1984]

The particle size distribution was determined by using a COULTER LS-230 particle-size distribution analyzer.

4.2 Adhesive Preparation

4.2.1. Material

Depolymerized latex is used as base polymer.

Three types of rosin tackifiers are used.

1. Rosin which melts with NaOH aqueous solution by 50/50 %wt from local company. Rosin was dispersed in water at 50% concentration,
2. SE376A, aqueous dispersion of modified rosin with anionic stabilizer from eka chemicals (N.Z). Ltd.,. New Zealand,
3. SE790G, aqueous dispersion of modified rosin with polymeric stabilizer from eka chemical(N.Z.).Ltd.,. New Zealand

Corona-treated Polypropylene film is used as a substrate in this experiment.

4.3. Preparation of Adhesive Film

Adhesive compounds were produced by mixing depolymerized latex with tackifiers by Heiddph RZR2050 electronic mixer at 400 rpm for 5 minutes. The adhesives were cast on a polypropylene film substrate by using a hand-coating device as shown in Figure 4.3.1. Then the coated substrate was heated for 4 minutes at 100 °C in the hotpack vacuum oven. The test pieces were cut into 1inch wide strips. Then they were conditioned at room temperature for 72 hours before testing. The thickness of adhesive film was control led by using 0.35 mm. string diameter.

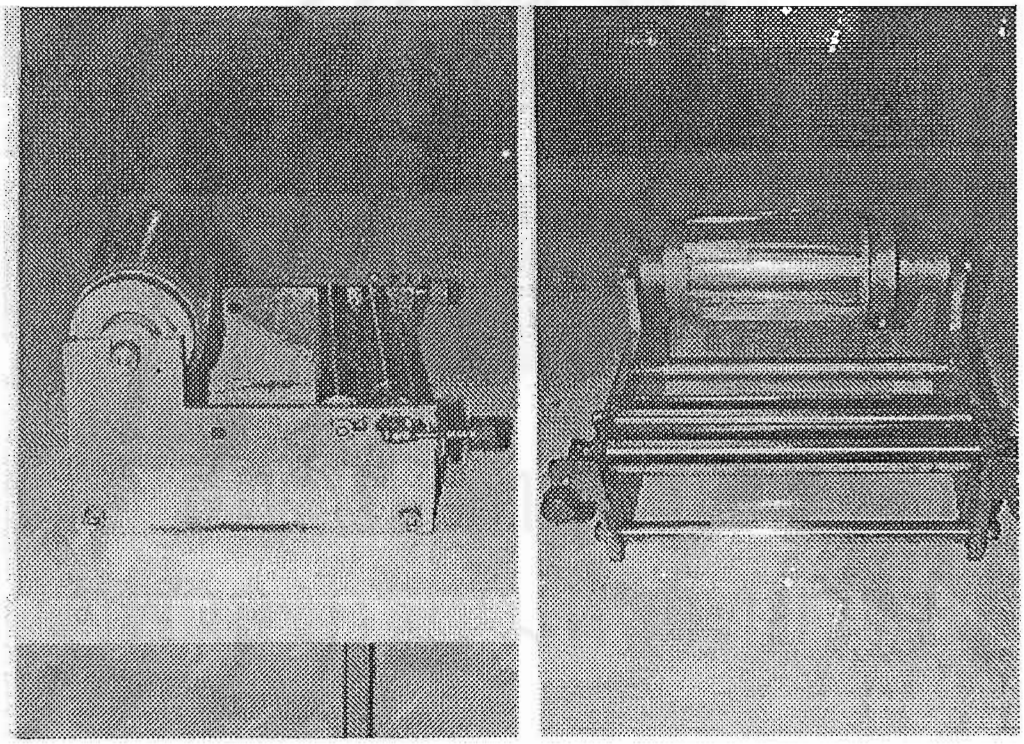


Figure 4.3.1 Hand-coating device.

4.4. Test of Adhesive

4.4.1. 180°Peel Adhesion [PSTC,1997].

Peel tests were performed in PSTC-1(Pressure Sensitive Tape Council) using stainless steel surface. Stainless surfaces were cleaned by swabbing with acetone and MEK to remove adhesive traces, then rinsing with tap water and drying, respectively. Next, apply the adhesive tape to the test surface using 1 kg of load roller at speed 12 inch per minute. The Lloyd 2000R instrument which can be operated in both tension and compression mode was used to perform 180^0 peel testing of PSAs samples. The crosshead speed was 12 inch per minute with the accuracy of ±0.5% of the set speed. Each peeling test using interchangeable load cells had an overall force ranging from 0.25 N to 10kN.

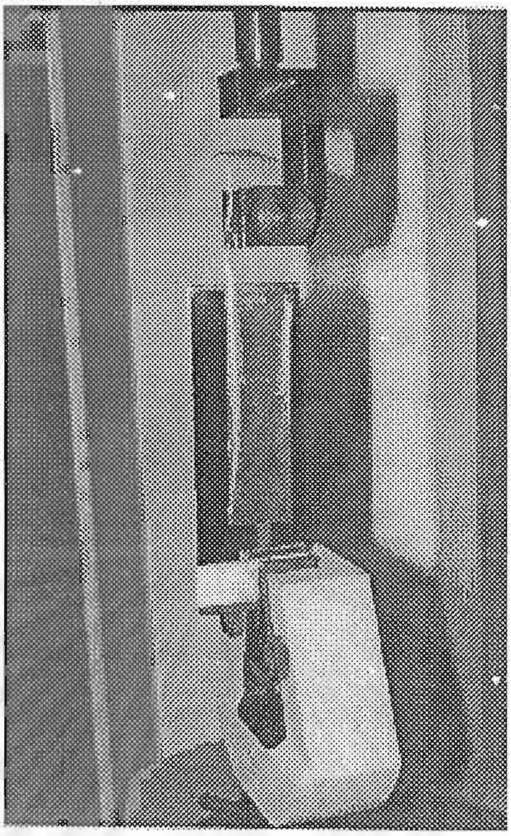


Figure 4.4.1. 180°Peel adhesion test.

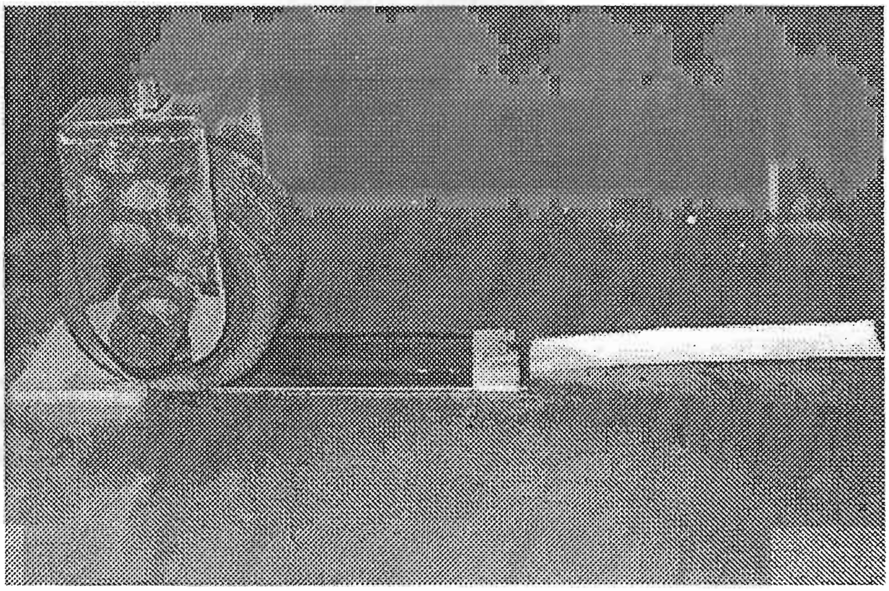


Figure 4.4.2. Load Roller (1kg)

4.4.2 Loop tack[FINAT,1999]

A tensile tester and vertical jaw with separation rate of 300mm per minute with an accuracy of ±2% was used in this experiment. Test pieces were strips taken from a representative sample of PSA. Each sample of the strip was 25 mm wide and minimum length of 175 mm. The cut should be clean and straight. At first, hold the two ends of the adhesive-coated material strip and form a loop by bringing the two ends together. Then, clamp the loop end into the top jaw of tester and leave the loop hang vertically downwards. Next, start the machine and bring the loop into contact with the stainless plate at a speed of 300 mm per minute. When full contact over the stainless plate has been achieved (25mm x 25mm) reverse the direction of the machine immediately. Allow separation to take place at a speed of 300 mm per minute. Then, record the maximum force that completely separates the loop from the surface.

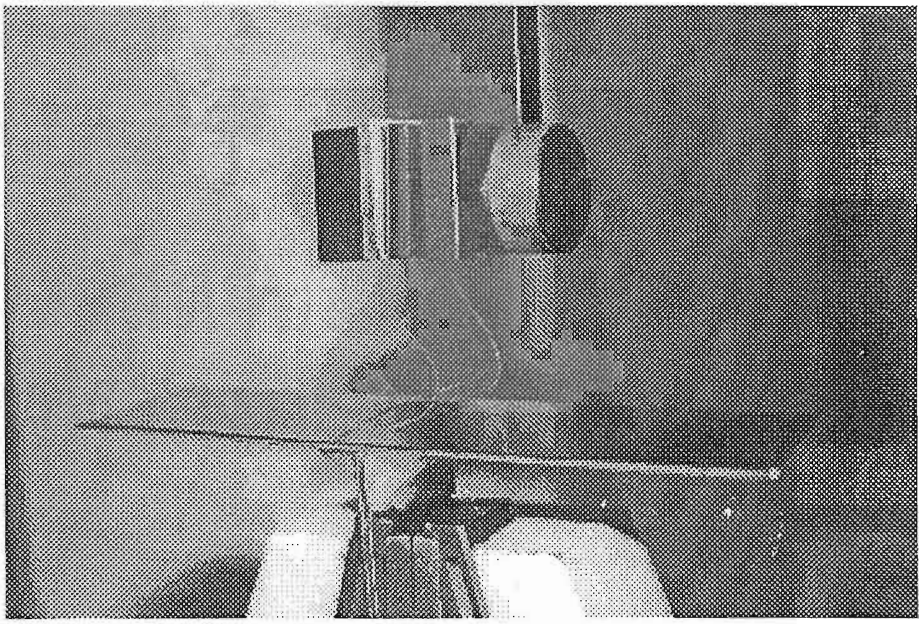


Figure 4.4.2. Loop tack test.

4.4.3 Holding time [PSTC,1997].

This test was performed according to PSTC-7 with a stainless surface. The first step was to apply a weight to the end of the tape which was attached to a given surface. The contact area between the adhesive and the glass was 1x1 inch. An applied load 1 kg was used. Then, measure the time when the tape was removed from the given surface.

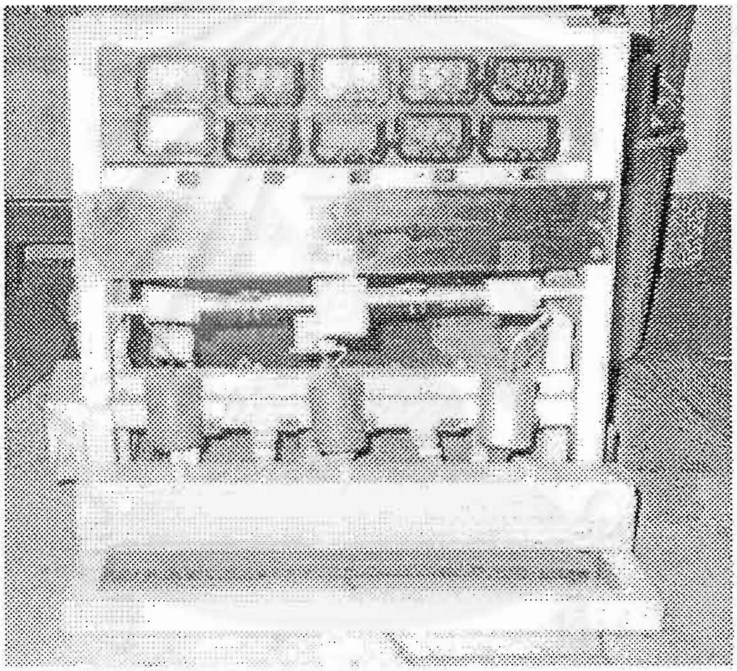


Figure 4.4.4 Holding time test.

4.5 Experimental Design

The designed formulation of PSA with selected additives in the present study was based on the percentage by latex weight. Latex depolymerization time was measured in hour. Central Composite Design (CCD) experiment was used to vary, the following four factor variables:

1. Latex depolymerization time (1 to 5 hours).
2. Amount of Rosin ester (2 to 66 phr).
3. Amount of SE376A (2 to 66 phr).
4. Amount of SE790G (2 to 66 phr).

The quantity of above factors were varied at five levels. In the CCD, the codes of -2, -1, 0, +1, +2 were assigned. The formulation of PSA is shown in AppendixB.

CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the results and discussion are divided into two major parts namely the latex depolymerization and properties analysis of PSA. The CCD experiment is applied to analyze the effect of indepent variables on properties of PSA.

5.1 Analysis of Latex

5.1.1 Latex Depolymerization

The relationship between the intrinsic viscosity of depolymerized latex and reaction time is shown in Figure 5.1.1.

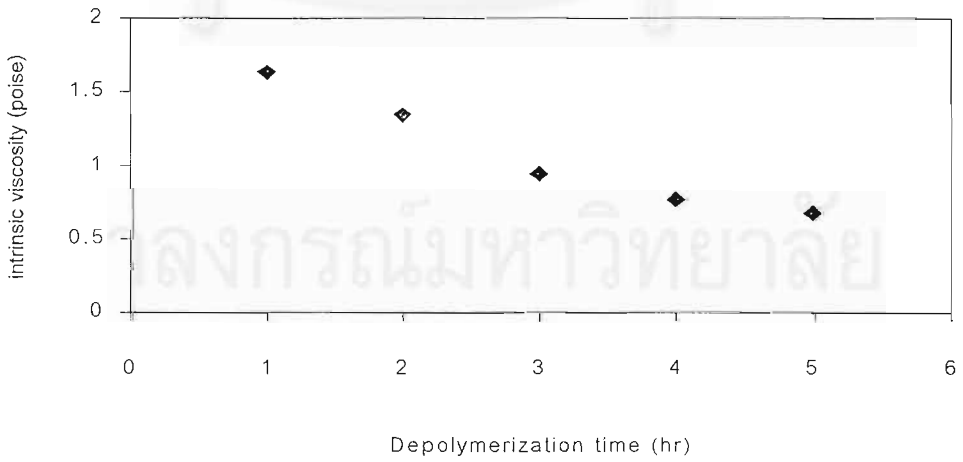


Figure 5.1.1. Relationship between intrinsic viscosity and reaction time.

Figure 5.1.1. shows that the intrinsic viscosity of depolymerized HA-latex 1 phr of $K_2S_2O_8$ and 15 phr of propanol at 60°C decreases from 1.631 to 0.676 poise. as reaction time increases from 1 to 5 hours.

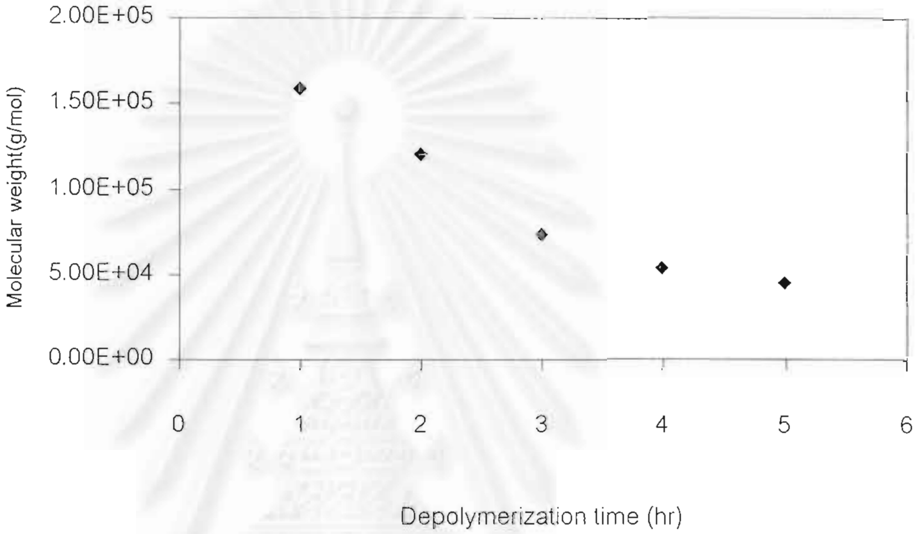


Figure 5.1.2 The relation between molecular weight and reaction time.

The viscosity-average molecular weight, (M_v) of depolymerized latexes are estimated from Mark-Houwink equation by using the Mark-Houwink constants K of 33.1 x 10^{-5} and a of 0.71. Figure 5.1.2 illustrates the relationship between the molecular weight and reaction time. The molecular weight decreases from 1.58 x 10^5 to 0.46 x 10^5 g/mol as the increasing in reaction time.

5.1.2 Particle Size Diameter of Latex.

Figure 5.1.3 to 5.1.8 show the particle-size distribution of the depolymerized latex at 0 to 5 hours. Table 5.1.1 shows the list of Means particle-size diameter of depolymerized latex at various of latex depolymerization time. The Mode of particle-size diameters of depolymerized latex are 0.829 μm. The Median particle-size diameters of depolymerized latex range from 0.906 to 0.962 μm. Some depolymerized latex has larger particle size diameters. This might be the result of adding $K_2S_2O_8$ or propanol rapidly, and these additives have affected the coagulation of the latex. According to Blackley the propanol (a water-miscible organic solvent) is one of chemical destabilizing agents [Blackley,1966]. The coagulated latex shifts the Mean of diameter particle-size. Therefore, the Mean of diameter particle-size is not used in this analysis. The Median particle-size diameter is the best-estimated value to demonstrate the average particle-size diameter of the experiment. The distribution, mode, and Median of particle-size diameter of depolymerized latex are almost the same before depolymerization. This suggests that rubber particles are not broken during the depolymerization.

Table 5.1.1. List of diameter particle-size of depolymerized latex.

Depolymerization time (Hour)	Median diameter (micrometer,μm)	Mode diameter (micrometer,μm)
0	0.645	0.688
1	0.906	0.829
2	0.928	0.829
3	0.943	0.829
4	0.962	0.829
5	0.940	0.829

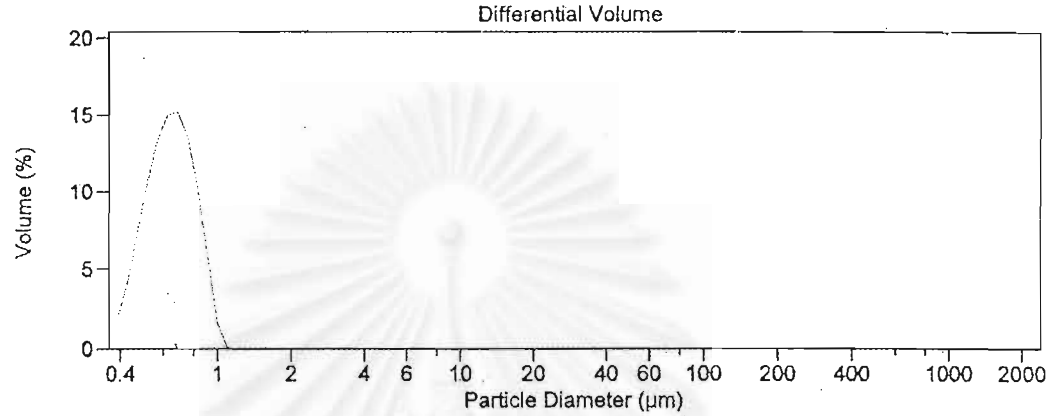


Figure 5.1.3 Particle-size diameter of HA latex

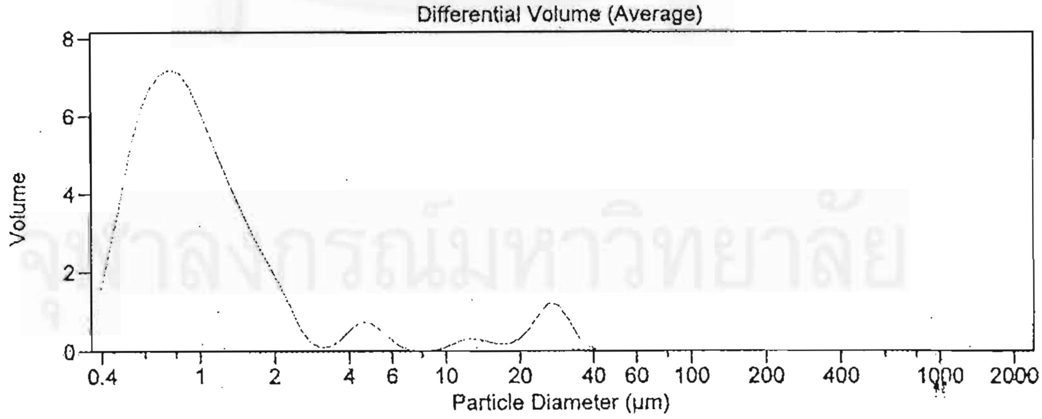


Figure 5.1.4. Particle-size diameter of 1-hour-depolymerized latex

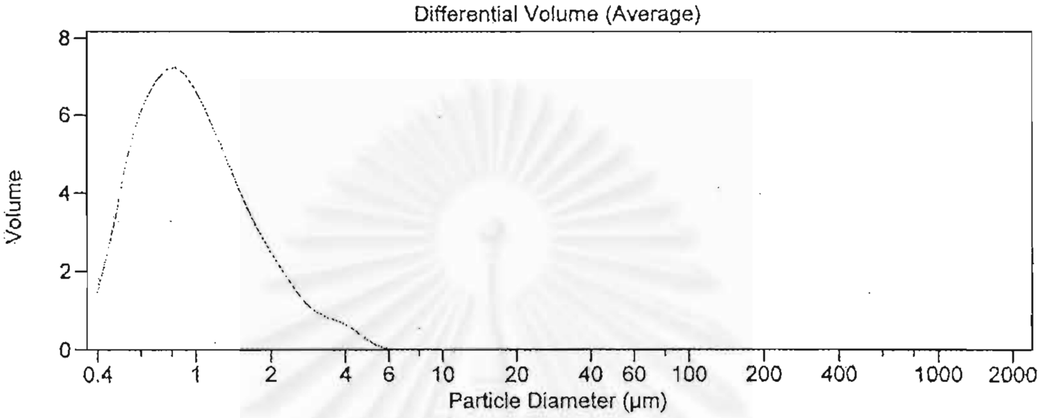


Figure 5.1.5 Particle-size diameter of 2-hour-depolymerized latex

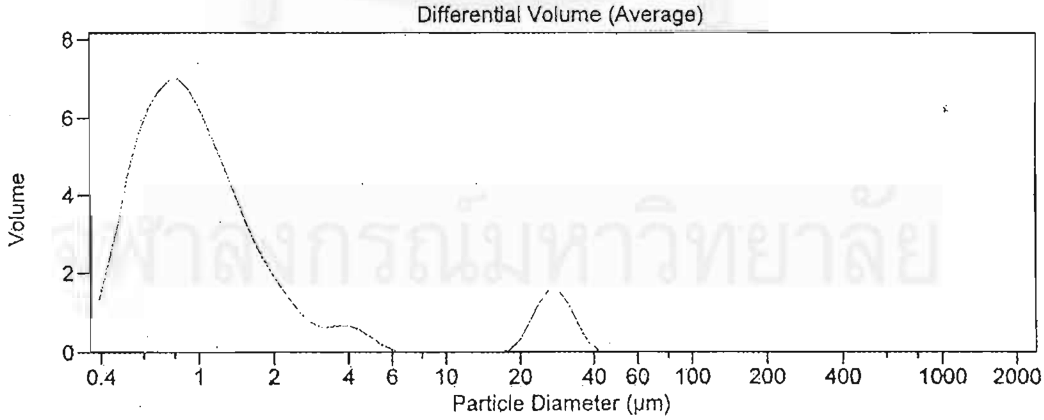


Figure 5.1.6. Particle-size diameter of 3-hour-depolymerized latex

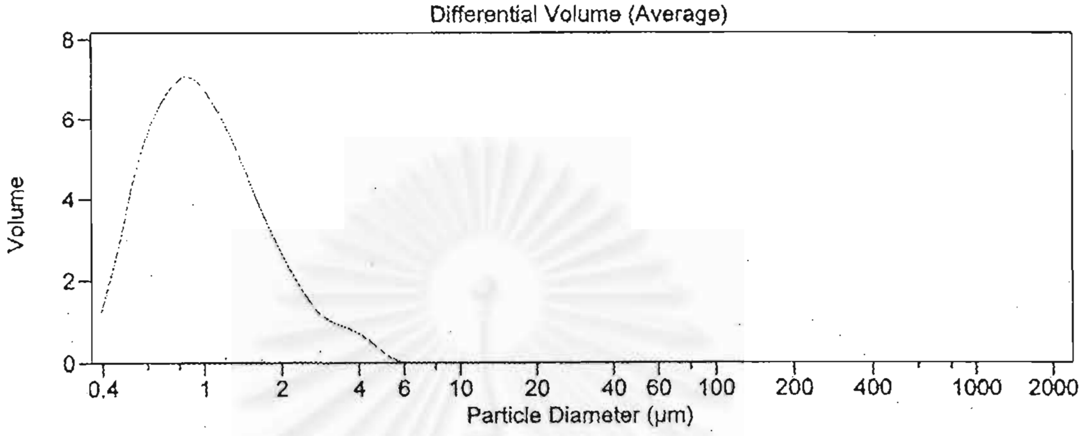


Figure 5.1.7. Particle-size diameter of 4-hour-depolymerized latex

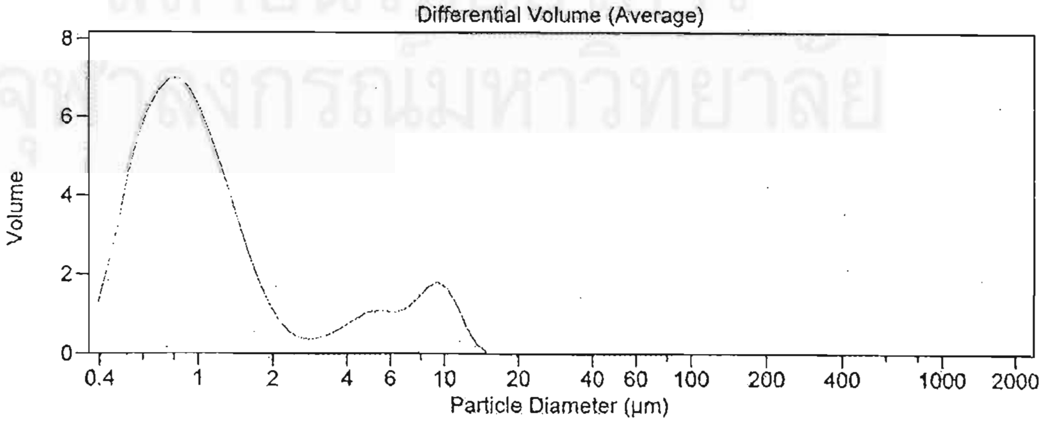


Figure 5.1.8. Particle-size diameter of 5-hour-depolymerized latex

5.1.3 The Raman Spectrum of Depolymerized Latex.

The Raman spectrum in the proper wavenumber of 0-4000 cm^{-1} is used to identify the functional group of polyisoprene or natural rubber. (In this work, the qualitative analysis is only concerned.) The results are shown in Figure 5.1.9. - Figure 5.3.14. All Raman spectrums of depolymerized latex have a few differences from normal HA-latex. The spectrum shows the functional group of polyisoprene, which are C=C, C-C , C-H, CH_2 ,and CH_3. The strong intensity bands at 1600 cm^{-1}, 2900 cm^{-1} and 200 cm^{-1} have been observed. These wavenumbers indicate the present of C=C, C-H, and C-C functional group respectively. The Raman experiment does not show C=O functional group because the C=O peak overlaps the C=C peak. So, it can be concluded that the depolymerization reaction time at 1 to 5 hours affects only on molecular weight with minimal change in the chemical bond of the latex.

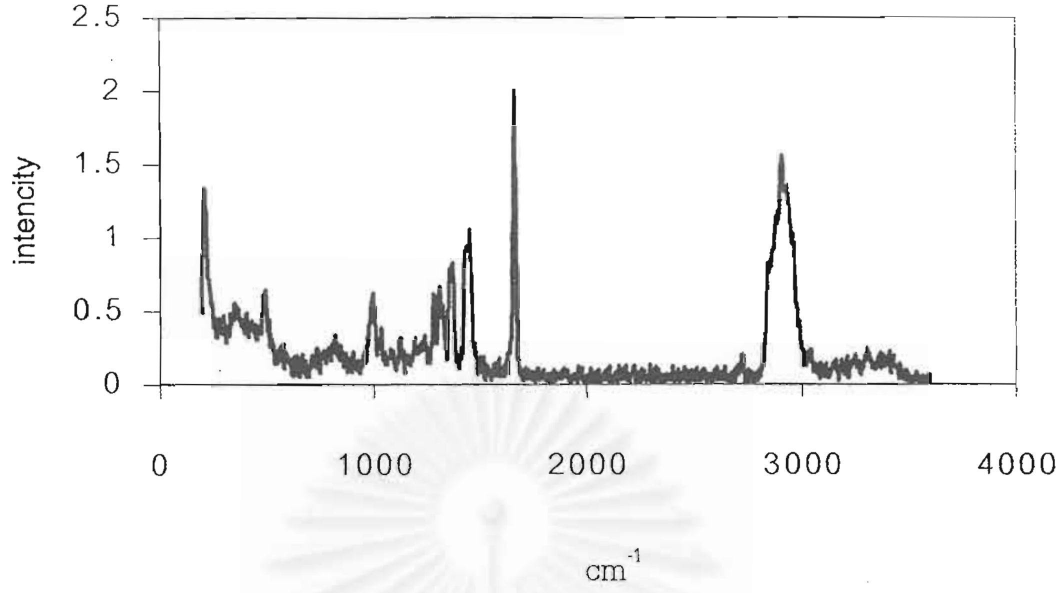


Figure 5.1.9 Raman spectrum of HA latex

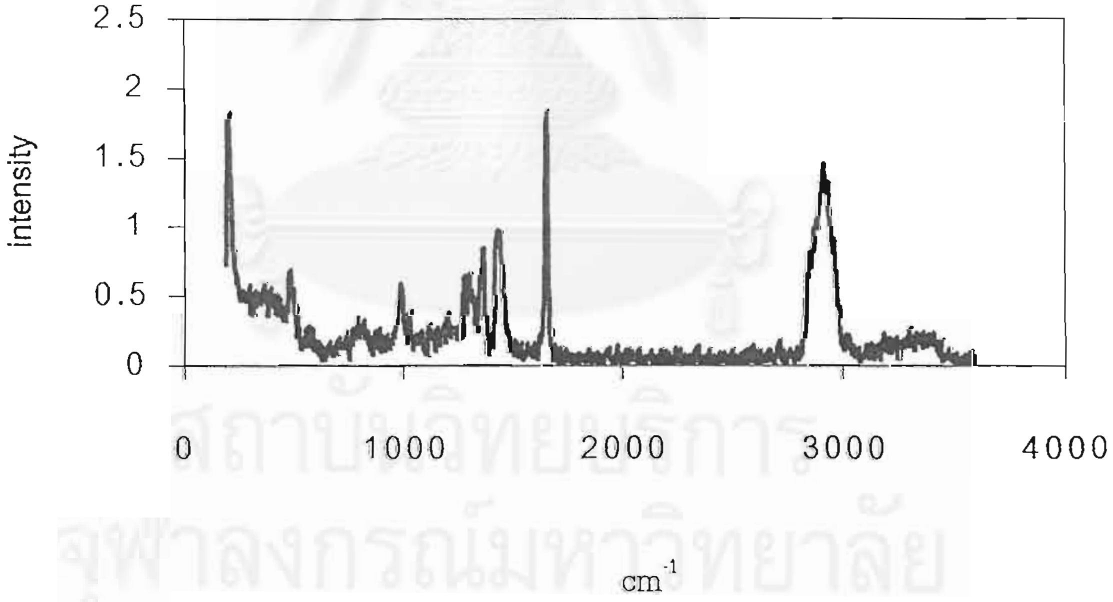


Figure 5.1.10 Raman spectrum of 1-hour-depolymerized HA-latex

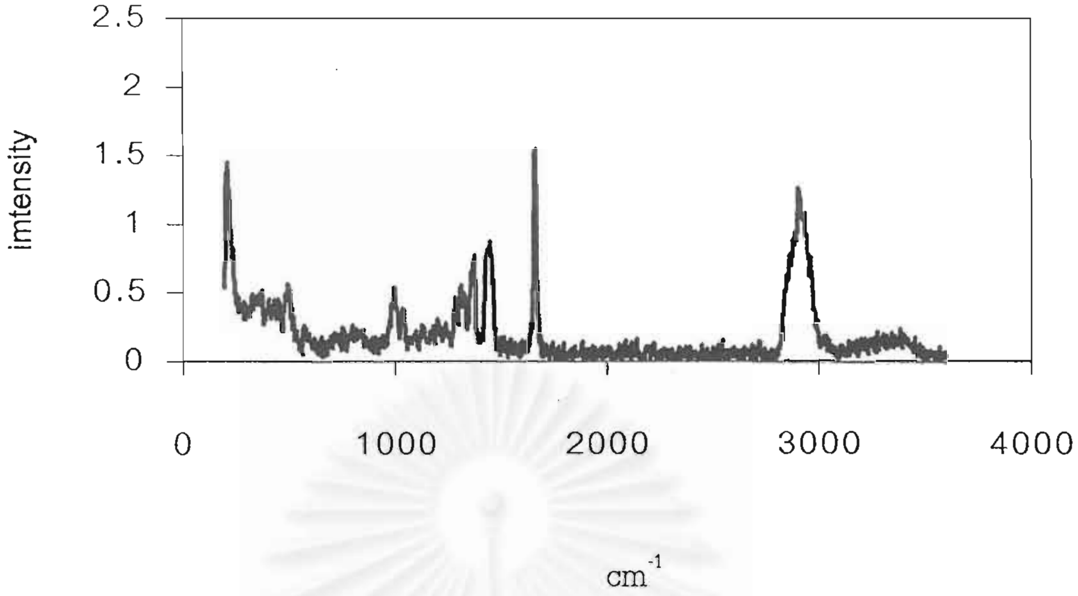


Figure 5.1.11 Raman spectrum of 2-hour-depolymerized HA-latex

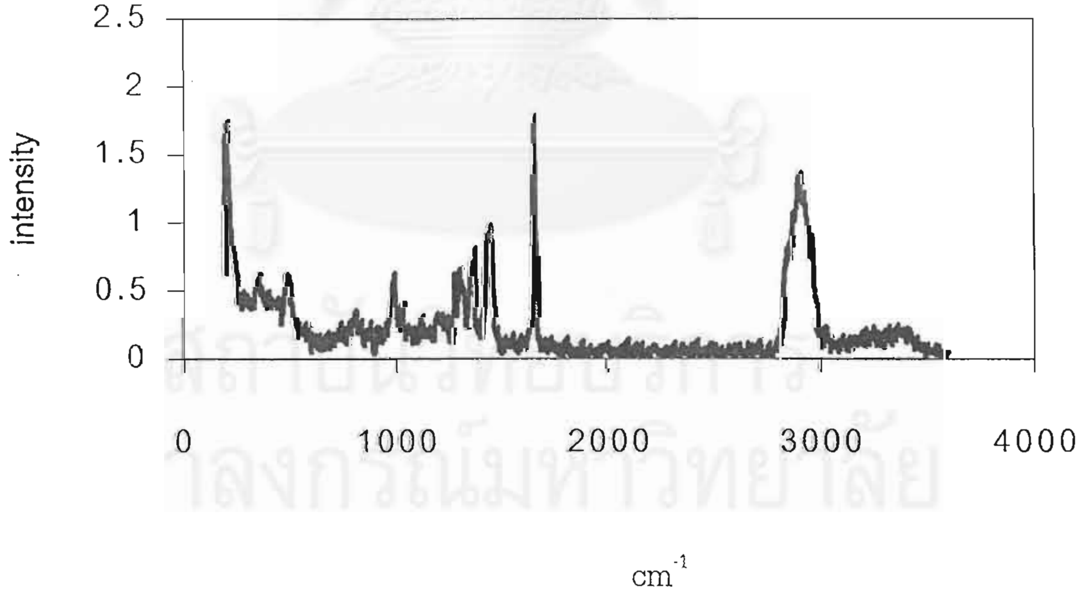


Figure 5.1.12 Raman spectrum of 3-hour-depolymerized HA-latex

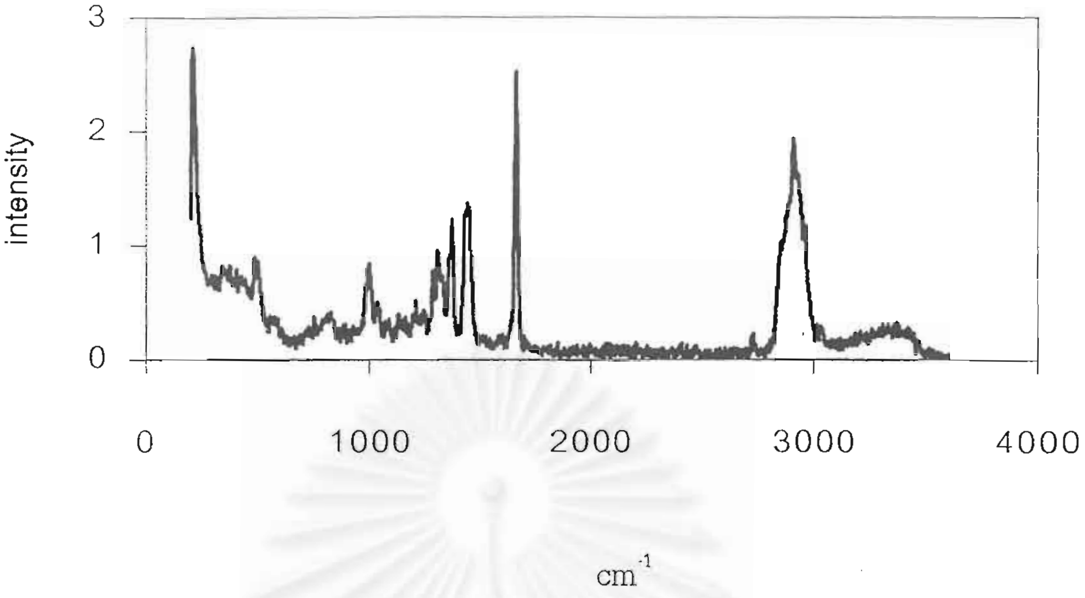


Figure 5.1.13 Raman spectrum of 4-hour-depolymerized HA-latex

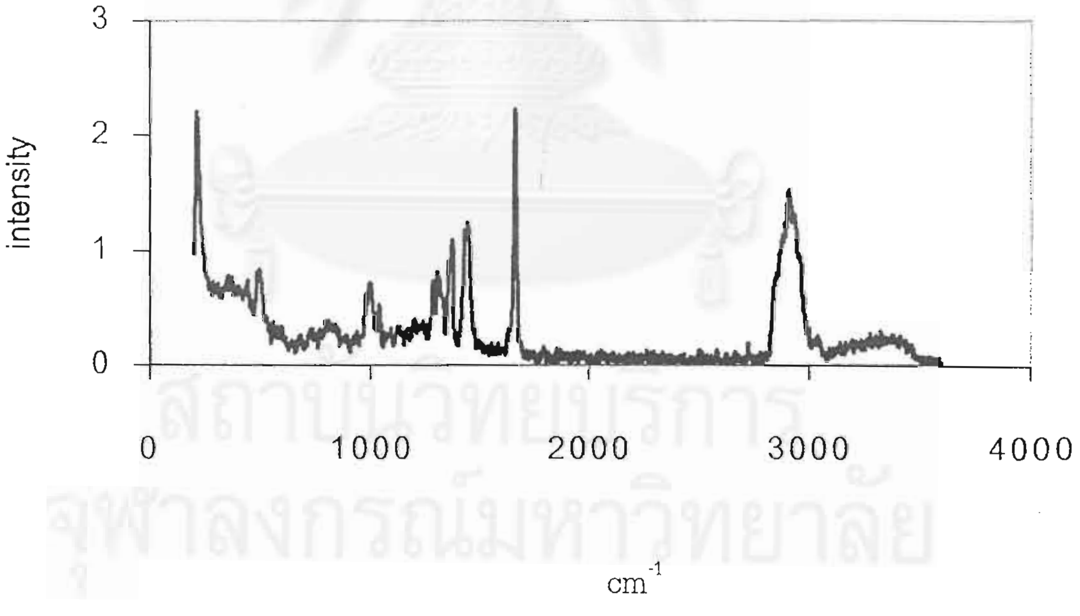


Figure 5.1.14 Raman spectrum of 5-hour-depolymerized HA-latex

Mechanism of the depolymerized latex, in the presence of $K_2S_2O_8$ and propanol, is shown in Figure 5.1.15. The rubber chain is oxidized by a radical initiator at double bond as shown in Step (1). It gives the most likely possible structure as shown in Step (2). The added propanol is expected to react partly with the reactive aldehydic carbon to give the most stable oxidation degraded product as shown in Step (3).[Tangpakdee,1998] As the result of Raman spectoscopy, this depolymerization reaction does not change the main structure of latex. It does not break the particle size of latex during the reaction (Further details in Particle-size Analysis).

From the experiments, molecular weight is reduced faster at initial stage and will be slower when the depolymerization time increases.

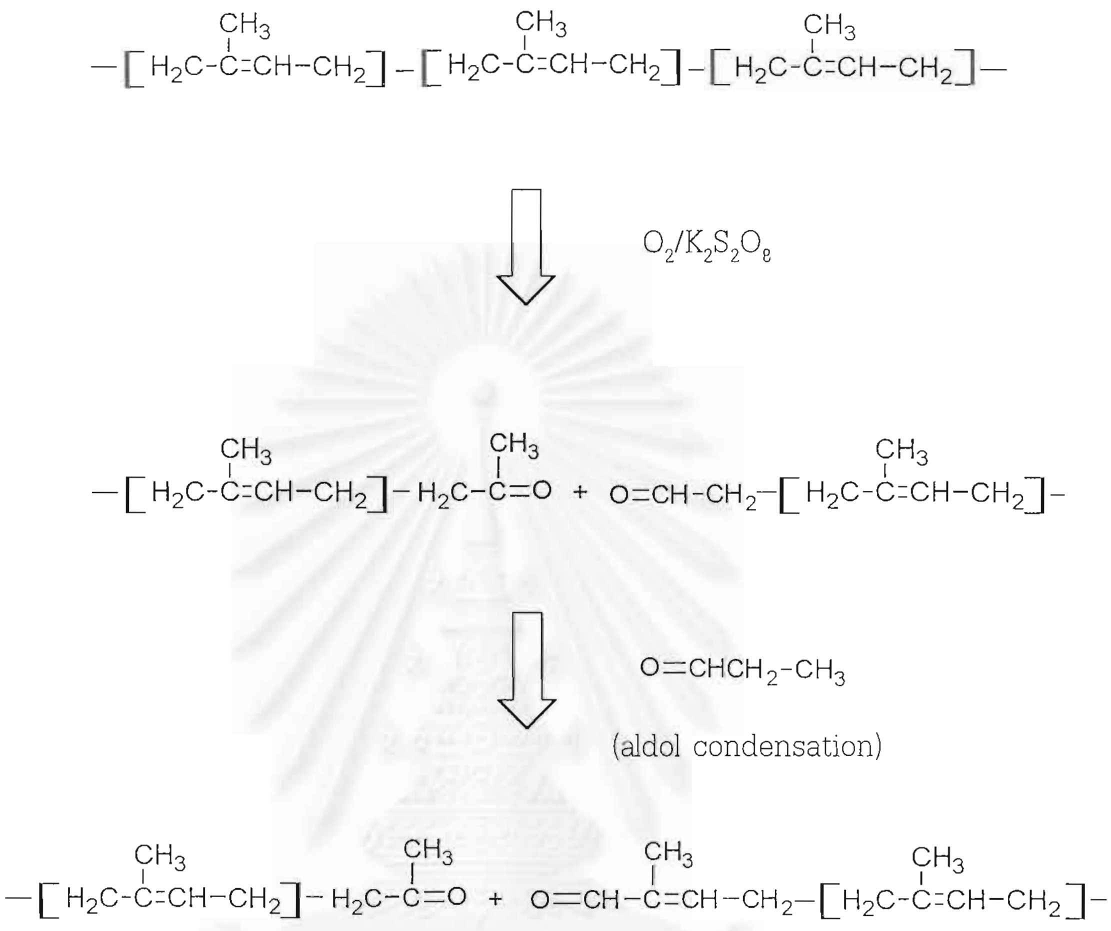


Figure 5.1.15. Presumed mechanism of oxidative degraded reaction of HA-latex. [Tangpakdee,1998]

5.2 Analysis of PSA properties

5.2.1. Regression Analysis

From the results of all properties tested of PSA, empirical models can be derived to reveal the relationship between physical properties, time of latex depolymerization, and the various amount of the selected additives. Variable codes are used to represent the time of latex depolymerization, and the quantity of the additives applied in the present study. Empirical models in term of the response surface equations are derived. All of physical properties of PSA, 180°peel adhesion, tack and holding time are shown in Table 5.2.1. The data can be analysed using multiple regression analysis to estimate the corresponding regression coefficient of the regression analysis which are depicted in Appendix C. The response surface equation of 180° peel adhesion, tack and holding time of PSA are shown in Equation (5-1), (5-2), and (5-3)

$$\begin{aligned} y_{180\ \text{peel adhesion}} = {} & 3.043 + 0.05x_1 + 0.458x_2 + 0.629x_3 + 0.692x_4 - 0.081x_1x_2 \\ & - 0.025x_1x_3 + 0.131x_1x_4 - 0.1x_2x_3 - 0.319x_2x_4 + 0.212x_3x_4 \\ & + 0.049x_1^2 + 0.049x_2^2 + 0.199x_3^2 + 0.286x_4^2 \end{aligned} \quad (5\text{-}1)$$

$$\begin{aligned} y_{\text{tack}} = {} & 3.519 + 0.012x_1 - 0.818x_2 + 0.878x_3 + 1.033x_4 + 0.180x_1x_2 \\ & - 0.133x_1x_3 - 0.161x_1x_4 - 0.395x_2x_3 - 0.293x_2x_4 + 0.389x_3x_4 \\ & - 0.135x_1^2 - 0.161x_2^2 + 0.125x_3^2 + 0.193x_4^2 \end{aligned} \quad (5\text{-}2)$$

$$\begin{aligned} y_{\text{holding time}} = {} & 110.43 - 25.79x_1 + 31.84x_2 - 30.57x_3 - 24.94x_4 + 1.818x_1x_2 \\ & + 13.98x_1x_3 - 6.546x_1x_4 - 16.82x_2x_3 + 20.13x_2x_4 - 4.286x_3x_4 \\ & + 9.275x_1^2 - 4.547x_2^2 + 6.161x_3^2 - 8.256x_4^2 \end{aligned} \quad (5\text{-}3)$$

The aforementioned variable codes: x_1, x_2, x_3, and x_4 represent time of latex depolymerization, quantity of rosin ester, SE376A, and SE790G respectively. Table 5.2.2 shows the regression coefficients derived from the regression analysis of various properties investigated of PSA and the variable code of time of latex depolymerization and additives quantity. Tables 5.2.3 to 5.2.5 demonstrate the error between the 180°peel adhesion, tack, and holding time, which is derived from the actual experiments and estimated by calculations.

Table 5.2.1 Result of all physical properties of PSA.

Experiment Number	Codified factors				Response		
	x_1	x_2	x_3	x_4	180° peel adhesion(N/in)	Tack (N/in^2)	holding time (min)
1	-	-	-	-	1.55	1.556	186.67
2	+	-	-	-	2.40	3.310	111.00
3	-	+	-	-	3.80	2.290	220.00
4	+	+	-	-	3.20	1.687	190.00
5	-	-	+	-	3.45	5.137	135.67
6	+	-	+	-	2.70	3.281	90.67
7	-	+	+	-	4.00	1.354	85.75
8	+	+	+	-	4.35	3.411	140.33
9	-	-	-	+	3.65	5.147	68.00
10	+	-	-	+	3.60	3.218	45.00
11	-	+	-	+	3.40	1.812	270.00
12	+	+	-	+	4.30	3.713	138.33
13	-	-	+	+	4.80	7.385	24.33
14	+	-	+	+	6.30	8.038	5.00
15	-	+	+	+	5.60	5.446	97.50
16	+	+	+	+	5.20	3.587	20.67

Table 5.2.1 Result of all physical properties of PSA.(continue)

Experiment number	Codified factors				Response		
	x_1	x_2	x_3	x_4	180° peel adhesion(N/in)	Tack (N/in^2)	Holding time (min)
17	-2	0	0	0	2.58	2.472	219.33
18	2	0	0	0	2.55	2.563	58.25
19	0	-2	0	0	1.30	3.882	29.00
20	0	2	0	0	4.10	0.946	138.00
21	0	0	-2	0	2.15	2.014	165.00
22	0	0	2	0	4.45	5.096	87.67
23	0	0	0	-2	2.35	1.709	108.00
24	0	0	0	2	4.95	5.951	29.33
25	0	0	0	0	3.10	3.506	95.00
26	0	0	0	0	3.05	3.531	118.00
27	0	0	0	0	2.95	3.536	120.00
28	0	0	0	0	3.14	3.503	110.00
29	0	0	0	0	3.05	3.540	115.00
30	0	0	0	0	3.05	3.479	105.00
31	0	0	0	0	2.95	3.540	110.00

Table 5.2.2 Coefficients derived from the multiple regression analysis for the physical properties of PSA.

Equation : $y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{44}x_4^2$

Where : y = Property

x_1 = Code of time of latex depolymerization

x_2 = Code of Rosin ester

x_3 = Code of SE790G

x_4 = Code of SE790G

b = Regression coefficients

y	b_0	b_1	b_2	b_3	b_4	b_{12}	b_{13}	b_{14}	b_{23}	b_{24}	b_{34}	b_{11}	b_{22}	b_{33}	b_{44}
Physical properties of PSA															
180°peel adhesion (N/in)	3.0428	0.0500	0.4583	0.6291	0.6917	-0.0812	-0.0250	0.1312	-0.1000	-0.3188	0.2125	0.0487	0.0487	0.1987	0.2861
Tack (N/in^2)	3.5193	0.0125	-0.8185	0.8779	1.0335	0.1796	-0.1330	-0.1616	-0.3946	-0.2930	0.3891	-0.1347	-0.1606	0.1246	0.1934
Holding time (min)	110.43	-25.79	31.84	-30.57	-24.94	1.8175	13.99	-6.55	-16.82	20.13	-4.29	9.28	-4.55	6.16	-8.26

Table 5.2.3. Experiment and calculated error of 180^0 peel adhesion of PSA

Exp. No.	180^{o}peel adhesion(N/inch)		Error	%error
	Experiment	Calculation		
1	1.550	1.614	-0.0643	4.15
2	2.400	1.664	0.7357	30.65
3	3.800	3.531	0.2691	7.08
4	3.200	3.256	-0.0561	1.75
5	3.450	2.698	0.7525	21.81
6	2.700	2.648	0.0525	1.94
7	4.000	4.214	-0.2141	5.35
8	4.350	3.839	0.5107	11.74
9	3.650	2.948	0.7021	19.24
10	3.600	3.523	0.0773	2.15
11	3.400	3.589	-0.1893	5.57
12	4.300	3.839	0.4607	10.71
13	4.800	4.881	-0.0811	1.69
14	6.300	5.356	0.9441	14.99
15	5.600	5.123	0.4775	8.53
16	5.200	5.273	-0.0725	1.39

Table 5.2.3. Experiment and calculated error of 180^0 peel adhesion of PSA (continued)

Exp. No.	180°peel adhesion(N/inch)		error	%error
	Experiment	Calculation		
17	2.850	3.137	-0.2873	10.08
18	2.550	3.337	-0.7873	30.87
19	1.300	2.321	-1.0207	78.52
20	4.100	4.154	-0.0539	1.31
21	2.150	2.579	-0.4291	19.96
22	4.450	5.096	-0.6455	14.51
23	2.350	2.804	-0.4535	19.30
24	4.950	5.570	-0.6203	12.53
25	3.100	3.043	0.0575	1.85
26	3.050	3.043	0.0075	0.25
27	2.950	3.043	-0.0925	3.14
28	3.150	3.043	0.1075	3.41
29	3.050	3.043	0.0075	0.25
30	3.050	3.043	0.0075	0.25
31	2.950	3.043	-0.0925	3.14

Table 5.2.4. Experiment and calculated error of tack of PSA.

Exp. No.	Tack(N/in^2)		Error	%error
	Experiment	Calculation		
1	1.556	2.098	-0.542	34.826
2	3.310	2.203	1.107	33.447
3	2.290	1.160	1.130	49.332
4	1.687	1.884	-0.197	11.66
5	5.137	4.031	1.106	21.536
6	3.281	3.754	-0.473	14.407
7	1.354	1.765	-0.411	30.332
8	3.411	2.106	1.305	38.256
9	5.147	4.229	0.918	17.83
10	3.218	3.938	-0.720	22.371
11	1.812	2.270	-0.458	25.259
12	3.713	2.597	1.116	30.065
13	7.385	7.619	-0.233	3.1618
14	8.038	6.945	1.093	13.597
15	5.446	4.331	1.116	20.483
16	3.587	4.276	-0.689	19.194

Table 5.2.4. Experiment and calculated error of tack of PSA.(continued)

Exp. No.	Tack(N/in^2)		error	%error
	Experiment	Calculation		
17	2.472	2.889	-0.417	16.857
18	2.563	2.939	-0.376	14.659
19	3.882	4.514	-0.632	16.273
20	0.946	0.907	0.040	4.1755
21	2.014	2.145	-0.131	6.5094
22	5.096	5.757	-0.661	12.965
23	1.709	2.076	-0.367	21.457
24	5.951	6.377	-0.426	7.1501
25	3.506	3.519	-0.013	0.3793
26	3.531	3.519	0.012	0.3314
27	3.536	3.519	0.017	0.4723
28	3.503	3.519	-0.016	0.4653
29	3.540	3.519	0.021	0.5847
30	3.479	3.519	-0.040	1.1584
31	3.540	3.519	0.021	0.5847

Table 5.2.5. Experiment and calculated error of holding time of PSA.

Exp. No.	Holding time(min)		error	%error
	Experiment	Calculation		
1	186.67	170.81	15.86	8.50
2	111.00	100.72	10.28	9.27
3	220.00	224.23	-4.23	1.92
4	190.00	161.41	28.59	15.05
5	135.67	123.90	11.77	8.68
6	90.67	109.75	-19.08	21.04
7	85.75	110.05	-24.30	28.34
8	140.33	103.17	37.16	26.48
9	68.00	102.33	-34.33	50.48
10	45.00	6.05	38.95	86.56
11	270.00	236.28	33.72	12.49
12	138.33	147.27	-8.94	6.46
13	24.33	38.27	-13.94	57.31
14	5.00	-2.06	7.06	141.27
15	97.50	104.95	-7.45	7.64
16	70.67	71.89	-1.22	1.72

Table 5.2.5. Experiment and calculated error of holding time of PSA.(continued)

Exp. No.	Holding time(min)		error	%error
	Experiment	Calculation		
17	219.33	199.11	20.22	9.22
18	58.25	95.95	-37.70	64.72
19	29.00	28.55	0.45	1.54
20	138.00	155.93	-17.93	12.99
21	165.00	196.22	-31.22	18.92
22	87.67	73.93	13.74	15.67
23	108.00	127.29	-19.29	17.86
24	29.33	27.52	1.81	6.16
25	95.00	110.43	-15.43	16.24
26	118.00	110.43	7.57	6.42
27	120.00	110.43	9.57	7.98
28	110.00	110.43	-0.43	0.39
29	115.00	110.43	4.57	3.97
30	105.00	110.43	-5.43	5.17
31	110.00	110.43	-0.43	0.39

5.2.2 Analysis of Variance (ANOVA)

Regression coefficients depict all of physical properties of PSA by regression analysis. The appropriate test of the response surface equations from the designed experiment are carried out by variance analysis of the data from all experiments. Analysis of variance of 180° peel adhesion, tack and holding time are shown in Table 5.2.6 to 5.2.8. Statistic t_o test of coefficients of 180° peel adhesion, tack and holding time are shown in Table 5.2.9 to 5.2.11.The details of the calculation are summarized in AppendixC.

From the ANOVA table demonstrated in Table 5.2.6, it is found that the F_o of 180° peel adhesion is 5.879 compared with the critical F-distribution at the level of significance at 0.025 (degree of confidence is 97.5%) $F_{0.025,14,16}$ is 2.185. It appears that F_o is greater than $F_{0.025,14,16}$, hence the hypothesis of $H_o : b_1 = b_2 = ... = b_k = 0$ is rejected. This experiment shows that there is at least one variable among latex depolymerization time (phr of Rosin ester, phr of SE376G, and phr of SE790A.) which is influential on 180° peel adhesion of PSA. The coefficient of determination, R^2, is 0.835. It means that the relationship between the overall variance of 180° peel adhesion caused by the variation of the latex depolymerization time (phr of rosin ester, phr of SE376G, and phr of SE790A) which is 83.5%.

From Table 5.2.7, it is found that the F_o of tack is 6.294 when compared with the critical F-distribution at the level of significance at 0.1 (degree of confidence is 97.5%) $F_{0.025,14,16}$ is 2.185. It shows that one of variables is influential on Tack. The coefficient of determination, R^2, is to 0.847. It means that the relationship between the overall variance of Tack caused by the variation of the latex depolymerization time, phr of rosin ester, phr of SE376G, and phr of SE790A which is to 84.7%.

From Table 5.2.8, it is found that the F_o of holding time is 9.414 when compared with the critical F-distribution at the level of significance at 0.025 (degree of confidence is 97.5%) $F_{0.025,14,16}$ is 2.815. It shows that one of variables is influential on holding time. The coefficient of determination, R^2, is 0.892. It means that the relationship between the overall variance of holding time caused by the variation of the latex depolymeriation time, phr of rosin ester, phr of SE376G, and phr of SE790A which is 89.2%

The statistical t_o of the regression coefficients of the multiple regression equation for all physical properties are shown in table 5.2.9 to 5.2.11. The calculation method is shown in Appendix C. For example, in the case of 180° peel adhesion when compared with the statistical t_o of each coefficient and the critical t-distribution at the level of significant at 0.05 from Appendix D, the $t_{0.05,16}$ is 1.740. It appears that the statistical t_o of the regression coefficient testing is greater than the critical t-distribution at $t_{0.05,16}$. This experiment can imply that the regression coefficients from the test is significant to the response surface equation. Then, if the statistical t_o of any regression coefficients is less than $t_{0.05,16}$, the particular regression coefficient is not significant to the response surface equation. It can be deleted from the equation as shown in Table 5.2.9 to 5.2.11. Therefore, the response surface equation of 180° peel adhesion, tack, and holding time from Equation (5-1), (5-2), and (5-3) can be rewritten as follows

$$y_{180^\circ \text{peel adheion}} = 3.043 + 0.458x_2 + 0.629x_3 + 0.691x_4 - 0.286x_4^2 - 0.319x_2x_4 \quad (5\text{-}4)$$

$$y_{\text{tack}} = 3.519 - 0.878x_2 + 0.878x_3 + 1.034x_4 - 0.395x_2x_3 \quad (5\text{-}5)$$

$$y_{\text{holding time}} = 110.429 - 25.79x_1 + 31.84x_2 - 30.57x_3 - 24.94x_4$$

$$- 16.82x_2x_3 + 20.13x_2x_4 \quad (5\text{-}6)$$

Table 5.2.6 ANOVA table for the multiple regression analysis of the interaction of latex depolymerization time, phr of Rosin ester, phr of SE376G, and phr of SE790A on the 180° peel adhesion.

Source of Variation	Sum of square	Degree of freedom	Mean Square	F_o
Regression	***32.59***	***14***	***2.328***	5.879
- First order terms	26.084	4	6.521	16.467
-Second order terms	6.506	10	0.651	1.644
Error	***6.345***	***16***	***0.396***	
-Lack of fit	6.313	10	0.631	
-Pure error	0.032	6	0.005	
Total	***38.935***	***30***	$R^2 = 0.835$	

Table 5.2.7 ANOVA table for the multiple regression analysis of the interaction of latex depolymerization time, phr of Rosin ester, phr of SE376G, and phr of SE790A on Tack.

Source of Variation	Sum of square	Degree of freedom	Mean Square	F_o
Regression	***70.50***	***14***	***5.035***	6.294
- First order terms	60.22	4	15.05	18.812
-Second order terms	10.28	10	1.03	1.28
Error	***12.793***	***16***	***0.80***	
-Lack of fit	12.790	10	1.28	
-Pure error	0.003	6	0.0005	
Total	***82.84***	***30***	$R^2 = 0.847$	

Table 5.2.8 ANOVA table for the multiple regression analysis of the interaction of latex depolymerization time, phr of Rosin ester, phr of SE376G, and phr of SE790A on Holding time.

Source of Variation	Sum of square	Degree of freedom	Mean Square	F_o
Regression	***98924.881***	***14***	***7066.063***	9.414
- First order terms	77667.466	4	19416.862	25.870
-Second order terms	21257.415	10	2125.742	2.832
Error	***12008.98***	***16***	***750.56***	
-Lack of fit	11571.27	10	1157.13	
-Pure error	437.71	6	72.95	
Total	***110933.86***	***30***	$R^2 = 0.892$	

Table 5.2.9 Statistic t_o test of coefficients testing for interactions of latex depolymerization time, phr of Rosin ester, phr of SE376G, and phr of SE790A on 180° peel adhesion at the level of significance of 0.10

Regression Coefficient		t_o	Hypothesis test ($t_{0.05,18}$=1.740)
b_o	3.043	12.79	Significance
b_1	0.050	0.39	No significance
b_2	0.458	3.57	Significance
b_3	0.629	4.89	Significance
b_4	0.691	5.38	Significance
b_{11}	-0.049	0.41	No significance
b_{22}	0.049	0.41	No significance
b_{33}	0.198	1.69	No significance
b_{44}	0.286	2.43	Significance
b_{12}	-0.081	-0.52	No significance
b_{13}	-0.025	-0.16	No significance
b_{14}	0.131	0.83	No significance
b_{23}	-0.100	-0.64	No significance
b_{24}	-0.319	-2.02	Significance
b_{34}	0.212	1.35	No significance

Table 5.2.10 Statistic t_o test of coefficients testing for interactions of latex depolymerization time, phr of Rosin ester, phr of SE376G, and phr of SE790A on tack at the level of significance of 0.10

Regression Coefficient		t_o	Hypothesis test ($t_{o(0.05,16)}$=1.746)
b_o	3.519	10.41	Significance
b_1	0.012	0.07	No significance
b_2	-0.818	-4.48	Significance
b_3	0.878	4.81	Significance
b_4	1.034	5.66	Significance
b_{11}	-0.135	-0.81	No significance
b_{22}	-0.161	-0.96	No significance
b_{33}	0.125	0.75	No significance
b_{44}	0.193	0.16	No significance
b_{12}	0.180	0.80	No significance
b_{13}	-0.133	-0.59	No significance
b_{14}	-0.162	-0.72	No significance
b_{23}	-0.395	-1.77	Significance
b_{24}	-0.293	-1.31	No significance
b_{34}	0.389	1.74	No significance

Table 5.2.11 Statistic t_o test of coefficients testing for interactions of latex depolymerization time, phr of Rosin ester, phr of SE376G, and phr of SE790A on Holding time at the level of significance of 0.050

Regression Coefficient		t_o	Hypothesis test ($t_{c(0.025,16)}$=2.120)
b_o	110.429	10.67	Significance
b_1	-25.79	-4.61	Significance
b_2	31.8433	5.69	Significance
b_3	-30.572	-5.47	Significance
b_4	-24.942	-4.46	Significance
b_{11}	9.275	1.81	No significance
b_{22}	-4.547	-0.89	No significance
b_{33}	6.162	1.20	No significance
b_{44}	-8.256	-1.61	No significance
b_{12}	1.818	0.27	No significance
b_{13}	13.985	2.04	No significance
b_{14}	-6.546	-0.96	No significance
b_{23}	-16.818	-2.46	Significance
b_{24}	20.131	2.94	Significance
b_{34}	-4.286	-0.63	No significance

From the regression coefficient test with statistical t_o, the response surface equation can be derived to show the relationship between the physical properties of PSA and the variable code of latex depolymerization time, phr of Rosin ester, phr of SE376G and phr of SE790A as shown in Table 5.2.12.

Table 5.2.12 Coefficients derived from the multiple regression analysis using t-distribution analysis for the physical properties of PSA.

Equation : $y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4 + b_{34}x_3x_4 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{44}x_4^2$

Where : y = Property

x_1 = Code of latex depolymerization time

x_2 = Code of Rosin ester

x_3 = Code of SE790G

x_4 = Code of SE790G

b = Regression coefficients

y	b_0	b_1	b_2	b_3	b_4	b_{12}	b_{13}	b_{14}	b_{23}	b_{24}	b_{34}	b_{11}	b_{22}	b_{33}	b_{44}
Physical properties of PSA															
180° peel adhesion (N/in)	3.0428		0.4583	0.6291	0.6917					-0.3188					0.2861
Tack (N/in^2)	3.5193		-0.8185	0.8779	1.0335				-0.3946						
Holding time (min)	110.43	-25.79	31.84	-30.57	-24.94				-16.82	20.13					

5.3 Effect of the latex depolymerization time and quantity of additives studied on the physical properties of PSA.

Response surface methodology is used in order to show the relationship between the properties of PSA and the variable factors as shown in Figure 5.3.1 to 5.3.18., by using the Equation 5.2-1 to 5.2-3 to plot graphs. The effects of the latex depolymerization time and amount of tackifier to physical properties of PSA are presented and discussed in the following section.

5.3.1 180° peel adhesion

Interaction of latex depolymerization time and phr of tackifier

Figures 5.3.1 to 5.3.3 show the interaction of latex depolymerization time and, phr of Rosin ester, phr of SE376A, and phr of SE790G on 180°peel adhesion respectively. At low phr of Rosin ester, 180° peel adhesion increases while the latex depolymerization time increases. However, at high phr of Rosin ester, 180°peel adhesion slightly decreases as latex depolymerization time increases according to Figure 5.3.1.

In Figure 5.3.2, phr of SE376A between 2 to 30phr, 180°peel adhesion increases as depolymerization time increases. If phr ofSE376A increases over 30 phr, 180°peel adhesion become greater as well. But latex depolymerization time has a slight effect on 180°peel adhesion. At 2-hour-depolymerization time and 10 phr of SE376A, the 180°peel adhesion go down to the lowest point.

In Figure 5.3.3, at low phr of SE790G, 180° peel adhesion decreases at the increase of the latex depolymerization. However, this will only happen if the phr of

SE790G is less than 22 phr of SE790G. After 22 phr of SE790G, 180°peel adhesion increases when latex depolymerization time increases.

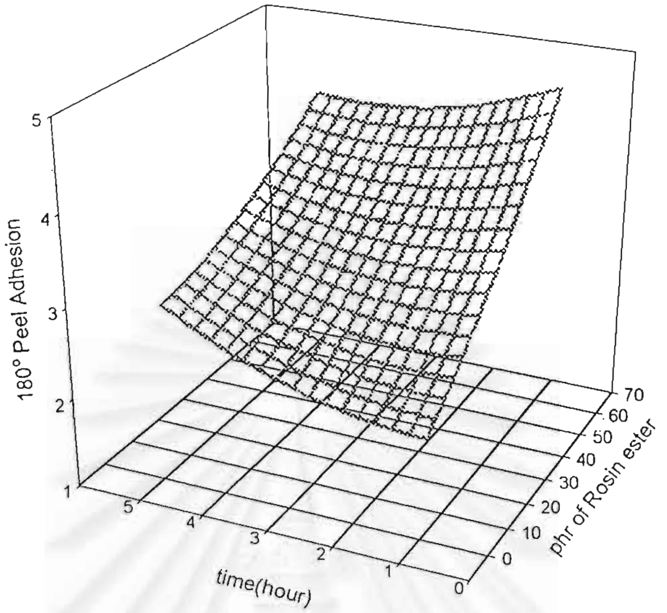
Interaction of Rosin ester, SE376A, and SE790G

Figures 5.3.4 to 5.3.6 show the effects of Rosin ester, SE376A, and SE790G on 180°peel adhesion. From Figure 5.3.4, if Rosin ester and/or SE376A increase, 180° peel adhesion increases.

In Figure 5.3.5, at low phr of Rosin ester or phr of SE790G, 180°peel adhesion increases as phr of SE790G or phr of Rosin ester increases. At high phr of SE790G, if phr of Rosin ester increases, 180° peel adhesion decreases. At high phr of Rosin ester, 180° peel adhesion decreases to the minimum level and go up as phr of SE790G increases.

According to Figure 5.3.6, the interaction between SE376A and SE790G on 180°peel adhesion decreases to the minimum point at 17 phr of SE376A and 25 phr of SE790G.

Effect of latex depolymerization time and rosin ester
on 180° peel adhesion



Effect of latex depolymerization time and rosin ester
on 180° peel adhesion

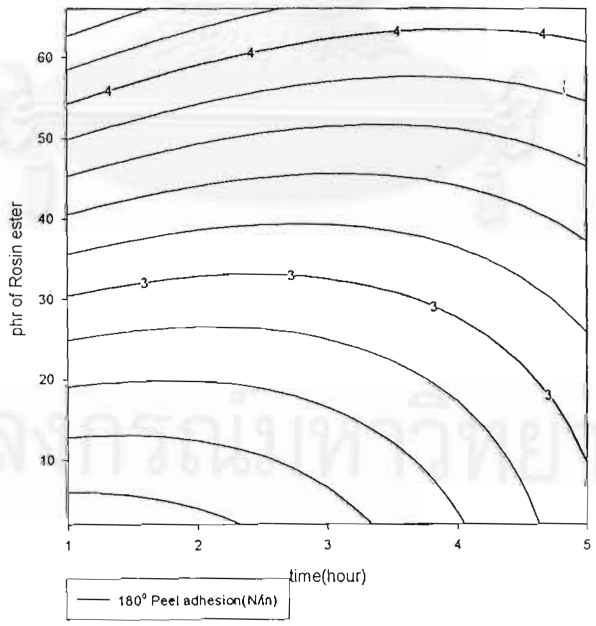
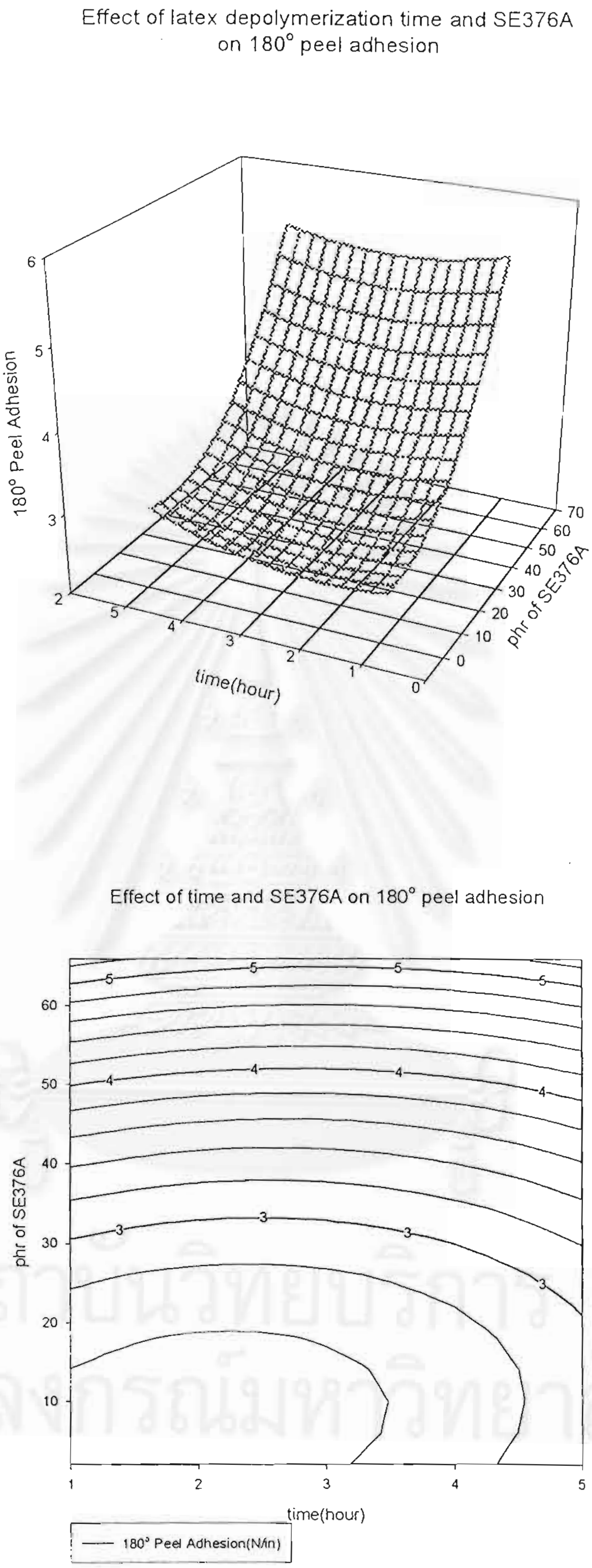


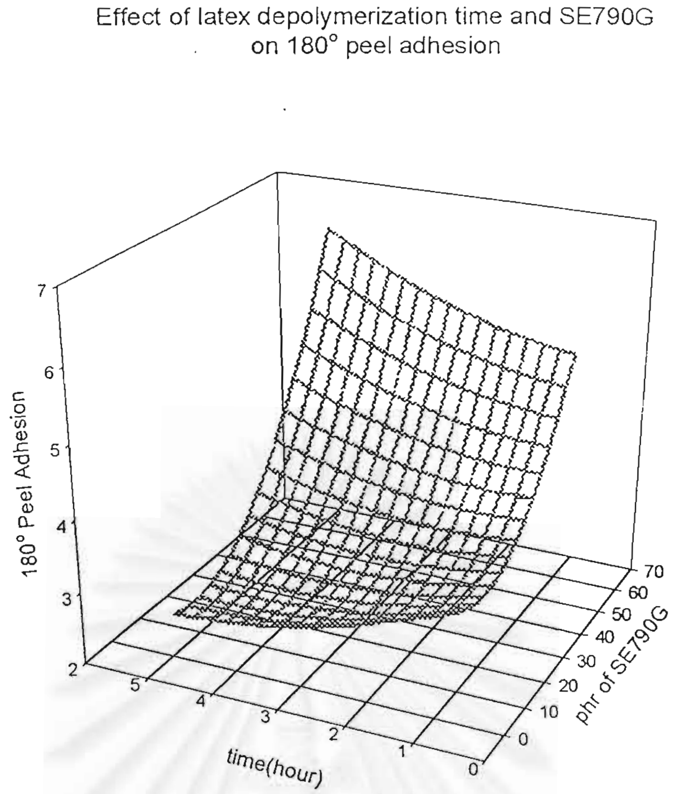
Figure 5.3.1. Effect of latex depolymerization time and rosin ester on 180°peel adhesion



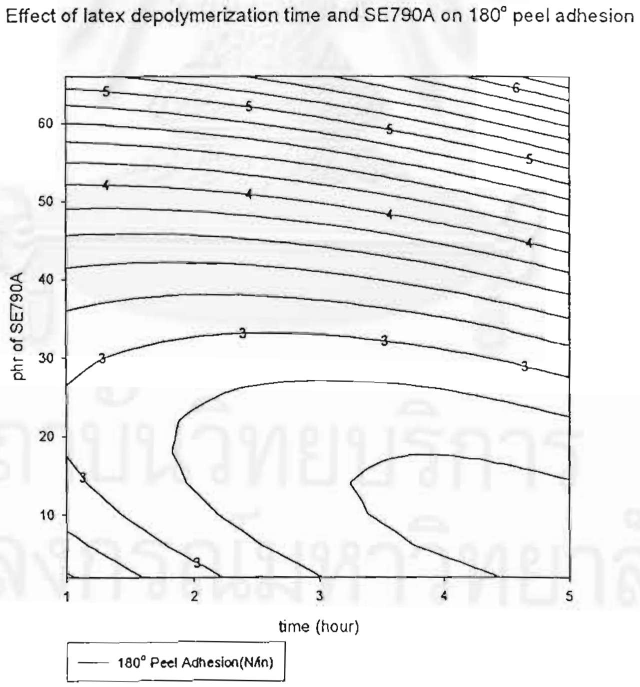
Effect of latex depolymerization time and SE376A on 180° peel adhesion

Effect of time and SE376A on 180° peel adhesion

Figure 5.3.2. Effect of latex depolymerization time and SE376A on 180°peel adhesion



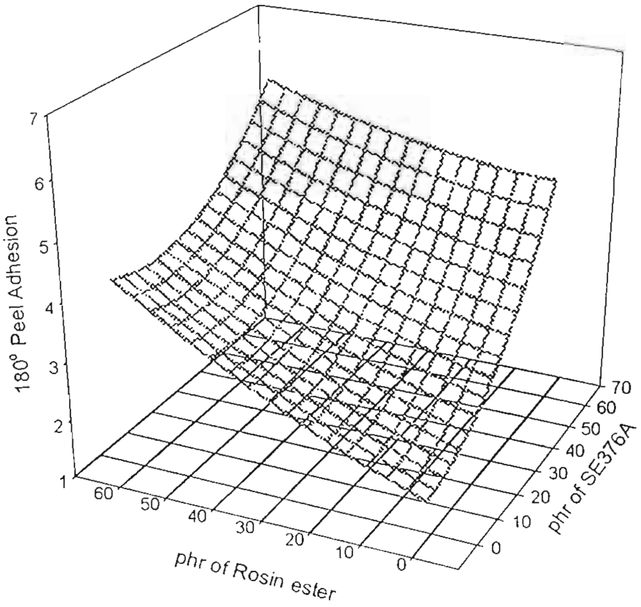
Effect of latex depolymerization time and SE790G on 180° peel adhesion



Effect of latex depolymerization time and SE790A on 180° peel adhesion

Figure 5.3.3. Effect of latex depolymerization time and SE790G on 180°peel adhesion

Effect of rosin ester and SE376A on 180° peel adhesion



Effect of rosin ester and SE376A on 180°peel adhesion

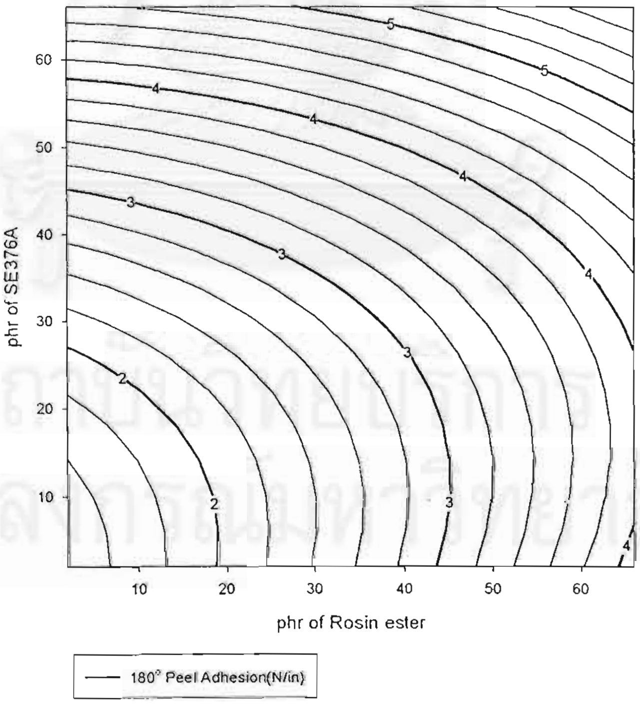
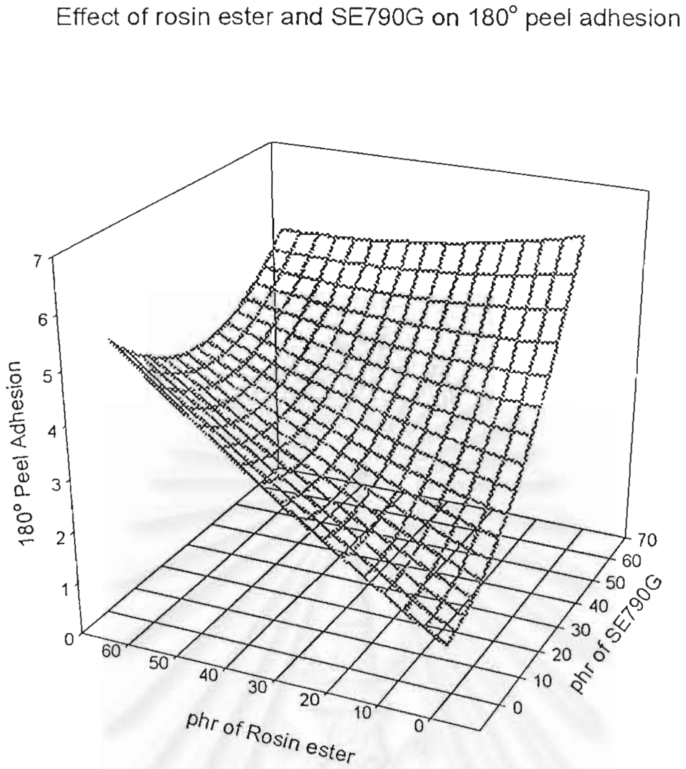


Figure 5.3.4. Effect of rosin ester and SE376A on 180°peel adhesion.



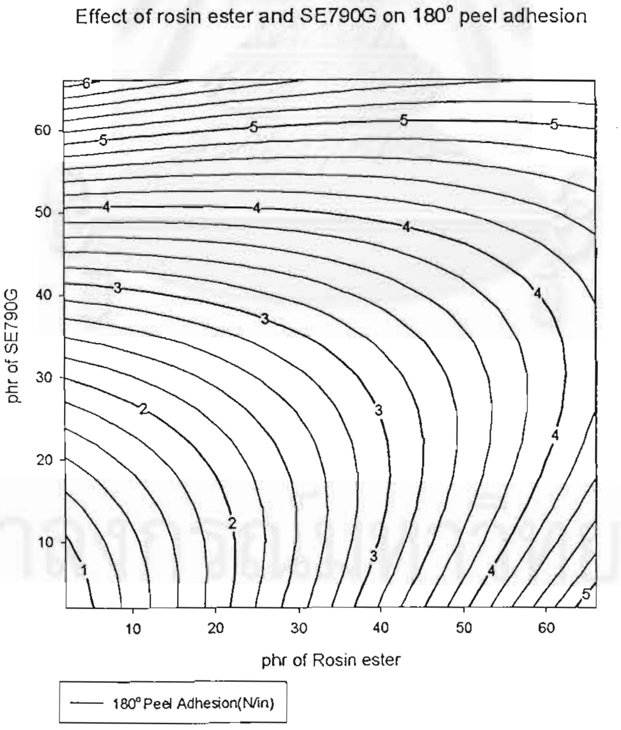
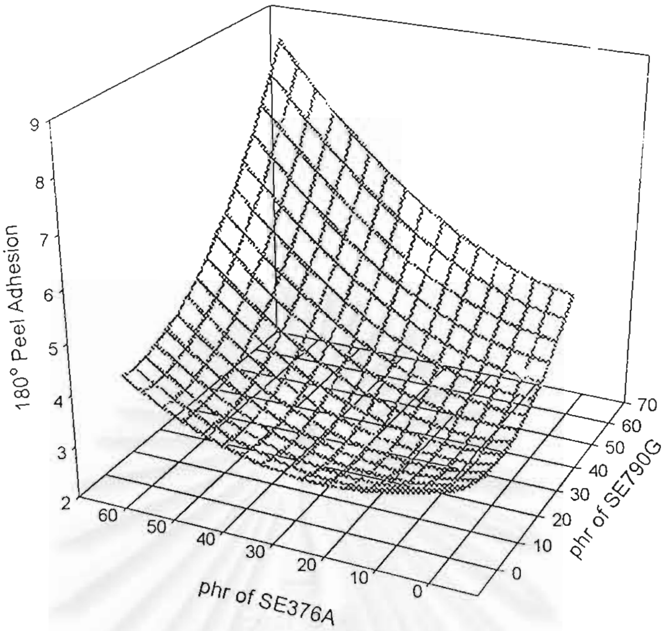


Figure 5.3.5. Effect of rosin ester and SE790G on 180°peel adhesion

Effect of SE376A and SE790G on 180° peel adhesion



Effect of SE376A and SE790G on 180° peel adhesion

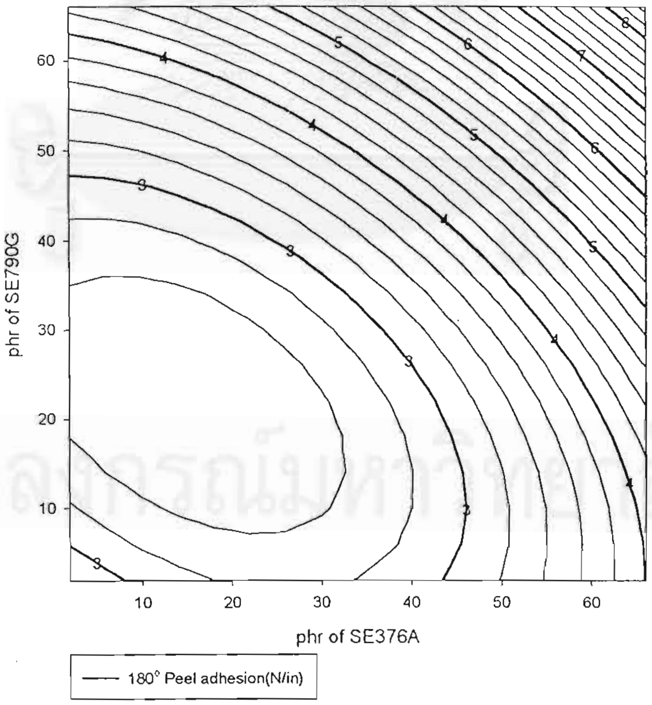


Figure 5.3.6. Effect of SE376A and SE790G on 180°peel adhesion

From the experiment it may be concluded that molecular weight of latex will decreases when depolymerization time increases. This leads to the increase of chain mobility and diffusion rate of adhesives that may possibly result in the increase of 180°peel adhesion as shown by the figures obtained from RSM using regression analysis. However, the depolymerization time might has no significant effect for 180°peel adhesion regarding Table 5.2.9 while the 180° peel adhesion increases if phr of tackifiers increase as shown in Figures 5.3.1. to 5.3.3. When considering the effect of tackifiers on 180°peel adhesion in pairs (phr of Rosin ester and SE376A, phr of Rosin ester and SE790G, SE376A and SE790G), 180°peel adhesion may likely increases if the contents of the tackifiers increase as shown by the figure obtain from RSM. According to Benedek, it was believed that the chain mobility and diffusion rate of PSA are also increased by adding tackifiers. [Benedek,1996]

In addition the changing amounts of tackifiers are significant for the production of 180°peel adhesion equation. This adhesion depends on phr of tackifiers in adhesive more than the depolymerization time.

5.3.2 Tack

Interaction of latex depolymerization time and phr of tackifier

Figures 5.3.7 to 5.3.9 show the interaction of latex depolymerization time, phr of Rosin ester, phr of SE376A, and phr of SE790G on tack. From Figure 5.3.7, at constant phr of Rosin ester, tack increases to the maximum point and then it decreases as latex depolymerization time increases. At the same latex depolymerization time, tack increases to the maximum point and decreases after that due to the increasing phr of Rosin ester.

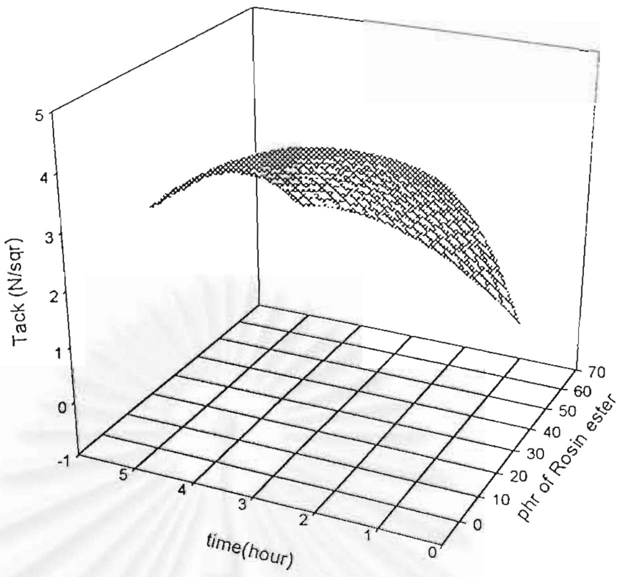
From Figures 5.3.8 and 5.3.9, at constant phr of tackifier (SE376A or SE790G), tack increases to the maximum point. After that it decreases because of the increasing latex depolymerization time. At the same latex depolymerization time, tack increases as phr of tackifier (SE376A or SE790G) increases.

Interaction of Rosin ester, SE376A, and SE790G

Figures 5.3.10 to 5.3.12 show the effect of Rosin ester, SE376A, and SE790G on tack. At low phr of SE376A and SE790G, phr of Rosin ester has a slight effect on tack. Tack increases gently before reaching the critical point after that it decreases slightly, due to the increasing phr of Rosin ester. At high phr of SE376A and SE790G, tack decreases as Rosin ester increases. At low phr of Rosin ester, tack increases when phr of SE376A or SE790G increases. At high phr of Rosin ester, the rate of tack decreases as shown in Figures 5.3.10 and 5.3.11.

From Figure 5.3.12, an increase in phr of SE376A and SE790G has no effect on tack at low phr of these resins. According to the graph, tack increases when these resins are added up to the critical point.

Effect of latex depolymerization time and rosin ester on tack



Effect of latex depolymerization time and rosin ester on tack

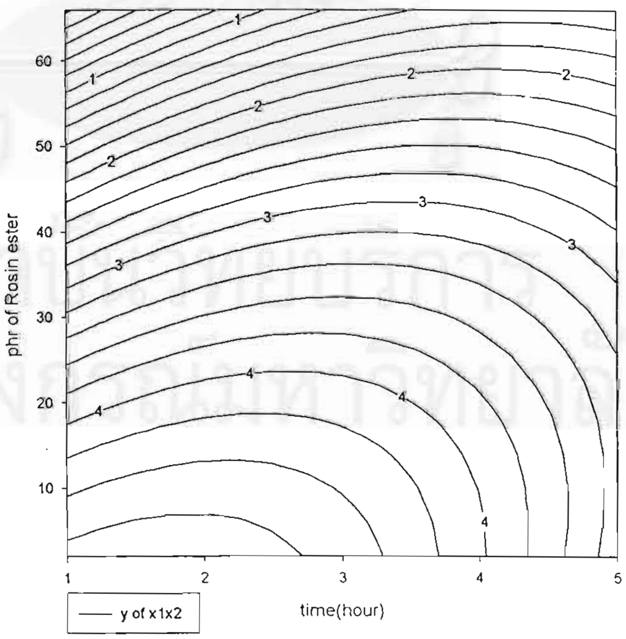
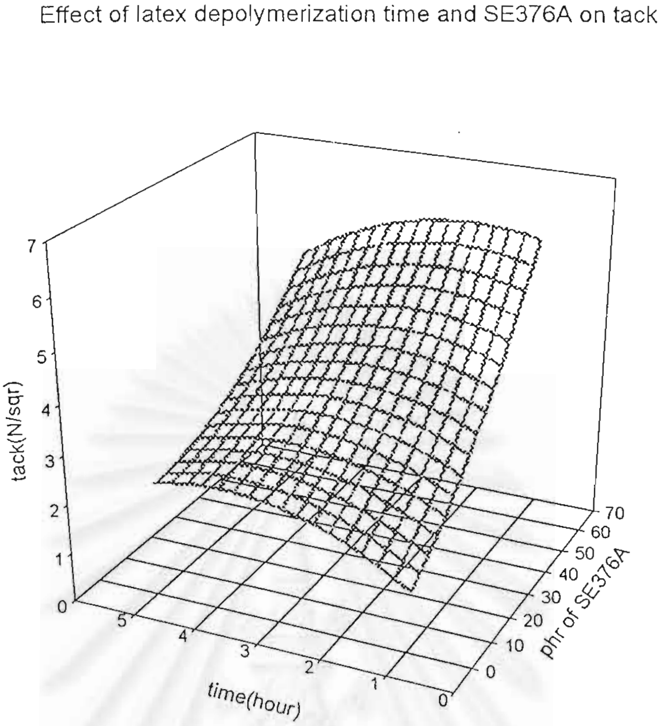


Figure 5.3.7. Effect of latex depolymerization time and rosin ester on tack



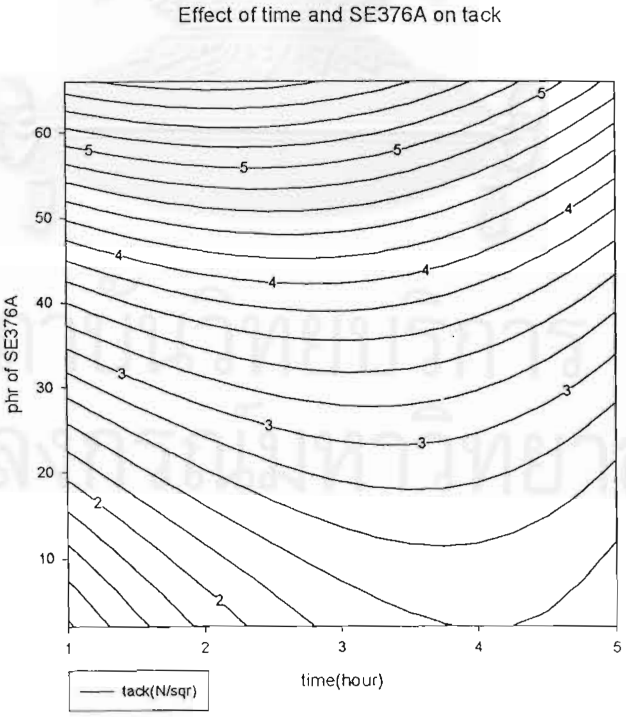
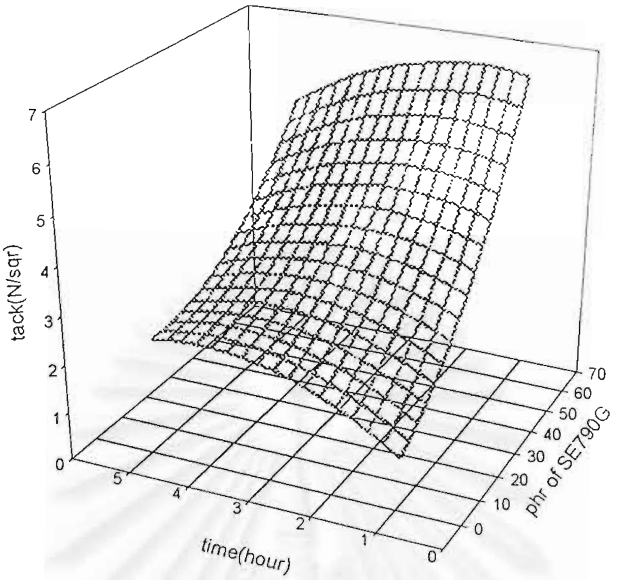


Figure 5.3.8. Effect of latex depolymerization time and SE376A on tack

Effect of latex depolymerization time and SE790G on tack



Effect of latex depolymerization time and %SE790G on tack

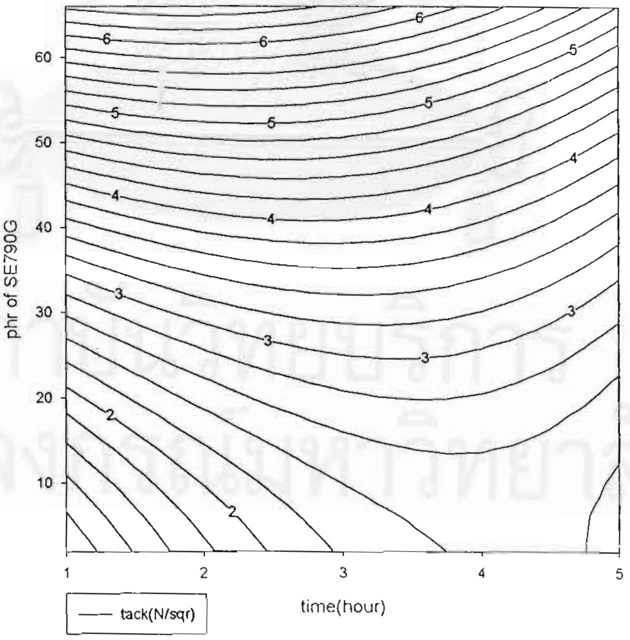
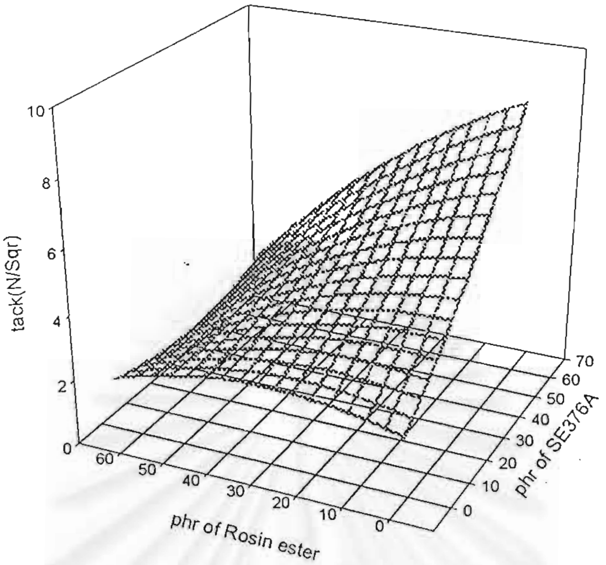


Figure 5.3.9. Effect of latex depolymerization time and SE790G on tack

Effect of rosin ester and SE376A on tack



Effect of rosin ester and SE376A on tack

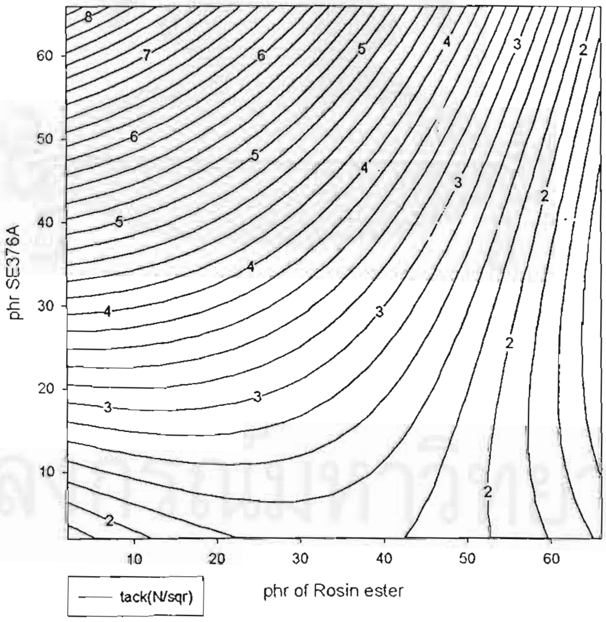


Figure 5.3.10. Effect of rosin ester and SE376A on tack

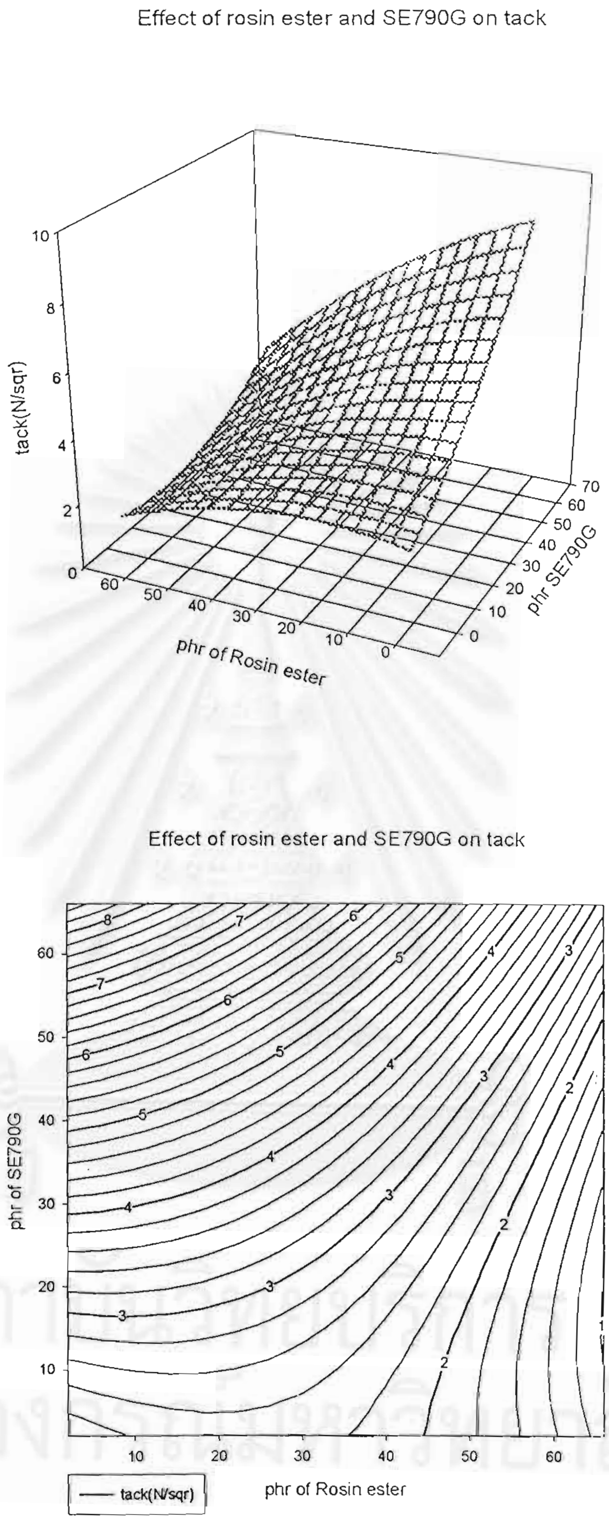
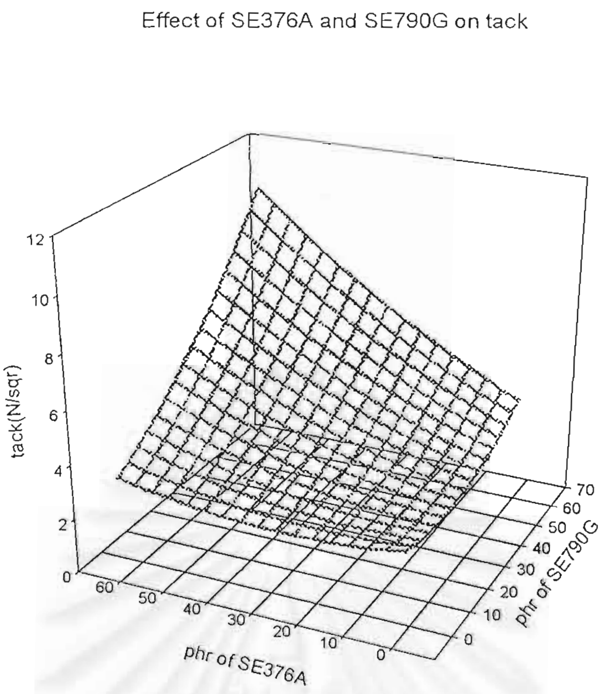


Figure 5.3.11. Effect of rosin ester and SE790G on tack


Effect of SE376A and SE790G on tack

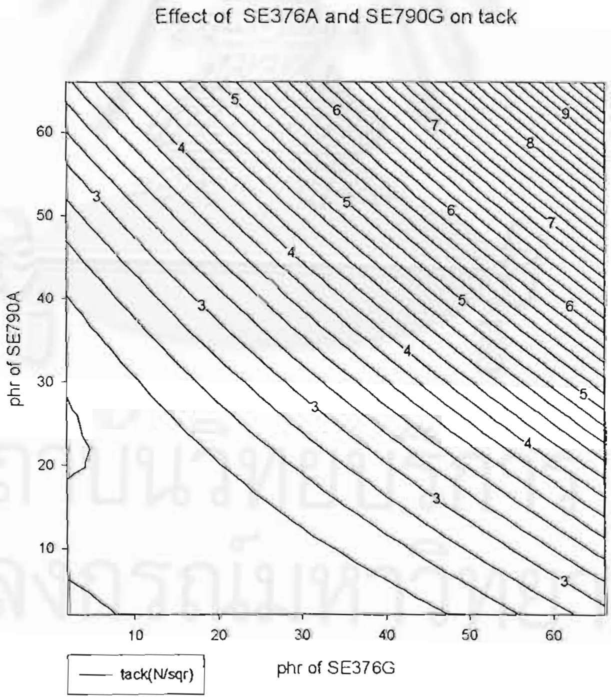

Effect of SE376A and SE790G on tack

Figure 5.3.12. Effect of Se376A and SE790G on tack

The high molecular weight of latex may affects the poor wetting ability, because the molecules of latex flow with more difficulty than low molecular weight latex. Decreasing molecular weight increases chain mobility and wetting ability of adhesives. Then, tack should increases if molecular weight decreases. From ANOVA table 5.3.10, tack depends on tackifiers more than molecular weight of latex. Normally, tack may increases if the quantity of tackifiers also increase regarding Benedek, tackifiers will add more chain mobility of adhesive, but in Rosin ester only.[Benedek,1996] Since in preparing Rosin ester it is difficult to make it stable and have the particle-size as small as commercial grade. All this possibly results in making tack decreases. Tack decreases if phr of Rosin ester increases, because large particles sizes of Rosin ester lead to latex coagulation. This effect will increase elastic property of adhesive and reduce the viscous property of adhesive as shown in Figure 5.3.7.

On the other hand, RSM shows that tack should increases if phr of SE376A and/or SE790G increase together. This is the ability of the tackifiers to increase the chain mobility of adhesive as shown in Figure 5.3.8, 5.3.9 and 5.3.12. Moreover, tack increases if phr of Rosin ester decreases when phr of SE376A or SE790G increases as shown in Figure 5.3.10 and 5.3.11.

5.3.3 Holding time

Interaction of latex depolymerization time and phr of tackifier

Figures 5.3.13 to 5.3.15 show the interaction of latex depolymerization time, phr of Rosin ester, phr of SE376A, and phr of SE790G on holding. At the same phr of Rosin ester, holding time decreases, the if latex depolymerization time increases. Moreover, at the same latex depolymerization time, holding time increases if phr of Rosin ester increases as shown in Figure 5.3.13.

In Figure 5.3.14, at low phr of SE376A, holding time decreases resulting from the increase in latex depolymerization time. Between 1 and 3 hours of latex depolymerization time, holding time decreases when phr of SE376A increase. After 3 hours of latex depolymerization time, holding time decreases until phr of SE376A is over 45.

From Figure 5.3.15, holding time decreases as the latex depolymerization time increases. When phr of SE790G increases, holding time increases. After reaching the critical point it decreases. Latex depolymerization time and phr of SE790G on holding time are 3.50 hours and 4 phr of SE790G at estimated critical point point of the interaction.

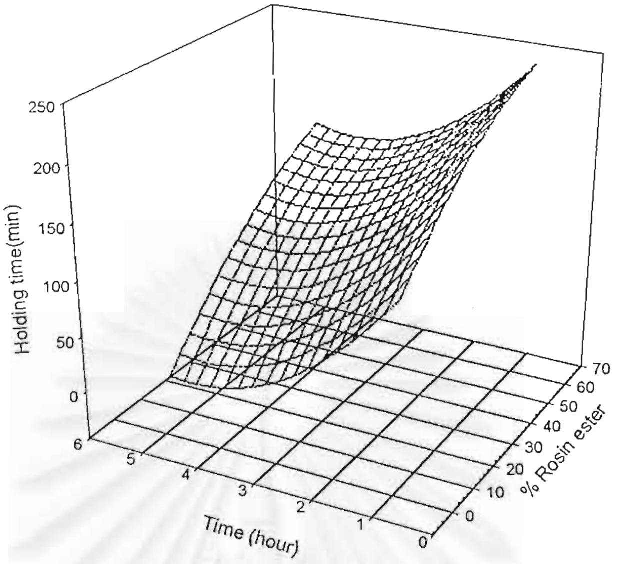
Interaction of Rosin ester, SE376A, and SE790G

Figures 5.3.16 to 5.3.18 show the effect of Rosin ester, SE376A, and SE790G on holding time. At low phr of SE376A, holding time increases, if Rosin ester increases. Rosin ester has slightly affected holding time at high phr of SE376A. At low phr of Rosin ester, an increase in SE376A has little effect on holding time. At high phr of Rosin ester, holding time decreases while phr of SE376A increases as shown in Figure 5.3.16.

At low phr of Rosin ester, holding time decreases as phr of SE790G increases. The holding time continues to increase to the highest point at 40 phr Rosin ester and then it decreases. At low phr of SE790G, the change of phr of Rosin ester has little effect on holding time. At high phr of SE790G, holding time increases, if phr of Rosin ester increases. The estimated minimum point of the interaction of phr of Rosin ester and phr of SE790G are 33 phr of Rosin ester and 8 phr of SE790G as shown in Figure 5.3.17.

From Figure 5.3.18 holding time decreases as a result of the increase in phr of SR790A at all phr of SE376A. At first, holding time increases until it reaches the critical point at 15 phr ofSE790G. After that it decreases when phr of SE376A increases.

Effect of latex depolymerization time and rosin ester on holding time



Effect of time and rosin ester on holding time

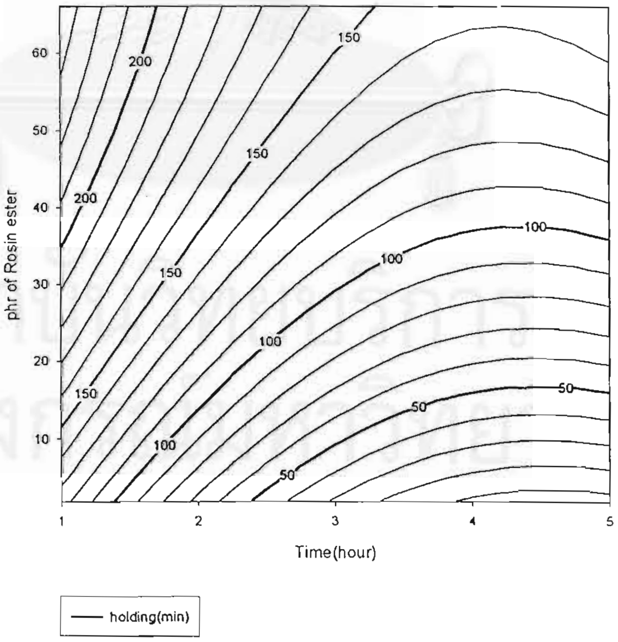
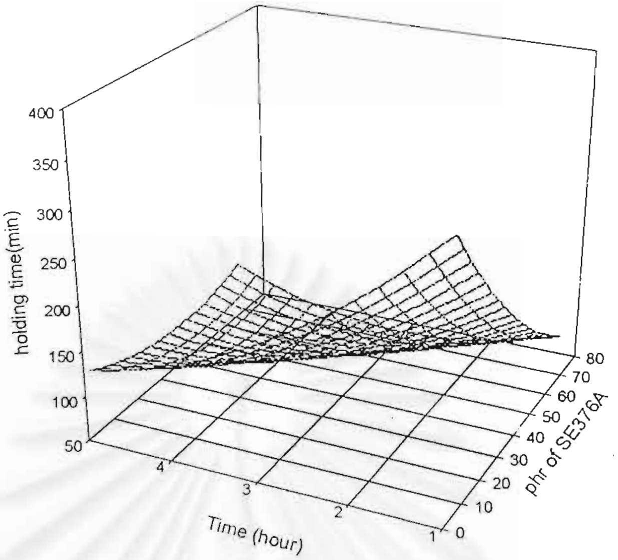


Figure 5.3.13. Effect of latex depolymerization time and rosin ester on holding time.

Effect of time and SE376A on holding time



Effect of latex depolymerization time and SE376A on holding time

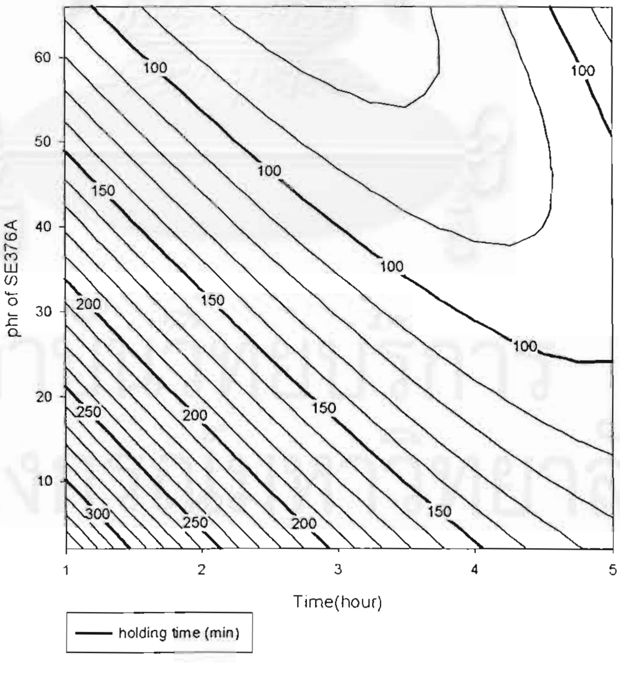
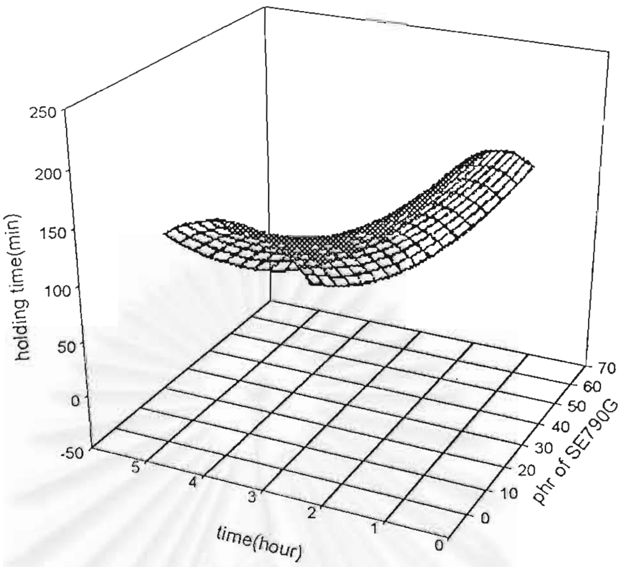


Figure 5.3.14. Effect of latex depolymerization time and SE376A on holding time

Effect of latex depolymerization time and SE790G on holding time



Effect of latex depolymerization time and SE790G on holding time

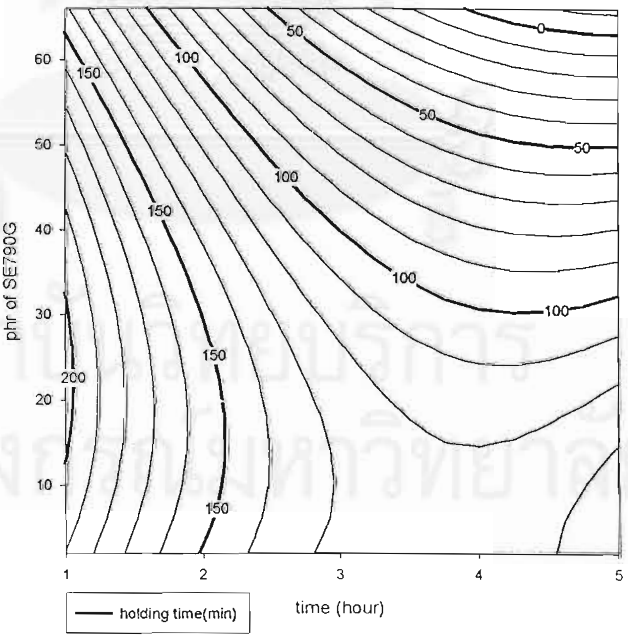
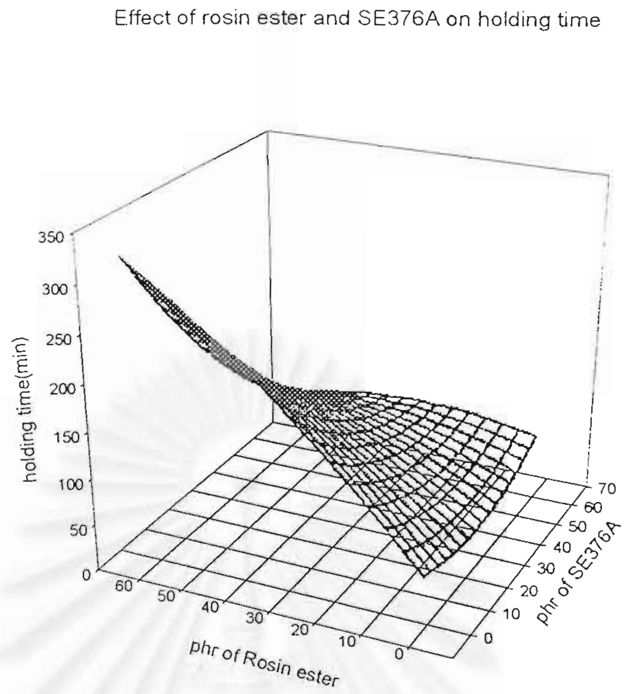


Figure 5.3.15. Effect of latex depolymerization time and SE790G on holding time


Effect of rosin ester and SE376A on holding time

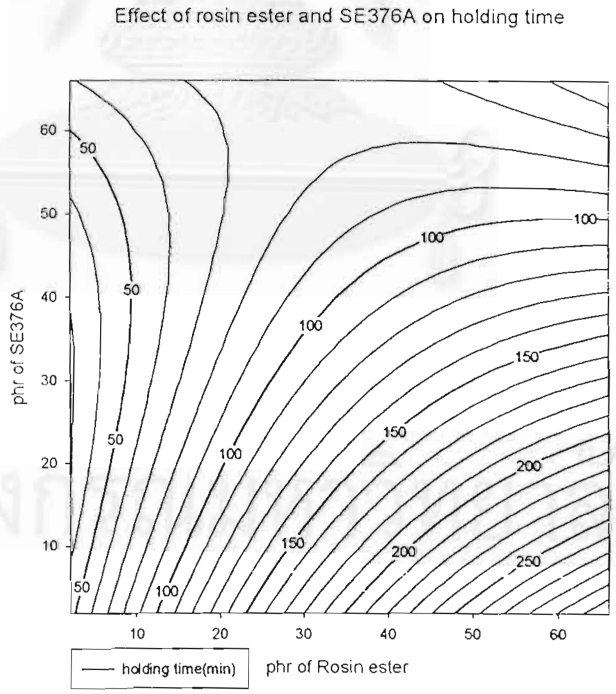
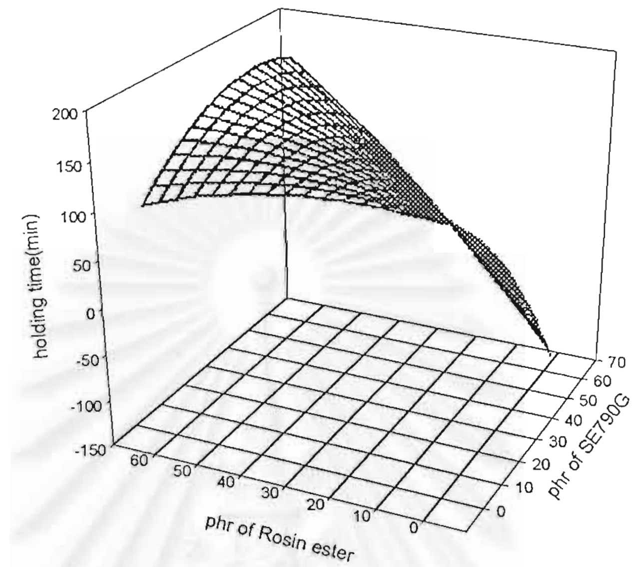

Effect of rosin ester and SE376A on holding time

Figure 5.3.16. Effect of rosin ester and SE376A on holding time


Effect of rosin ester and SE790G on holding time

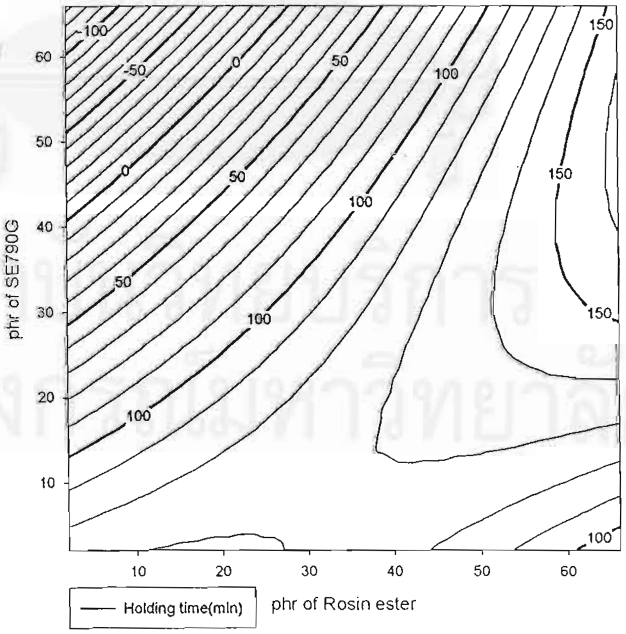
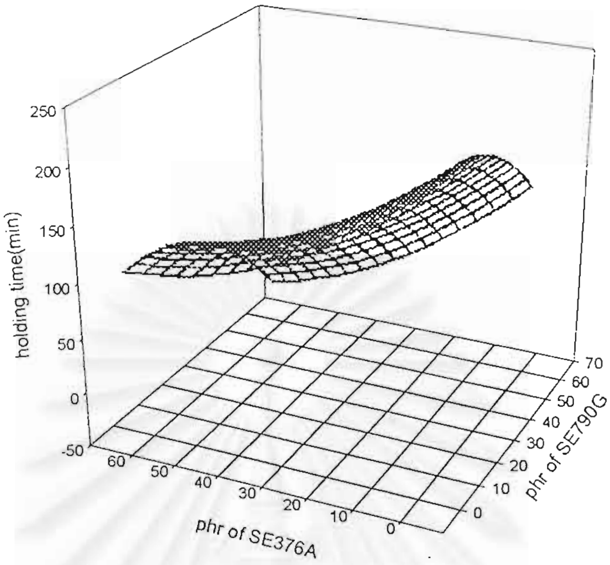

Effect of rosin ester and SE790G on holding time

Figure 5.3.17. Effect of rosin ester and SE790G on holding time

Effect of SE376A and SE790G on holding time



Effect of SE376A and SE790G on holding time

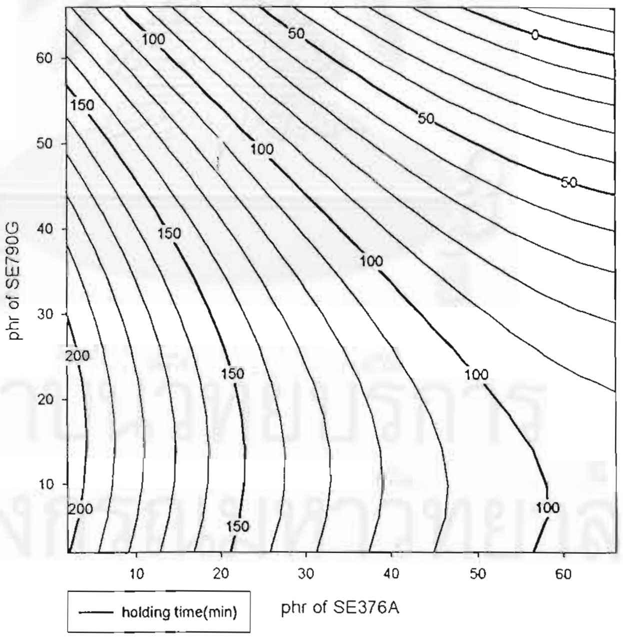


Figure 5.3.18. Effect of SE376A and SE790G on holding time

Shear holding properties of adhesive depends on latex depolymerization time and the amount of tackifiers as shown in Table 5.3.11. The ANOVA table shows the significant term for holding time.

At low latex depolymerization time, the depolymerized reaction produces adhesives that have higher molecular weight, so the shear strength of the adhesives is high.This is in agreement with the results given by Benedek. [Benedek,1996] Large particle-size of Rosin ester leads to latex coagulation and improves the elastic property of adhesives. From RSM using regression model it appears that holding time trend to increases if Rosin ester increases and latex depolymerization time decreases as shown in Figure 5.3.13. In contrast, holding time trend to increases, when SE376A or SE790G decreases and depolymerization time decreases as shown in Figure 5.3.14 and 5.3.15.

Holding time likely increases if Rosin ester increases but SE376A or SE790G decreases as shown in Figure 5.3.16 and 5.3.17. In addition, holding time incline to decreases if SE376A and SE790G decrease as shown in Figure 5.3.18, this is the result from adding tackifier to improve the chain mobility of adhesive and decrease the shear strength of adhesive with reference to Benedek. [Benedek,1996] However, SE790G has a unique qualification which helps to increase holding time when used in a small quantity.

CHAPTER VI

CONCLUSION AND RECOMMENDATION

Thus far, it can not be specified which type of PSAs is the best as their performance depends on the purpose of applications. It can be concluded that the characteristics of peel and tack depend on the quantity and type of tackifiers that are added into the rubber latex which is the water-base polymer.

Holding time depends on the latex depolymerization time, quantity, and types of tackifiers. Since these factors directly affect the shear strength of adhesive which in turn, determines the value of holding time. If the depolymerization time is short, high molecular weight rubber remains and high strength of shear is obtained. Thus the holding time increases. If the quantity of tackifiers increases, the strength of shear will become smaller. In this case, the decrease of the holding time results.

The increase in chain mobility can raise the tack and peel strength of PSA. This research found that adding more tackifier content into adhesive and increases the depolymerization time result in the increase in chain mobility. As a consequent, the tack and peel strength is higher. However, the effect of tackifier content on peel and tack is much stronger than the depolymerization time. However, depolymerization time of rubber latex increase, the holding time will decrease. This result is the same as the increase in the quantity of tackifier, i.e. SE376A and SE790G. On the other hand, if the quantity of Rosin ester increases, holding time will rise.

Currently, there is no commercial production of PSA in Thailand. Consequently, the cost of production of PSA according to this study is compares to those of acrylic waster base PSA elsewhere. The price of PSA would vary on its property and pricing standard of each company as shown in Table 6.1. The testing standards of each company are different from this research. The study has compared the lowest price against cost of PSA which can be illustrated in term of formula and properties as follows.

Table 6.1 Cost of Acrylic PSAs in Thailand, 2000.

Code	company	Tack	Adhesion (kg/in)	Cohesion(hr)	coating thickness,m	price (Baht/kg)
SE1212	Eternal	$<4^1$	0.8^3	$>8^4$	25-28	50
ER-7005-40	Eternal	$<7^1$	1^3	$>20^4$	25-28	55
SE6101-M	Eternal	$<6^1$	1^3	$>24^4$	25-28	63
SE1211	Eternal	$<4^1$	0.6^3	$>10^4$	25-28	45
PS-35T	Rohm and haas adhesive	$>1.1^2$	$1.2\text{-}1.8^4$	$>10^5$	22	45
PS-24	Rohm and haas adhesive	$>0.9^2$	$0.8\text{-}1.0^4$	$>8^5$	22	42
STC-99	Rohm and haas adhesive	$1.1\text{-}1.5^2$	$1.8\text{-}2.3^4$	$10\text{-}15^5$	22	50
R9319	Union carbide	$<5^1$	$0.5\text{-}1.0^3$	$>8^5$	25-28	57
R9321	Union carbide	$<4^1$	$0.7\text{-}1.0^3$	$>8^5$	25-28	57

^{1}PSTC6, 30°C, ^{2}FINAT, 25°C, ^{3} PSTC1, 30°C, ^{4} PSTC1, 25°C,^{5} PSTC7, 30°C

The rubber latex PSA's in this research using this formulation (1 hour of depolymerized latex, 50 phr of Rosin ester, 50 phr of SE376a and 50 phr of SE790G) have the estimated cost about 38 baht per kilogram. This PSA has 2.85 N/inch of 180°peel, 2.472 N/in^2 of tack and 219.33 min of holding time. The above estimation of adhesive cost carried out based on 40 Baht per $US., using CIF method. As for the rubber latex PSA's coat, its price will be the same as Acrylic water-based. However, if the exchange rate for Thai Baht against U.S. dollars becomes more appreciated the price of tackifiers will be lower. Thus, PSA production for industrial use will become more feasible.

Recommendation for further studies

However, there are some disadvantages of rubber latex PSA. Its color can change when it is stored for sometime. Moreover, the aging time of rubber latex is quite short compared with that of acrylic water-based.

Further development should emphasize on the study of how the adding of antioxidant or filler affect the physical properties of PSA and economic price. The use of rubber latex, which can be produced in Thailand, will be feasible especially if other raw materials (i.e. tackifier) can be obtained at a more competitive price.

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APPENDIX

APPENDIX A

EXPERIMENTAL DATA

A1 Data of inherent viscosity and reduced viscosity

TABLE A1.1 Data of viscosity of depolymerization HA latex at 1 hour.

Concentration (g/dl)	t1	t2	t3	t4	t5	t(avg)	ln(t/t0)/c	((t/t0)-1)/c
0.16	195.78	196.39	195.84	195.81	196.20	196.004	1.594	1.816
0.128	190.00	186.66	185.47	186.63	184.32	186.616	1.609	1.787
0.08	172.66	172.93	172.62	172.85	172.93	172.798	1.613	1.722
0.048	164.13	164.06	164.16	164.09	164.45	164.178	1.622	1.687

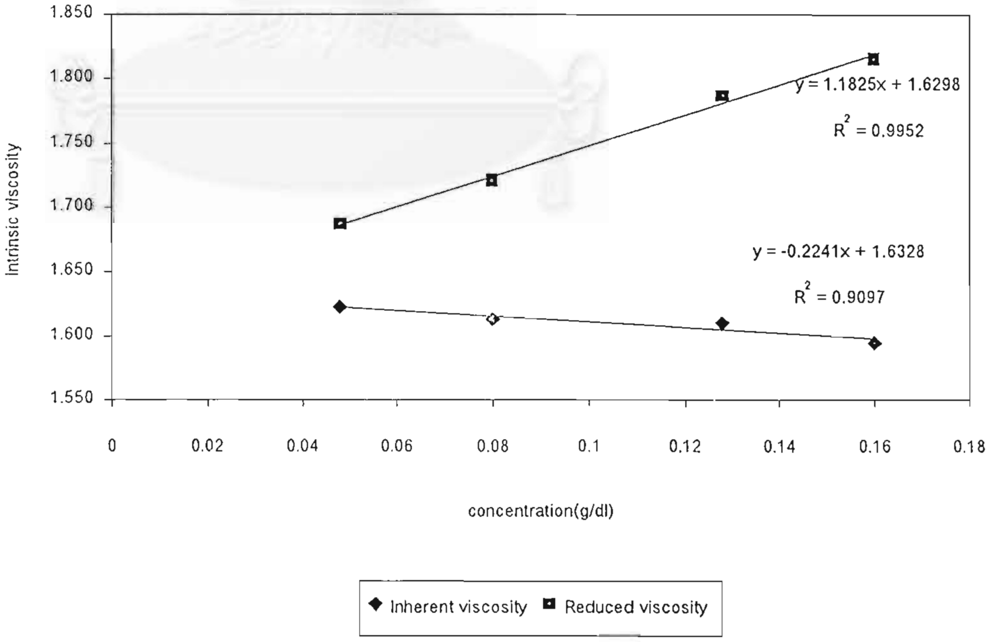


Figure A1.1. Reduced and inherent viscosity vs concentration curves for 1-hour-depolymerized rubber latex in toluene at 25^0

TABLE A1.2 Data of viscosity of depolymerization HA latex at 2 hours.

Concentration (g/dl)	t1	t2	t3	t4	t5	t(avg)	ln(t/t0)/c	((t/t0)-1)/c
0.16	185.06	185.48	185.64	185.32	185.21	185.342	1.244	1.377
0.128	178.58	178.65	178.58	178.65	178.6	178.612	1.267	1.375
0.08	168.09	168.02	169.09	168.04	168.85	168.418	1.292	1.361

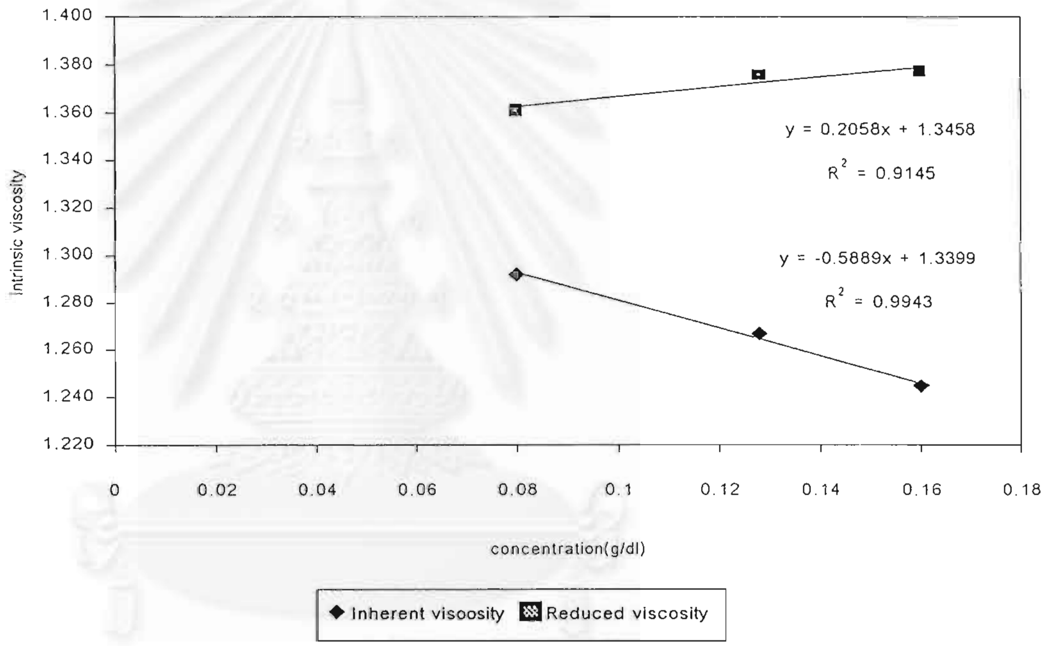


Figure A1.2. Reduced and inherent viscosity vs concentration curves for 2-hour-depolymerized rubber latex in toluene at 25^0

TABLE A1.3 Data of viscosity of depolymerization HA latex at 3 hours.

Concentration (g/dl)	t1	t2	t3	t4	t5	t(avg)	ln(t/t0)/c	((t/t0)-1)/c
0.16	176.51	176.11	175.81	176.12	175.65	176.040	0.923	0.994
0.128	170.45	171.00	171.22	170.88	171.44	170.998	0.926	0.983
0.08	163.56	163.72	163.65	163.68	163.76	163.674	0.935	0.971
0.048	158.80	158.91	158.99	158.82	158.76	158.856	0.936	0.957

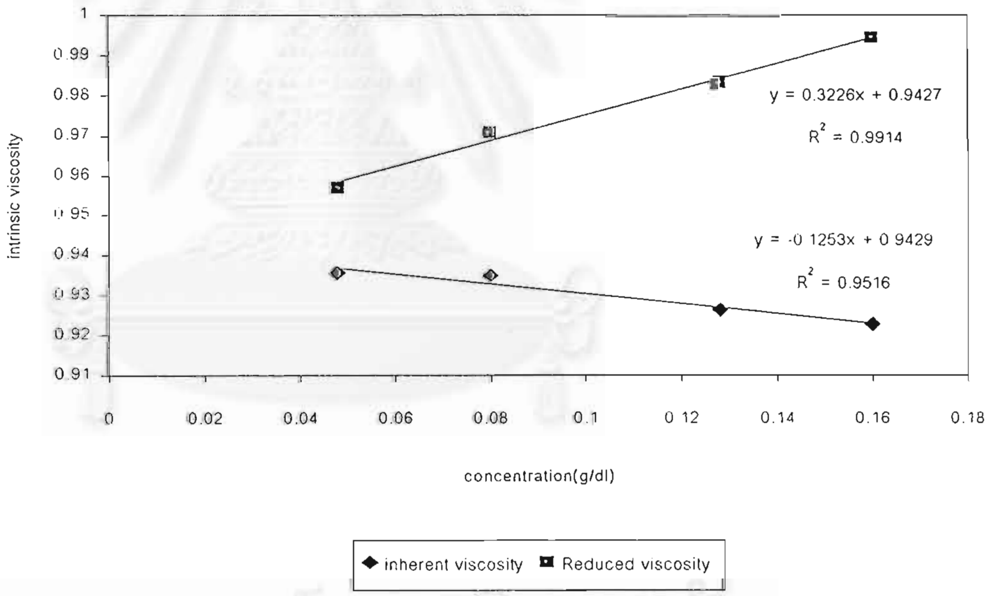


Figure A1.3. Reduced and inherent viscosity vs concentration curves for 3-hour-depolymerized rubber latex in toluene at 25^0

TABLE A1.4 Data of viscosity of depolymerization HA latex at 4 hours.

Concentration (g/dl)	t1	t2	t3	t4	t5	t(avg)	ln(t/t0)/c	((t/t0)-1)/c
0.16	170.61	170.93	170.92	170.94	170.93	170.866	0.736	0.781
0.128	167.01	166.92	166.95	166.94	167.03	166.970	0.740	0.776
0.08	161.20	161.24	161.20	161.32	161.35	161.262	0.749	0.772
0.048	157.18	157.68	157.81	157.32	157.48	157.494	0.756	0.770

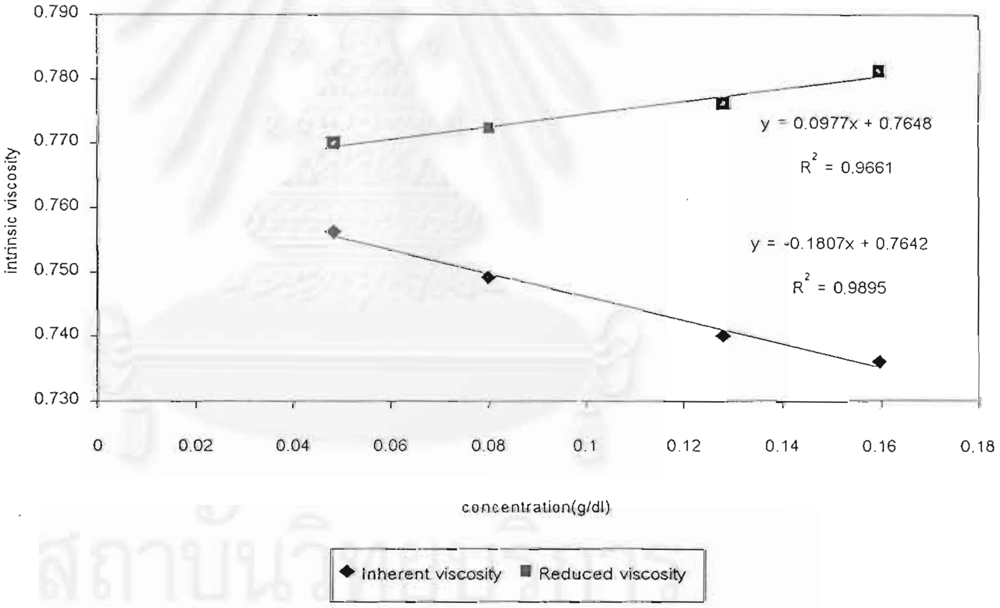


Figure A1.4. Reduced and inherent viscosity vs concentration curves for 4-hour-depolymerized rubber latex in toluene at 25^0

TABLE A1.5 Data of viscosity of depolymerization HA latex at 5 hours.

Concentration (g/dl)	t1	t2	t3	t4	t5	t(avg)	ln(t/t0)/c	$((t/t_o)-1)/c$
0.16	162.21	162.10	162.39	162.95	162.84	162.498	0.422	0.437
0.128	160.36	160.23	160.35	160.41	160.27	160.324	0.423	0.434
0.08	156.82	156.98	157.25	157.20	157.32	157.114	0.424	0.431
0.048	155.06	155.21	154.94	154.93	154.86	155.000	0.424	0.428

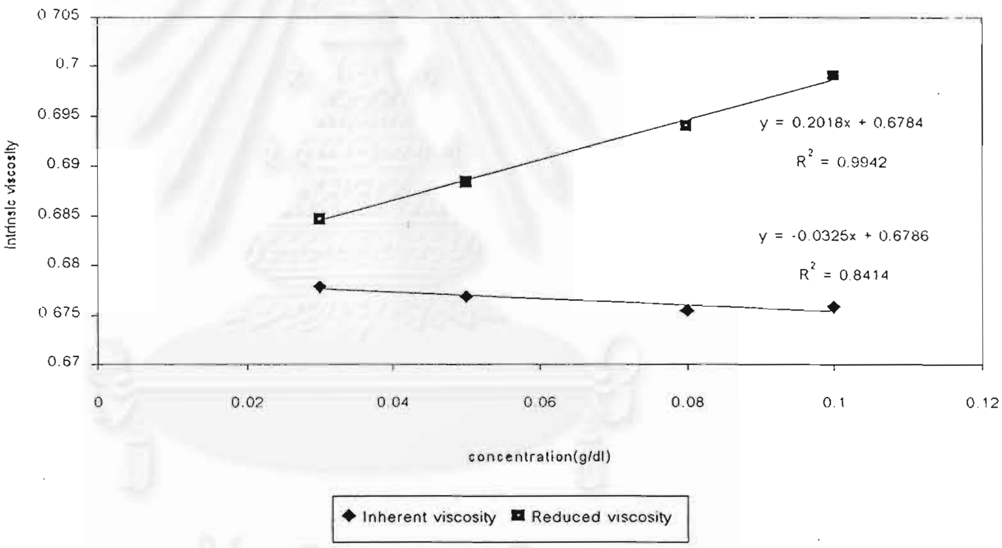


Figure A1.5. Reduced and inherent viscosity vs concentration curves for 5-hour-depolymerized rubber latex in toluene at 25^0

APPENDIX B

EXPERIMENTAL DESIGN

B1 Experimental design

Two experimental designs were planned in this study. One was 2^4 factorial design [Schmidt,1994] for an investigation of effects of key parameters on initial rate. The other was the, central composite design (CCD)[Schmidt,1994], an expansion of the first design to both extremes in order to construct the response surface equation.

Four experimental parameters were of interest: X1 = Depolymerization time (Hr), X2 = amount of rosin aqueous (phr of latex), X3 = amount of snowtack 376A (phr of latex), X4 = amount of snowtack 790G (phr of latex). In the first design, all factors were studied at two levels (+1 and -1). Table B1 shows the first design experiment. Levels of these factors can be determined from their actual values as expressed in the equations below. The number subtracted from the actual value is the actual value at level 0,while the divisor is the difference between actual values per level.

$$X1 = \frac{\text{depolymerization time} - 3}{1}$$

$$X2 = \frac{\text{amount of rosin aqueous} - 34}{16}$$

$$X3 = \frac{\text{amount of snowtack 376A} - 34}{16}$$

$$X4 = \frac{\text{amount of snowtack 790G} - 34}{16}$$

Table B1.1.Experimental design planning. Codified and actual levels of the factors.

Exp. On	Codified factors				Actual factors			
	X1	X2	X3	X4	X1	X2	X3	X4
1	-	-	-	-	2	18	18	18
2	+	-	-	-	4	18	18	18
3	-	+	-	-	2	50	18	18
4	+	+	-	-	4	50	18	18
5	-	-	+	-	2	18	50	18
6	+	-	+	-	4	18	50	18
7	-	+	+	-	2	50	50	18
8	+	+	+	-	4	50	50	18
9	-	-	-	+	2	18	18	50
10	+	-	-	+	4	18	18	50
11	-	+	-	+	2	50	18	50
12	+	+	-	+	4	50	18	50
13	-	-	+	+	2	18	50	50
14	+	-	+	+	4	18	50	50
15	-	+	+	+	2	50	50	50
16	+	+	+	+	4	50	50	50

Table B1.2.Levels of experiment factors

Experiment factors	Levels				
	-2	-1	0	1	2
Depolymerization time (Hr) = X1	1	2	3	4	5
Amount of rosin aqueous (% of latex) = X2	2	18	34	50	66
Amount of snowtack 376 (% of latex) = X3	2	18	34	50	66
Amount of snowtack 790A (% of latex) = X4	2	18	34	50	66

The effect of these experiment plans were determined by applying the Yates's algorithm [Box et al.,1978] to the actual experiments. Then, the factors are expanded to a central composite (CCD), as shown in Tables B2 and B3, by introducing the extreme levels (Barker, 1985) : Depolymerization time at 1 and 5 Hr, amount of rosin aqueous at 2 and 66 phr, amount of snowtack 376A at 2 and 66 phr, amount of snowtack 790G at 2 and 66 phr.

Table B1.3.Experimental design planning, codified and actual levels for the central composite design (CCD)

Exp. On	Codified factors				Actual factors			
	X1	X2	X3	X4	X1	X2	X3	X4
17	-2	0	0	0	1	34	34	34
18	+2	0	0	0	5	34	34	34
19	0	-2	0	0	3	2	34	34
20	0	+2	0	0	3	66	34	34
21	0	0	-2	0	3	34	2	34
22	0	0	+2	0	3	34	66	34
23	0	0	0	-2	3	34	34	2
24	0	0	0	+2	3	34	34	66
25	0	0	0	0	3	34	34	34
26	0	0	0	0	3	34	34	34
27	0	0	0	0	3	34	34	34
28	0	0	0	0	3	34	34	34
29	0	0	0	0	3	34	34	34
30	0	0	0	0	3	34	34	34
31	0	0	0	0	3	34	34	34

APPENDIX C

Calculation Method

C.1. Viscosity and Molecular Weight Calculation

The molecular weight of latex was calculated using Mark Houwink Equation (C1-1)

$$[\eta] = KM_v^a \qquad \text{(C-1)}$$

where $[\eta]$ = intrinsic viscosity

K,a = constant

The intersection of relative viscosity and specific viscosity at o% concentration from Appendix A is the intrinsic viscosity. The relation between relative viscosity and intrinsic viscosity and the relation between specific viscosity and intrinsic viscosity are shown in Equation C.1-2 and C.1-3. For example, the intrinsic viscosity of 1 hour of latex depolymerization time is 1.6313. From Figure C.1.1, the molecular weight of 1 hour of latex depolymerization time is 158,852.53.

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \qquad \textbf{(C.1-2)}$$

$$\frac{\ln \eta_r}{c} = [\eta] + k''[\eta]^2 c \qquad \textbf{(C.1-3)}$$

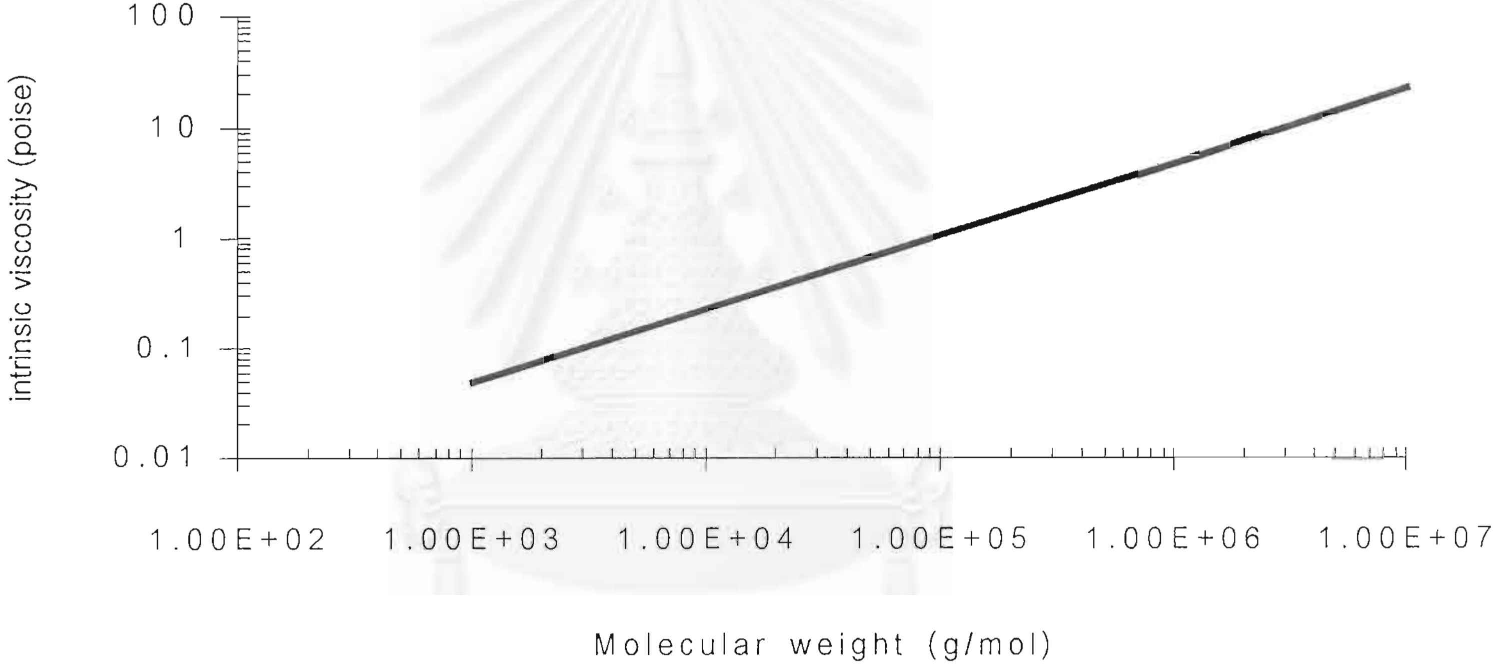


Figure C.1.1 Intrinsic viscosity-molecular weight relationship for natural rubber.

C.2. Estimation of multiple linear regression coefficients

The study of response surface methodology of response of PSA will be carried out by creating mathematical model with 2nd order polynomial equation as below.

$$
\begin{aligned}
Y_o = {} & b_o+b_1x_1+b_2x_2+b_3x_3+b_4x_4+b_{12}x_1x_2+b_{13}x_1x_3+b_{14}x_1x_4+b_{23}x_2x_3 \\
& +b_{24}x_2x_4+b_{34}x_3x_4+b_{11}x_1^2+b_{22}x_2^2+b_{33}X_3^2+b_{44}x_4^2 \qquad \text{(C2-1)}
\end{aligned}
$$

Using multiple linear regression analysis as follows can do the estimation of coefficient of the above equation by matrix calculation.

For example, the result of 180°peel adhesion (Table 5.2.3) can be written in matrix on the next pages.

$$X = \left|\begin{array}{ccccccccccccccc}
X_0 & X_1 & X_2 & X_3 & X_4 & X_1^2 & X_2^2 & X_3^2 & X_4^2 & X_1X_2 & X_1X_3 & X_1X_4 & X_2X_3 & X_2X_4 & X_3X_4 \\
1 & -1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 \\
1 & -1 & 1 & -1 & -1 & 1 & 1 & 1 & 1 & -1 & 1 & -1 & -1 & -1 & -1 \\
1 & 1 & 1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & 1 \\
1 & -1 & -1 & 1 & -1 & 1 & 1 & 1 & 1 & 1 & -1 & 1 & -1 & 1 & -1 \\
1 & 1 & -1 & 1 & -1 & 1 & 1 & 1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 \\
1 & -1 & 1 & 1 & -1 & 1 & 1 & 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 \\
1 & 1 & 1 & 1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & -1 & 1 & -1 & -1 \\
1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & -1 & 1 & -1 & -1 \\
1 & 1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 \\
1 & -1 & 1 & -1 & 1 & 1 & 1 & 1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 \\
1 & 1 & 1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & -1 & 1 & -1 & 1 & -1 \\
1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & 1 \\
1 & 1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & -1 & 1 & 1 & -1 & -1 & 1 \\
1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & -2 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 2 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & -2 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 2 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & -2 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 2 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & -2 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 4 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}\right| ,Y = \left|\begin{array}{c}
1.550 \\ 2.400 \\ 3.800 \\ 3.200 \\ 3.450 \\ 2.700 \\ 4.000 \\ 4.350 \\ 3.650 \\ 3.600 \\ 3.400 \\ 4.300 \\ 4.800 \\ 6.300 \\ 5.600 \\ 5.200 \\ 2.850 \\ 2.550 \\ 1.300 \\ 4.100 \\ 2.150 \\ 4.450 \\ 2.350 \\ 4.950 \\ 3.100 \\ 3.050 \\ 2.950 \\ 3.150 \\ 3.050 \\ 3.050 \\ 2.950
\end{array}\right|$$

Calculating (X'X) and inverse matrix of (X'X) and (X'Y) will get

$X'X =$

$$\left|\begin{matrix}
31 & 0 & 0 & 0 & 0 & 24 & 24 & 24 & 24 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 24 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 24 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 24 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 24 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
24 & 0 & 0 & 0 & 0 & 48 & 16 & 16 & 16 & 0 & 0 & 0 & 0 & 0 & 0 \\
24 & 0 & 0 & 0 & 0 & 16 & 48 & 16 & 16 & 0 & 0 & 0 & 0 & 0 & 0 \\
24 & 0 & 0 & 0 & 0 & 16 & 16 & 48 & 16 & 0 & 0 & 0 & 0 & 0 & 0 \\
24 & 0 & 0 & 0 & 0 & 16 & 16 & 16 & 48 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 16 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 16 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 16 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 16 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 16 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 16
\end{matrix}\right|$$

$X'X^{-1}=$

$$\left|\begin{matrix}
1/7 & 0 & 0 & 0 & 0 & -1/28 & -1/28 & -1/28 & -1/28 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1/24 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1/24 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1/24 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1/24 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1/28 & 0 & 0 & 0 & 0 & 47/1344 & 5/1344 & 5/1344 & 5/1344 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1/28 & 0 & 0 & 0 & 0 & 5/1344 & 47/1344 & 5/1344 & 5/1344 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1/28 & 0 & 0 & 0 & 0 & 5/1344 & 5/1344 & 47/1344 & 5/1344 & 0 & 0 & 0 & 0 & 0 & 0 \\
-1/28 & 0 & 0 & 0 & 0 & 5/1344 & 5/1344 & 5/1344 & 47/1344 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/16 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/16 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/16 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/16 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/16 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1/16
\end{matrix}\right|$$

$$X'Y = \begin{vmatrix} 0y \\ 1y \\ 2y \\ 3y \\ 4y \\ 11y \\ 22y \\ 33y \\ 44y \\ 12y \\ 13y \\ 14y \\ 23y \\ 24y \\ 34y \end{vmatrix} = \begin{vmatrix} 108.8 \\ 1.7 \\ 11 \\ 15.6 \\ 16.1 \\ 84.4 \\ 84.4 \\ 89.2 \\ 92 \\ -0.8 \\ 0.1 \\ 1.6 \\ -1.1 \\ -5.6 \\ 2.9 \end{vmatrix}$$

Therefore, multiple linear regression coefficients can be estimated from

$$b = (X'X)^{-1}(X'Y) = \begin{vmatrix} b_0 \\ b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_{11} \\ b_{22} \\ b_{33} \\ b_{44} \\ b_{12} \\ b_{13} \\ b_{14} \\ b_{23} \\ b_{24} \\ b_{34} \end{vmatrix} = \begin{vmatrix} 3.0428 \\ 0.0500 \\ 0.4583 \\ 0.6291 \\ 0.6917 \\ 0.0487 \\ 0.0487 \\ 0.1987 \\ 0.2861 \\ -0.0812 \\ -0.0250 \\ 0.1312 \\ -0.1000 \\ -0.3188 \\ 0.2125 \end{vmatrix}$$

Therefore, the response surface equation can be written in 2nd order polynomial equation showing the relationship between 180°peel adhesion and the code showing the latex depolymerization time and quantity of tackifiers as in the equation below.

$$Y_{180\text{ peel adhesion}} = 3.043 + 0.05x_1 + 0.458x_2 + 0.629x_3 + 0.692x_4 - 0.081x_1x_2 - 0.025x_1x_3 + 0.131x_1x_4 - 0.1x_2x_3 - 0.319x_2x_4 + 0.212x_3x_4 + 0.049x_1^2 + 0.049x_2^2 + 0.199x_3^2 + 0.286x_4^2$$

For other responses, regression analysis method can also be used to estimate coefficient of response surface equation.

C.3. Analysis of Variance

C.3.1 Total sum of square of responses (y) calculate from

$$SS_T = \sum_{i=1}^{n} y_i^2 - \frac{G^2}{n} \qquad (C.3.-1)$$

$$= (1.550^2+2.400^2+...+3.540^2) - \frac{(1.55 + 2.4 + ... + 3.54)^2}{31}$$

$$= 38.935$$

C.3.2 Regression sum of square calculated from

$$SS_R = SS_{R1} + SS_{R2} \qquad (C.3-2)$$

a. First order term of regression: sum of square calculated from

$$SS_{R1} = \sum_{i=1}^{k} b_i(iy) \qquad (C.3\text{-}3)$$

$$= (0.050)(1.7)+(0.458)(11.5)+(0.629)(15.6)+(0.691)(16.1)$$

$$= 26.084$$

Mean square of coefficient of 1st order term of regression is

$$MS_1 = \frac{SS_{R1}}{k} = 26.084/4 = 6.521 \qquad (C.3\text{-}4)$$

When k is degree of freedom

b. Second order term of regression: sum of square calculated from equation

$$SS_{R2} = b_o(0y)+\sum_{i=1}^{k}\sum_{j=1}^{k} b_{ij}(ijy) - \frac{G^2}{n} \qquad (C.3\text{-}5)$$

$$= (3.043)(108.8)+[(-0.049)(84.4)+(0.049)(84.4)+...+$$

$$(0.212)(2.9)+(0.286)(92) - \frac{(1.55 + 2.4 + ... + 3.54)^2}{31}$$

$$= 6.506$$

Mean square of coefficient of 1st order term of regression is

$$MS_2 = SS_{R2}/(k(k+1)/2) = 6.506/10 = 0.651 \qquad (C.3\text{-}6)$$

When k is degree of freedom

Therefore, regression sum of square can be calculated from equation C.3-2 as follows,

$$SS_R = 26.084+6.506 = 32.59$$

Mean square of coefficient of regression is

$$MS_R = \frac{SS_R}{\frac{k(k+3)}{2}} = \frac{32.59}{14} = 2.328 \qquad (C.3\text{-}7)$$

C.3.3 Error sum of square calculated from

$$SS_E = \sum_{i=1}^{n} (y_i - y_{cal,i})^2 \qquad (C.3\text{-}8)$$

$$= (1.55\text{-}1.614)^2+(2.4\text{-}1.664)^2+...+(2.950\text{-}3.043)^2$$

$$= 6.345$$

and $$MS_E = \frac{SS}{n-1-\frac{k(k+3)}{2}} = \frac{6.345}{16} = 0.396 \qquad (C.3\text{-}9)$$

Pure error sum of square calculated from equation

$$SS_{PE} = \sum_{u=1}^{n} (y_{1u} - \bar{y}_1)^2 \qquad (C.3.10)$$

By $\bar{y}$ is the average of center response equals

$$\bar{y} = \frac{3.1+3.05+2.95+3.15+3.05+3.05+2.95}{7} = 3.04$$

then

$$SS_{PE} = (3.1\text{-}3.043)^2+(3.05\text{-}3.043)^2+...+(2.95\text{-}3.043)^2 = 0.032$$

and

$$MS_{PE} = \frac{SS_{PE}}{n_1-1} = \frac{0.032}{7-1} = 0.005$$

Therefore

$$SS_{LOF} = SS_E - SS_{PE} = 6.345 - 0.032 = 6.313$$

and

$$MS_{LOF} = \frac{SS_{LOF}}{n_2 - \frac{k(k+3)}{2}} = 0.631$$

C.4. Calculation of statistic value of F_o

The test for the significance of regression is a test to determine if there is a linear relationship between the response y and a subset of the independent variable $X_1, X_2, \ldots, X_k$. the appropriate hypotheses are

H_o : $B_1 = B_2 = \ldots = B_k = 0$

H_1 : $B_I \neq 0$ for at least one I

Rejection of H_o in the above equation if $F_c > F_{\alpha, \nu_1, \nu_2}$ implies that at least one variable in the model contributes significantly to the fit. On the other hand, in case H_o is accepted, if $F_o < F_{\alpha, \nu_1, \nu_2}$; H implies that response has no relationship with independent variables $X_1, X_2, \ldots, X_k$.

C.4.1 Statistic value F_o of regression analysis calculated from equation

$$F_o = \frac{MS_R}{MS_E} = \frac{32.59}{6.521} = 5.879 \qquad \text{(C.4-1)}$$

As for the statistic value F_o of SS_{R1} and SS_{R2} can be calculated by the same method

C.5. Calculation of statistic value t_o

There is incessant interest in testing hypotheses on the individual regression coefficients. Such test would be useful in determining the value of each of the independent variables in the regression model.[Montgomery,1984].

The hypotheses for testing the significance of any individual regression coefficient, b_I, are

$$H_o \quad : \quad b_i = 0$$

$$H_I \quad : \quad b_i \neq 0$$

If H_o:b_i = 0 is not rejected, then this indicates that X_I can be deleted from the model. The hypothesis H_o : b_I = 0 is rejected if $t_o >| t|_{\alpha/2,\nu_1}$.

Statistic value t_o of each regression coefficient calculated from

$$t_o = \frac{b_i}{\sqrt{MS_E C_{ii}}} \qquad \text{(C.5-1)}$$

when b_i = coefficient I

MS_E = Mean square of error

C_{ii} = matrix $(X'X)^{-1}$ of i row and i column

For example, statistic value t_o of b_1 coefficient in the response surface equation of 180°peel adhesion to

$$t_o = \frac{0.050}{\sqrt{(0.396)(0.04167)}} = 0.39$$

For statistic value t_o of each b_i coefficient in the response surface equation can be calculated by the same method

C.6 Coefficient of determination

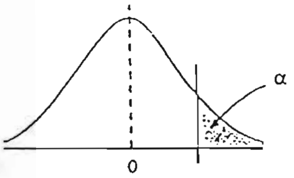
Coefficient of determination of regression analysis of 180°peel adhesion calculated from

$$R^2 = 1- \frac{SS_E}{SS_T} = 1-\frac{6.345}{38.935} = 0.835 \qquad \text{(C.6-1)}$$

APPENDIX D

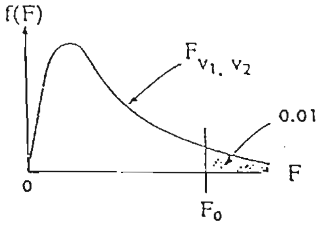
TABLE OF STATISTICAL t AND F DISTRIBUTION

Table D1.1 The critical value of t-distribution.



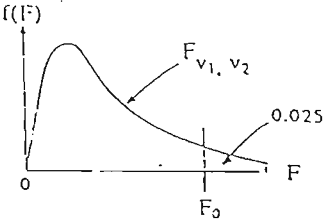
v \ α	.40	.25	.10	.05	.025	.01	.005	.0025	.001	.0005
1	.325	1.000	3.078	6.314	12.706	31.821	63.657	127.32	318.31	636.62
2	.289	.816	1.886	2.920	4.303	6.965	9.925	14.089	23.326	31.598
3	.277	.765	1.638	2.353	3.182	4.541	5.841	7.453	10.213	12.924
4	.271	.741	1.533	2.132	2.776	3.747	4.604	5.598	7.173	8.610
5	.267	.727	1.476	2.015	2.571	3.365	4.032	4.773	5.893	6.869
6	.265	.718	1.440	1.943	2.447	3.143	3.707	4.317	5.208	5.959
7	.263	.711	1.415	1.895	2.365	2.998	3.499	4.029	4.785	5.408
8	.262	.706	1.397	1.860	2.306	2.896	3.355	3.833	4.501	5.041
9	.261	.703	1.383	1.833	2.262	2.821	3.250	3.690	4.297	4.781
10	.260	.700	1.372	1.812	2.228	2.764	3.169	3.581	4.144	4.587
11	.260	.697	1.363	1.796	2.201	2.718	3.106	3.497	4.025	4.437
12	.259	.695	1.356	1.782	2.179	2.681	3.055	3.428	3.930	4.318
13	.259	.694	1.350	1.771	2.160	2.650	3.012	3.372	3.852	4.221
14	.258	.692	1.345	1.761	2.145	2.624	2.977	3.326	3.787	4.140
15	.258	.691	1.341	1.753	2.131	2.602	2.947	3.286	3.733	4.073
16	.258	.690	1.337	1.746	2.210	2.583	2.921	3.252	3.686	4.015
17	.257	.689	1.333	1.740	2.110	2.567	2.898	3.222	3.646	3.965
18	.257	.688	1.330	1.734	2.101	2.552	2.878	3.197	3.610	3.922
19	.257	.688	1.328	1.729	2.093	2.539	2.861	3.174	3.579	3.883
20	.257	.687	1.325	1.725	2.086	2.528	2.845	3.153	3.552	3.850
21	.257	.686	1.323	1.721	2.080	2.518	2.831	3.135	3.527	3.819
22	.256	.686	1.321	1.717	2.074	2.508	2.819	3.119	3.505	3.792
23	.256	.685	1.319	1.714	2.069	2.500	2.807	3.104	3.485	3.767
24	.256	.685	1.318	1.711	2.064	2.492	2.797	3.091	3.467	3.745
25	.256	.684	1.316	1.708	2.060	2.485	2.787	3.078	3.450	3.725
26	.256	.684	1.315	1.706	2.056	2.479	2.779	3.067	3.435	3.707
27	.256	.684	1.314	1.703	2.052	2.473	2.771	3.057	3.421	3.690
28	.256	.683	1.313	1.701	2.048	2.467	2.763	3.047	3.408	3.674
29	.256	.683	1.311	1.699	2.045	2.462	2.756	3.038	3.396	3.659
30	.256	.683	1.310	1.697	2.042	2.457	2.750	3.030	3.385	3.646
40	.255	.681	1.303	1.684	2.021	2.423	2.704	2.971	3.307	3.551
60	.254	.679	1.296	1.671	2.000	2.390	2.660	2.915	3.232	3.460
120	.254	.677	1.289	1.658	1.980	2.358	2.617	2.860	3.160	3.373
∞	.253	.674	1.282	1.645	1.960	2.326	2.576	2.807	3.090	3.291

Table D1.2 The critical value of F-distribution at the level of significant of 0.01



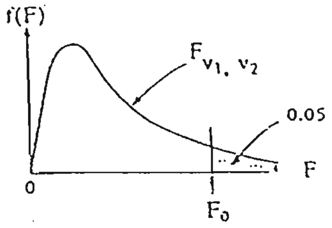
v_2 \ v_1	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
1	4052	4999.5	5403	5625	5764	5859	5928	5982	6022	6056	6106	6157	6209	6235	6261	6287	6313	6339	6366
2	98.50	99.00	99.17	99.25	99.30	99.33	99.36	99.37	99.39	99.40	99.42	99.43	99.45	99.46	99.47	99.47	99.48	99.49	99.50
3	34.12	30.82	29.46	28.71	28.24	27.91	27.67	27.49	27.35	27.23	27.05	26.87	26.69	26.60	26.50	26.41	26.32	26.22	26.13
4	21.20	18.00	16.69	15.98	15.52	15.21	14.98	14.80	14.66	14.55	14.37	14.20	14.02	13.93	13.84	13.75	13.65	13.56	13.46
5	16.26	13.27	12.06	11.39	10.97	10.67	10.46	10.29	10.16	10.05	9.89	9.72	9.55	9.47	9.38	9.29	9.20	9.11	9.02
6	13.75	10.92	9.78	9.15	8.75	8.47	8.26	8.10	7.98	7.87	7.72	7.56	7.40	7.31	7.23	7.14	7.06	6.97	6.88
7	12.25	9.55	8.45	7.85	7.46	7.19	6.99	6.84	6.72	6.62	6.47	6.31	6.16	6.07	5.99	5.91	5.82	5.74	5.65
8	11.26	8.65	7.59	7.01	6.63	6.37	6.18	6.03	5.91	5.81	5.67	5.52	5.36	5.28	5.20	5.12	5.03	4.95	4.86
9	10.56	8.02	6.99	6.42	6.06	5.80	5.61	5.47	5.35	5.26	5.11	4.96	4.81	4.73	4.65	4.57	4.48	4.40	4.31
10	10.04	7.56	6.55	5.99	5.64	5.39	5.20	5.06	4.94	4.85	4.71	4.56	4.41	4.33	4.25	4.17	4.08	4.00	3.91
11	9.65	7.21	6.22	5.67	5.32	5.07	4.89	4.74	4.63	4.54	4.40	4.25	4.10	4.02	3.94	3.86	3.78	3.69	3.60
12	9.33	6.93	5.95	5.41	5.06	4.82	4.64	4.50	4.39	4.30	4.16	4.01	3.86	3.78	3.70	3.62	3.54	3.45	3.36
13	9.07	6.70	5.74	5.21	4.86	4.62	4.44	4.30	4.19	4.10	3.96	3.82	3.66	3.59	3.51	3.43	3.34	3.25	3.17
14	8.86	6.51	5.56	5.04	4.69	4.46	4.28	4.14	4.03	3.94	3.80	3.66	3.51	3.43	3.35	3.27	3.18	3.09	3.00
15	8.68	6.36	5.42	4.89	4.56	4.32	4.14	4.00	3.89	3.80	3.67	3.52	3.37	3.29	3.21	3.13	3.05	2.96	2.87
16	8.53	6.23	5.29	4.77	4.44	4.20	4.03	3.89	3.78	3.69	3.55	3.41	3.26	3.18	3.10	3.02	2.93	2.84	2.75
17	8.40	6.11	5.18	4.67	4.34	4.10	3.93	3.79	3.68	3.59	3.46	3.31	3.16	3.08	3.00	2.92	2.83	2.75	2.65
18	8.29	6.01	5.09	4.58	4.25	4.01	3.84	3.71	3.60	3.51	3.37	3.23	3.08	3.00	2.92	2.84	2.75	2.66	2.57
19	8.18	5.93	5.01	4.50	4.17	3.94	3.77	3.63	3.52	3.43	3.30	3.15	3.00	2.92	2.84	2.76	2.67	2.58	2.49
20	8.10	5.85	4.94	4.43	4.10	3.87	3.70	3.56	3.46	3.37	3.23	3.09	2.94	2.86	2.78	2.69	2.61	2.52	2.42
21	8.02	5.78	4.87	4.37	4.04	3.81	3.64	3.51	3.40	3.31	3.17	3.03	2.88	2.80	2.72	2.64	2.55	2.46	2.36
22	7.95	5.72	4.82	4.31	3.99	3.76	3.59	3.45	3.35	3.26	3.12	2.98	2.83	2.75	2.67	2.58	2.50	2.40	2.31
23	7.88	5.66	4.76	4.26	3.94	3.71	3.54	3.41	3.30	3.21	3.07	2.93	2.78	2.70	2.62	2.54	2.45	2.35	2.26
24	7.82	5.61	4.72	4.22	3.90	3.67	3.50	3.36	3.26	3.17	3.03	2.89	2.74	2.66	2.58	2.49	2.40	2.31	2.21
25	7.77	5.57	4.68	4.18	3.85	3.63	3.46	3.32	3.22	3.13	2.99	2.85	2.70	2.62	2.54	2.45	2.36	2.27	2.17
26	7.72	5.53	4.64	4.14	3.82	3.59	3.42	3.29	3.18	3.09	2.96	2.81	2.66	2.58	2.50	2.42	2.33	2.23	2.13
27	7.68	5.49	4.60	4.11	3.78	3.56	3.39	3.26	3.15	3.06	2.93	2.78	2.63	2.55	2.47	2.38	2.29	2.20	2.10
28	7.64	5.45	4.57	4.07	3.75	3.53	3.36	3.23	3.12	3.03	2.90	2.75	2.60	2.52	2.44	2.35	2.26	2.17	2.06
29	7.60	5.42	4.54	4.04	3.73	3.50	3.33	3.20	3.09	3.00	2.87	2.73	2.57	2.49	2.41	2.33	2.23	2.14	2.03
30	7.56	5.39	4.51	4.02	3.70	3.47	3.30	3.17	3.07	2.98	2.84	2.70	2.55	2.47	2.39	2.30	2.21	2.11	2.01
40	7.31	5.18	4.31	3.83	3.51	3.29	3.12	2.99	2.89	2.80	2.66	2.52	2.37	2.29	2.20	2.11	2.02	1.92	1.80
60	7.08	4.98	4.13	3.65	3.34	3.12	2.95	2.82	2.72	2.63	2.50	2.35	2.20	2.12	2.03	1.94	1.84	1.73	1.60
120	6.85	4.79	3.95	3.48	3.17	2.96	2.79	2.66	2.56	2.47	2.34	2.19	2.03	1.95	1.86	1.76	1.66	1.53	1.38
∞	6.63	4.61	3.78	3.32	3.02	2.80	2.64	2.51	2.41	2.32	2.18	2.04	1.88	1.79	1.70	1.59	1.47	1.32	1.00

Table D1.3 The critical value of F-distribution at the level of significant of 0.025



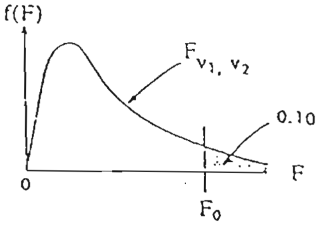
v_2 \ v_1	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
1	647.8	799.5	864.2	899.6	921.8	937.1	948.2	956.7	963.3	968.6	976.7	984.9	993.1	997.2	1001	1006	1010	1014	1018
2	38.51	39.00	39.17	39.25	39.30	39.33	39.36	39.37	39.39	39.40	39.41	39.43	39.45	39.46	39.46	39.47	39.48	39.49	39.50
3	17.44	16.04	15.44	15.10	14.88	14.73	14.62	14.54	14.47	14.42	14.34	14.25	14.17	14.12	14.08	14.04	13.99	13.95	13.90
4	12.22	10.65	9.98	9.60	9.36	9.20	9.07	8.98	8.90	8.84	8.75	8.66	8.56	8.51	8.46	8.41	8.36	8.31	8.26
5	10.01	8.43	7.76	7.39	7.15	6.98	6.85	6.76	6.68	6.62	6.52	6.43	6.33	6.28	6.23	6.18	6.12	6.07	6.02
6	8.81	7.26	6.60	6.23	5.99	5.82	5.70	5.60	5.52	5.46	5.37	5.27	5.17	5.12	5.07	5.01	4.96	4.90	4.85
7	8.07	6.54	5.89	5.52	5.29	5.12	4.99	4.90	4.82	4.76	4.67	4.57	4.47	4.42	4.36	4.31	4.25	4.20	4.14
8	7.57	6.06	5.42	5.05	4.82	4.65	4.53	4.43	4.36	4.30	4.20	4.10	4.00	3.95	3.89	3.84	3.78	3.73	3.67
9	7.21	5.71	5.08	4.72	4.48	4.32	4.20	4.10	4.03	3.96	3.87	3.77	3.67	3.61	3.56	3.51	3.45	3.39	3.33
10	6.94	5.46	4.83	4.47	4.24	4.07	3.95	3.85	3.78	3.72	3.62	3.52	3.42	3.37	3.31	3.26	3.20	3.14	3.08
11	6.72	5.26	4.63	4.28	4.04	3.38	3.76	3.66	3.59	3.53	3.43	3.33	3.23	3.17	3.12	3.06	3.00	2.94	2.88
12	6.55	5.10	4.47	4.12	3.89	3.73	3.61	3.51	3.44	3.37	3.28	3.18	3.07	3.02	2.96	2.91	2.85	2.79	2.72
13	6.41	4.97	4.35	4.00	3.77	3.60	3.48	3.39	3.31	3.25	3.15	3.05	2.95	2.89	2.84	2.78	2.72	2.66	2.60
14	6.30	4.86	4.24	3.89	3.66	3.50	3.38	3.29	3.21	3.15	3.05	2.95	2.84	2.79	2.73	2.67	2.61	2.55	2.49
15	6.20	4.77	4.15	3.80	3.58	3.41	3.29	3.20	3.12	3.06	2.96	2.86	2.76	2.70	2.64	2.59	2.52	2.46	2.40
16	6.12	4.69	4.08	3.73	3.50	3.34	3.22	3.12	3.05	2.99	2.89	2.79	2.68	2.63	2.57	2.51	2.45	2.38	2.32
17	6.04	4.62	4.01	3.66	3.44	3.23	3.16	3.06	2.98	2.92	2.82	2.72	2.62	2.56	2.50	2.44	2.38	2.32	2.25
18	5.98	4.56	3.95	3.61	3.38	3.22	3.10	3.01	2.93	2.87	2.77	2.67	2.56	2.50	2.44	2.38	2.32	2.26	2.19
19	5.92	4.51	3.90	3.56	3.33	3.17	3.05	2.96	2.88	2.82	2.72	2.62	2.51	2.45	2.39	2.33	2.27	2.20	2.13
20	5.87	4.46	3.86	3.51	3.29	3.13	3.01	2.91	2.84	2.77	2.68	2.57	2.46	2.41	2.35	2.29	2.22	2.16	2.09
21	5.83	4.42	3.82	3.48	3.25	3.09	2.97	2.87	2.80	2.73	2.64	2.53	2.42	2.37	2.31	2.25	2.18	2.11	2.04
22	5.79	4.38	3.78	3.44	3.22	3.05	2.93	2.84	2.76	2.70	2.60	2.50	2.39	2.33	2.27	2.21	2.14	2.08	2.00
23	5.75	4.35	3.75	3.41	3.18	3.02	2.90	2.81	2.73	2.67	2.57	2.47	2.36	2.30	2.24	2.18	2.11	2.04	1.97
24	5.72	4.32	3.72	3.38	3.15	2.99	2.87	2.78	2.70	2.64	2.54	2.44	2.33	2.27	2.21	2.15	2.08	2.01	1.94
25	5.69	4.29	3.69	3.35	3.13	2.97	2.85	2.75	2.68	2.61	2.51	2.41	2.30	2.24	2.18	2.12	2.05	1.98	1.91
26	5.66	4.27	3.67	3.33	3.10	2.94	2.82	2.73	2.65	2.59	2.49	2.39	2.28	2.22	2.16	2.09	2.03	1.95	1.88
27	5.63	4.24	3.65	3.31	3.08	2.92	2.80	2.71	2.63	2.57	2.47	2.36	2.25	2.19	2.13	2.07	2.00	1.93	1.85
28	5.61	4.22	3.63	3.29	3.06	2.90	2.78	2.69	2.61	2.55	2.45	2.34	2.23	2.17	2.11	2.05	1.98	1.91	1.83
29	5.59	4.20	1.61	3.27	3.04	2.88	2.76	2.67	2.59	2.53	2.43	2.32	2.21	2.15	2.09	2.03	1.96	1.89	1.81
30	5.57	4.18	3.59	3.25	3.03	2.87	2.75	2.65	2.57	2.51	2.41	2.31	2.20	2.14	2.07	2.01	1.94	1.87	1.79
40	5.42	4.05	3.46	3.13	2.90	2.74	2.62	2.53	2.45	2.39	2.29	2.18	2.07	2.01	1.94	1.88	1.80	1.72	1.64
60	5.29	3.93	3.34	3.01	2.79	2.63	2.51	2.41	2.33	2.27	2.17	2.06	1.94	1.88	1.82	1.74	1.67	1.58	1.48
120	5.15	3.80	3.23	2.89	2.67	2.52	2.39	2.30	2.22	2.16	2.05	1.94	1.82	1.76	1.69	1.61	1.53	1.43	1.31
∞	5.02	3.69	3.12	2.79	2.57	2.41	2.29	2.19	2.11	2.05	1.94	1.83	1.71	1.64	1.57	1.48	1.39	1.27	1.00

Table D1.4 The critical value of F-distribution at the level of significant of 0.05



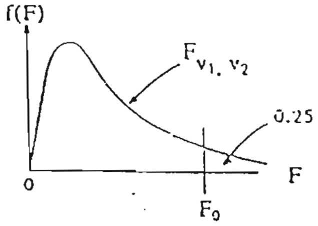
v_2 \ v_1	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5	241.9	243.9	245.9	248.0	249.1	250.1	251.1	252.2	253.3	254.3
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.41	19.43	19.45	19.45	19.46	19.47	19.48	19.49	19.50
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.74	8.70	8.66	8.64	8.62	8.59	8.57	8.55	8.53
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.77	5.75	5.72	5.69	5.66	5.63
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.53	4.50	4.46	4.43	4.40	4.36
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.84	3.81	3.77	3.74	3.70	3.67
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.57	3.51	3.44	3.41	3.38	3.34	3.30	3.27	3.23
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.12	3.08	3.04	3.01	2.97	2.93
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.90	2.86	2.83	2.79	2.75	2.71
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.85	2.77	2.74	2.70	2.66	2.62	2.58	2.54
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.61	2.57	2.53	2.49	2.45	2.40
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.51	2.47	2.43	2.38	2.34	2.30
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.42	2.38	2.34	2.30	2.25	2.21
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.35	2.31	2.27	2.22	2.18	2.13
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.29	2.25	2.20	2.16	2.11	2.07
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.24	2.19	2.15	2.11	2.06	2.01
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.19	2.15	2.10	2.06	2.01	1.96
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.15	2.11	2.06	2.02	1.97	1.92
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.11	2.07	2.03	1.98	1.93	1.88
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.08	2.04	1.99	1.95	1.90	1.84
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.25	2.18	2.10	2.05	2.01	1.96	1.92	1.87	1.81
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34	2.30	2.23	2.15	2.07	2.03	1.98	1.94	1.89	1.84	1.78
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32	2.27	2.20	2.13	2.05	2.01	1.96	1.91	1.86	1.81	1.76
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.18	2.11	2.03	1.98	1.94	1.89	1.84	1.79	1.73
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28	2.24	2.16	2.09	2.01	1.96	1.92	1.87	1.82	1.77	1.71
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27	2.22	2.15	2.07	1.99	1.95	1.90	1.85	1.80	1.75	1.69
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25	2.20	2.13	2.06	1.97	1.93	1.88	1.84	1.79	1.73	1.67
28	4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24	2.19	2.12	2.04	1.96	1.91	1.87	1.82	1.77	1.71	1.65
29	4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.72	2.18	2.10	2.03	1.94	1.90	1.85	1.81	1.75	1.70	1.64
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.89	1.84	1.79	1.74	1.68	1.62
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08	2.00	1.92	1.84	1.79	1.74	1.69	1.64	1.58	1.51
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.92	1.84	1.75	1.70	1.65	1.59	1.53	1.47	1.39
120	3.92	3.07	2.68	2.45	2.29	2.17	2.09	2.02	1.96	1.91	1.83	1.75	1.66	1.61	1.55	1.55	1.43	1.35	1.25
∞	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.52	1.46	1.39	1.32	1.22	1.00

Table D1.5 The critical value of F-distribution at the level of significant of 0.10.



v_2 \ v_1	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
1	39.86	49.50	53.59	55.83	57.24	58.20	58.91	59.44	59.86	60.19	60.71	61.22	61.74	62.00	62.26	62.53	62.79	63.06	63.33
2	8.53	9.00	9.16	9.24	9.29	9.33	9.35	9.37	9.38	9.39	9.41	9.42	9.44	9.45	9.46	9.47	9.47	9.48	9.49
3	5.54	5.46	5.39	5.34	5.31	5.28	5.27	5.25	5.24	5.23	5.22	5.20	5.18	5.18	5.17	5.16	5.15	5.14	5.13
4	4.54	4.32	4.19	4.11	4.05	4.01	3.98	3.95	3.94	3.92	3.90	3.87	3.84	3.83	3.82	3.80	3.79	3.78	3.76
5	4.06	3.78	3.62	3.52	3.45	3.40	3.37	3.34	3.32	3.30	3.27	3.24	3.21	3.19	3.17	3.16	3.14	3.12	3.10
6	3.78	3.46	3.29	3.18	3.11	3.05	3.01	2.98	2.96	2.94	2.90	2.87	2.84	2.82	2.80	2.78	2.76	2.74	2.72
7	3.59	3.26	3.07	2.96	2.88	2.83	2.78	2.75	2.72	2.70	2.67	2.63	2.59	2.58	2.56	2.54	2.51	2.49	2.47
8	3.46	3.11	2.92	2.81	2.73	2.67	2.62	2.59	2.56	2.54	2.50	2.46	2.42	2.40	2.38	2.36	2.34	2.32	2.29
9	3.36	3.01	2.81	2.69	2.61	2.55	2.51	2.47	2.44	2.42	2.38	2.34	2.30	2.28	2.25	2.23	2.21	2.18	2.16
10	3.29	2.92	2.73	2.61	2.52	2.46	2.41	2.38	2.35	2.32	2.28	2.24	2.20	2.18	2.16	2.13	2.11	2.08	2.06
11	3.23	2.86	2.66	2.54	2.45	2.39	2.34	2.30	2.27	2.25	2.21	2.17	2.12	2.10	2.08	2.05	2.03	2.00	1.97
12	3.18	2.81	2.61	2.48	2.39	2.33	2.28	2.24	2.21	2.19	2.15	2.10	2.06	2.04	2.01	1.99	1.96	1.93	1.90
13	3.14	2.76	2.56	2.43	2.35	2.28	2.23	2.20	2.16	2.14	2.10	2.05	2.01	1.98	1.96	1.93	1.90	1.88	1.85
14	3.10	2.73	2.52	2.39	2.31	2.24	2.19	2.15	2.12	2.10	2.05	2.01	1.96	1.94	1.91	1.89	1.86	1.83	1.80
15	3.07	2.70	2.49	2.36	2.27	2.21	2.16	2.12	2.09	2.06	2.02	1.97	1.92	1.90	1.87	1.85	1.82	1.79	1.76
16	3.05	2.67	2.46	2.33	2.24	2.18	2.13	2.09	2.06	2.03	1.99	1.94	1.89	1.87	1.84	1.81	1.78	1.75	1.72
17	3.03	2.64	2.44	2.31	2.22	2.15	2.10	2.06	2.03	2.00	1.96	1.91	1.86	1.84	1.81	1.78	1.75	1.72	1.69
18	3.01	2.62	2.42	2.29	2.20	2.13	2.08	2.04	2.00	1.98	1.93	1.89	1.84	1.81	1.78	1.75	1.72	1.69	1.66
19	2.99	2.61	2.40	2.27	2.18	2.11	2.06	2.02	1.98	1.96	1.91	1.86	1.81	1.79	1.76	1.73	1.70	1.67	1.63
20	2.97	2.59	2.38	2.25	2.16	2.09	2.04	2.00	1.96	1.94	1.89	1.84	1.79	1.77	1.74	1.71	1.68	1.64	1.61
21	2.96	2.57	2.36	2.23	2.14	2.08	2.02	1.98	1.95	1.92	1.87	1.83	1.78	1.75	1.72	1.69	1.66	1.62	1.59
22	2.95	2.56	2.35	2.22	2.13	2.06	2.01	1.97	1.93	1.90	1.86	1.81	1.76	1.73	1.70	1.67	1.64	1.60	0.57
23	2.94	2.55	2.34	2.21	2.11	2.05	1.99	1.95	1.92	1.89	1.84	1.80	1.74	1.72	1.69	1.66	1.62	1.59	1.55
24	2.93	2.54	2.33	2.19	2.10	2.04	1.98	1.94	1.91	1.88	1.83	1.78	1.73	1.70	1.67	1.64	1.61	1.57	1.53
25	2.92	2.53	2.32	2.18	2.09	2.02	1.97	1.93	1.89	1.87	1.82	1.77	1.72	1.69	1.66	1.63	1.59	1.56	1.52
26	2.91	2.52	2.31	2.17	2.08	2.01	1.96	1.92	1.88	1.86	1.81	1.76	1.71	1.68	1.65	1.61	1.58	1.54	1.50
27	2.90	2.51	2.30	2.17	2.07	2.00	1.95	1.91	1.87	1.85	1.80	1.75	1.70	1.67	1.64	1.60	1.57	1.53	1.49
28	2.89	2.50	2.29	2.16	2.06	2.00	1.94	1.90	1.87	1.84	1.79	1.74	1.69	1.66	1.63	1.59	1.56	1.52	1.48
29	2.89	2.50	2.28	2.15	2.06	1.99	1.93	1.89	1.86	1.83	1.78	1.73	1.68	1.65	1.62	1.58	1.55	1.51	1.47
30	2.88	2.49	2.28	2.14	2.03	1.98	1.93	1.88	1.85	1.82	1.77	1.72	1.67	1.64	1.61	1.57	1.54	1.50	1.46
40	2.84	2.44	2.23	2.09	2.00	1.93	1.87	1.83	1.79	1.76	1.71	1.66	1.61	1.57	1.54	1.51	1.47	1.42	1.38
60	2.79	2.39	2.18	2.04	1.95	1.87	1.82	1.77	1.74	1.71	1.66	1.60	1.54	1.51	1.48	1.44	1.40	1.35	1.29
120	2.75	2.35	2.13	1.99	1.90	1.82	1.77	1.72	1.68	1.65	1.60	1.55	1.48	1.45	1.41	1.37	1.32	1.26	1.19
∞	2.71	2.30	2.08	1.94	1.85	1.77	1.72	1.67	1.63	1.60	1.55	1.49	1.42	1.38	1.34	1.30	1.24	1.17	1.00

Table D1.6 The critical value of F-distribution at the level of significant of 0.25.



v_2 \ v_1	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
1	5.83	7.50	8.20	8.58	8.82	8.98	9.10	9.19	9.26	9.32	9.41	9.49	9.58	9.63	9.67	9.71	9.76	9.80	9.85
2	2.57	3.00	3.15	3.23	3.28	3.31	3.34	3.35	3.37	3.38	3.39	3.41	3.43	3.43	3.44	3.45	3.46	3.47	3.48
3	2.02	2.28	2.36	2.39	2.41	2.42	2.43	2.44	2.44	2.44	2.45	2.46	2.46	2.46	2.47	2.47	2.47	2.47	2.47
4	1.81	2.00	2.05	2.06	2.07	2.08	2.08	2.08	2.08	2.08	2.08	2.08	2.08	2.08	2.08	2.08	2.08	2.08	2.08
5	1.69	1.85	1.88	1.89	1.89	1.89	1.89	1.89	1.89	1.89	1.89	1.89	1.88	1.88	1.88	1.88	1.87	1.87	1.87
6	1.62	1.76	1.78	1.79	1.79	1.78	1.78	1.78	1.77	1.77	1.77	1.76	1.76	1.75	1.75	1.75	1.74	1.74	1.74
7	1.57	1.70	1.72	1.72	1.71	1.71	1.70	1.70	1.70	1.69	1.68	1.68	1.67	1.67	1.66	1.66	1.65	1.65	1.65
8	1.54	1.66	1.67	1.66	1.66	1.65	1.64	1.64	1.63	1.63	1.62	1.62	1.61	1.60	1.60	1.59	1.59	1.58	1.58
9	1.51	1.62	1.63	1.63	1.62	1.61	1.60	1.60	1.59	1.59	1.58	1.57	1.56	1.56	1.55	1.54	1.54	1.53	1.53
10	1.49	1.60	1.60	1.59	1.59	1.58	1.57	1.56	1.56	1.55	1.54	1.53	1.52	1.52	1.51	1.51	1.50	1.49	1.48
11	1.47	1.58	1.58	1.57	1.56	1.55	1.54	1.53	1.53	1.52	1.51	1.50	1.49	1.49	1.48	1.47	1.47	1.46	1.45
12	1.46	1.56	1.56	1.55	1.54	1.53	1.52	1.51	1.51	1.50	1.49	1.48	1.47	1.46	1.45	1.45	1.44	1.43	1.42
13	1.45	1.55	1.55	1.53	1.52	1.51	1.50	1.49	1.49	1.48	1.47	1.46	1.45	1.44	1.43	1.42	1.42	1.41	1.40
14	1.44	1.53	1.53	1.52	1.51	1.50	1.49	1.48	1.47	1.46	1.45	1.44	1.43	1.42	1.41	1.41	1.40	1.39	1.38
15	1.43	1.52	1.52	1.51	1.49	1.48	1.47	1.46	1.46	1.45	1.44	1.43	1.41	1.41	1.40	1.39	1.38	1.37	1.36
16	1.42	1.51	1.51	1.50	1.48	1.47	1.46	1.45	1.44	1.44	1.43	1.41	1.40	1.39	1.38	1.37	1.36	1.35	1.34
17	1.42	1.51	1.50	1.49	1.47	1.46	1.45	1.44	1.43	1.43	1.41	1.40	1.39	1.38	1.37	1.36	1.35	1.34	1.33
18	1.41	1.50	1.49	1.48	1.46	1.45	1.44	1.43	1.42	1.42	1.40	1.39	1.38	1.37	1.36	1.35	1.34	1.33	1.32
19	1.41	1.49	1.49	1.47	1.46	1.44	1.43	1.42	1.41	1.41	1.40	1.38	1.37	1.36	1.35	1.34	1.33	1.32	1.30
20	1.40	1.49	1.48	1.47	1.45	1.44	1.43	1.42	1.41	1.40	1.39	1.37	1.36	1.35	1.34	1.33	1.32	1.31	1.29
21	1.40	1.48	1.48	1.46	1.44	1.43	1.42	1.41	1.40	1.39	1.38	1.37	1.35	1.34	1.33	1.32	1.31	1.30	1.28
22	1.40	1.48	1.47	1.45	1.44	1.42	1.41	1.40	1.39	1.39	1.37	1.36	1.34	1.33	1.32	1.31	1.30	1.29	1.28
23	1.39	1.47	1.47	1.45	1.43	1.42	1.41	1.40	1.39	1.38	1.37	1.35	1.34	1.33	1.32	1.31	1.30	1.28	1.27
24	1.39	1.47	1.46	1.44	1.43	1.41	1.40	1.39	1.38	1.38	1.36	1.35	1.33	1.32	1.31	1.30	1.29	1.28	1.26
25	1.39	1.47	1.46	1.44	1.42	1.41	1.40	1.39	1.38	1.37	1.36	1.34	1.33	1.32	1.31	1.29	1.28	1.27	1.25
26	1.38	1.46	1.45	1.44	1.42	1.41	1.39	1.38	1.37	1.37	1.35	1.34	1.32	1.31	1.30	1.29	1.28	1.26	1.25
27	1.38	1.46	1.45	1.43	1.42	1.40	1.39	1.38	1.37	1.36	1.35	1.33	1.32	1.31	1.30	1.28	1.27	1.26	1.24
28	1.38	1.46	1.45	1.43	1.41	1.40	1.39	1.38	1.37	1.36	1.34	1.33	1.31	1.30	1.29	1.28	1.27	1.25	1.24
29	1.38	1.45	1.45	1.43	1.41	1.40	1.38	1.37	1.36	1.35	1.34	1.32	1.31	1.30	1.29	1.27	1.26	1.25	1.23
30	1.38	1.45	1.44	1.42	1.41	1.39	1.38	1.37	1.36	1.35	1.34	1.32	1.30	1.29	1.28	1.27	1.26	1.24	1.23
40	1.36	1.44	1.42	1.40	1.39	1.37	1.36	1.35	1.34	1.33	1.31	1.30	1.28	1.26	1.25	1.24	1.22	1.21	1.19
60	1.35	1.42	1.41	1.38	1.37	1.35	1.33	1.32	1.31	1.30	1.29	1.27	1.25	1.24	1.22	1.21	1.19	1.17	1.15
120	1.34	1.40	1.39	1.37	1.35	1.33	1.31	1.30	1.29	1.28	1.26	1.24	1.22	1.21	1.19	1.18	1.16	1.13	1.10
∞	1.32	1.39	1.37	1.35	1.33	1.31	1.29	1.28	1.27	1.25	1.24	1.22	1.19	1.18	1.16	1.14	1.12	1.08	1.00

VITA

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