SYNTHESIS OF NOVEL PRESSURE SENSITIVE ADHESIVES FOR LABEL APPLICATIONS

by

Şükrü Eren

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APPROVED BY:

Assoc. Prof. A. Ersin Acar ....
(Thesis Supervisor)

Assoc. Prof. Havva Yağcı Acar ....

Prof. Selim Küsefoğlu ....

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To My Mom and Dad,

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ABSTRACT

SYNTHESIS OF NOVEL PRESSURE SENSITIVE ADHESIVES FOR LABEL APPLICATIONS

In the label adhesives industry, the accepted pressure sensitive adhesives (PSA) are acrylic based water dispersions. These acrylic polymer emulsions have excellent ultraviolet (UV) and chemical resistance. However, their adhesion values alone are not enough for market requirements. Due to this, producers compound these acrylic polymers with tackifier resin dispersions especially for paper labels. In this study, it is aimed to produce label adhesive using a new approach. The goal is to develop a new one-pot polymerization process for the filmic label market. In one pot system, the purpose is to synthesize ready dispersions for label adhesives by adding the tackifier resin during the polymerization to the acrylic monomer. By doing so, it is hoped to eliminate high cost dispersing machines and high level of surfactants used in the dispersion process of the tackifier resin. Elimination of the surfactant coming from the tackifier resin dispersion is a potential solution for the whitening problem of the filmic labels. Another advantage is to save energy from the high cost dispersing process.

ÖZET

AKRİLAT BAZLI BASINCA DUYARLI ETİKET YAPIŞTIRICALARININ SENTEZİ

Etiket yapıştırıcıları endüstrisinde basınca duyarlı yapıştırıcılar genelde akrilat bazlı su dispersiyonlarıdır. Akrilik polimerler mükemmel kimyasal ve UV dayanımına sahiptirler. Ancak bu polimerlerin yapışma değerleri yalnız başlarına pazar ihtiyaçlarını karşılayabilecek kadar yeterli değildir. Bu yüzden, üreticiler kağıt etiketlerinde kullanılan akrilat polimerlerini yapışkanlık arttırıcı reçine dispersiyonları ile karıştırırlar. Bu araştırmada, yeni bir etiket yapıştırıcısı üretimi amaçlanmıştır. Filmik etiket pazarı için yeni bir polimerizasyon metodunun geliştirilmesi hedeflenilmektedir. Tek basamaklı sentez sistemindeki amaç, yapışkanlık arttırıcı reçineyi akrilik monomer polimerizasyonuna katarak kullanıma hazır etiket yapıştırıcısı dispersiyonların sentezidir. Böylece, yüksek maliyetli dispersiyon hazırlama makinelerinin ve yüksek miktarda kullanılan yüzey aktif maddenin kullanımının çıkarılması kolay olacaktır. Yapışkanlık arttırıcı reçine dispersiyonlarının hazırlanmasında kullanılan yüzey aktif maddenin çıkarılması, filmik etiketlerde yaşanan beyazlama problemi için bir çözümdür. Dispersiyon basamağının çıkarılmasının bir diğer avantajı ise yüksek maliyetli dispersiyon hazırlama makinelerinde kullanılan enerjiden tasarruf edilmesidir.

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LIST OF ACRONYMS/ABBREVIATIONS

M_n	Number average molar mas
M_w	Weight average molar mas
T_g	Glass transition Temperature
AA	Acrylic Acid
AFERA	European Association of The Self Adhesive Tape Industry
BA	Butyl Acrylate
BOPP	Biaxially-oriented Polypropylene
CTAs	Chain Transfer Agents
DCPD	Dicyclopentadiene
DiW	Diionized Water
DOE	Design of Experiment
DSC	Differential Scanning Calorimetry
EA	Ethyl Acrylate
HLB	Hydrophilic Lipophilic Balance
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
MAA	Methacrylic Acid
MMA	Methyl Methacrylate
PSA	Pressure Sensitve Adhesive
RE	Resin Number
SEC	Size Exclusion Chromatography
SS	Stainless Steel
STY	Styrene
TP	Tackifier Package
UV	Ultraviolet
2-EHA	2-EthyHexyl Acrylate

1. INTRODUCTION

1.1. What are Pressure Sensitive Adhesives?

In the history, the first pressure sensitive adhesives were used in medical applications as first aid tools about 150 years ago. In the mid-19th century, scientists added natural rubber to adhesive formulations that consists of just resins and beeswax. Towards the end of 19th century, natural rubber and zinc oxide containing adhesive have been developed. Due to this invention, it has been possible for chemical industry to produce adhesives in large quantities. However, the link between adhesive and solid surface was sometimes weak. Actual reason was the fact that wood rosins used in the formulations had large tendencies towards oxidation and therefore the tack was lost. Modification of the rosin structures was the solution to improve their stabilities [1].

Application of PSAs was limited to medical uses until 1930s. The first electrical insulating tape was developed towards 1930s. The adhesive mass was designed to adhere to itself. The problem with this tape was the lack of the cohesive strength which caused failures during unwinding. An important development in pressure sensitive tapes was in paint masking applications [1].

In World War II, due to lack of natural rubber scientists tried to find new materials. Polyisobutylene was one of the first polymers used instead of natural rubber. Scientists made detailed researches for many years about all other elastomers which can replace natural rubber in pressure sensitive products. As a result, polyacrylates and their copolymers were found to be the best replacements for the natural rubber [1].

There are two major application areas for pressure sensitive adhesives; tapes and labels. Different estimations about the total volume of PSA business have been mentioned. The United States consumption of PSA in 1980s is approximately about $2 billion. For tapes, it is $1.1 billion, while it is $640 million for labels. Large percentage of these products still consists of natural rubber. However, acrylate and styrene-butadiene block copolymers have grown fast and compete with natural rubber [1].

PSAs behave as viscoelastic materials. They are tacky and easily adhere to a variety of substrates via light pressure and short contact time. It is easy to understand that applied light pressure is ultimately essential so as to achieve adequate wet-out onto the solid surface to enable sufficient adhesion [2]. Tapes, labels, and protective films are some common PSA products. Even though PSAs can be produced by several methods such as solution polymerization, hot-melt processes, in recent years huge level of attention has been committed to the more environmentally friendly processes; acrylate based emulsion polymerization [3].

1.1.1. Pressure Sensitive Tapes

Tapes are the most important pressure sensitive products and have the largest volume all over the world (Figure 1.1). Classification of tapes can be done according to their area of application or their composition. The tapes may be categorized according to their composition into the following classes [1].

- Fabric tapes
- Paper tapes
- Film tapes
- Nonwoven fabric tapes
- Foil tapes
- Reinforced tapes
- Foam tapes
- Two-faced tapes
- Transfer tapes

Tapes can be categorized according to their function, in other words according their uses [1].

- Hospital and first aid tapes
- Office and graphic tapes
- Packaging and surface protection

- Building industry products
- Electrical tapes
- Automotive industry products
- Shoe industry tapes
- Appliance industry products
- Splicing tapes
- Corrosion protective tapes
- Miscellaneous tapes and pressure sensitive products

Figure 1.1. Tapes [4].

1.1.2. Pressure Sensitive Labels

One of the most widespread applications of pressure sensitive adhesives is in labels (Figure 1.2). In 1987, the most important pressure sensitive product in Europe was label. Label market in Europe was estimated as approximately 70% of the total PSA market. Labels are one the most considerable tools in the advertisement to support the sales [5].

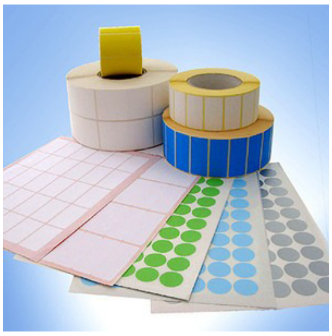


Figure 1.2. Paper labels [6].

Natural rubber-resin and acrylics are the major formulations for pressure sensitive labels. In the beginning, rubber-resin PSAs coming from natural raw materials were manufactured in large scales. These products had good performance in terms of adhesion but they failed in terms of resistance to the aging. Acrylics and carboxylated styrene-butadiene dispersions were introduced to the market with their higher performances and lower prices. Acrylics adhesives can be produced *via* solvent-based, water based and hot melt formulations. Labeling is one of the most important application areas for water born acrylic polymers [5].

1.2. Emulsion Polymerization

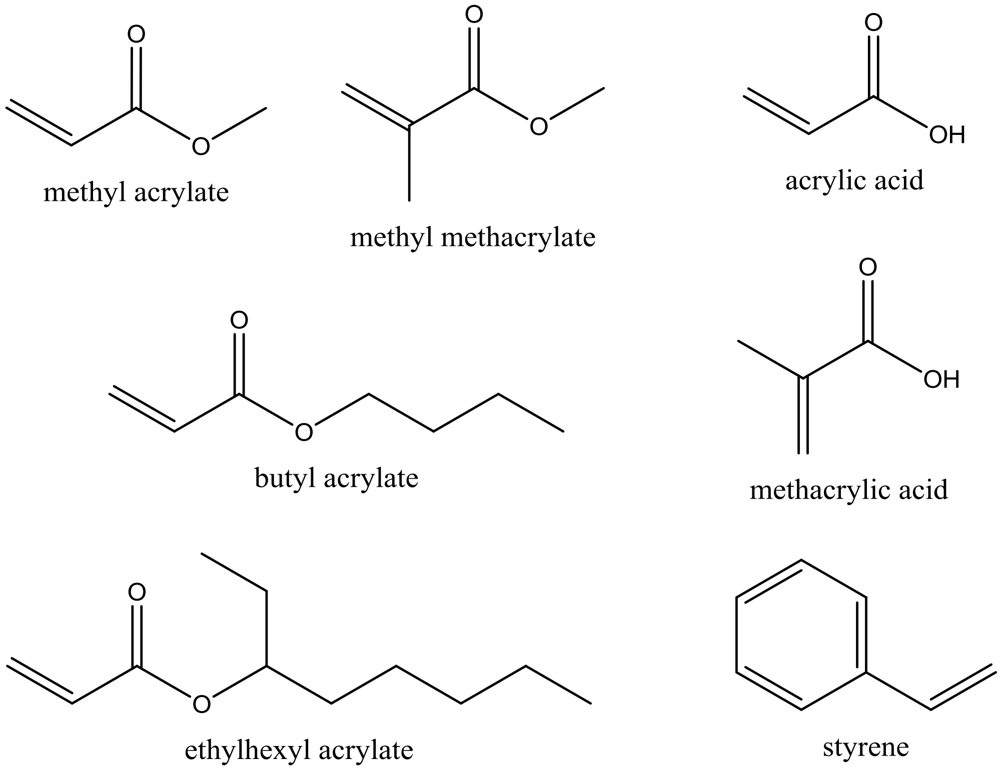
Free radical polymerization is the most widely used polymerization technique in chemical industry because of the ease of processibility. It is used for bulk polymerization processes like emulsion polymerization processes in which waterborne polymers are produced. With the help of emulsion polymerization, polymers are well dispersed in water during the production. The aqueous polymer dispersion is called as latex [7].

Basic component of emulsion polymerization is an emulsion consisting of two phases; the dispersed (oil) phase and aqueous phase. Oil phase includes monomer and monomer soluble particles, and continuous phase, in general water, and contains water soluble components. In addition, there are other components added to the polymerization at the beginning and/or at the end of the process. The main components of an emulsion polymerization are listed below [8].

- Monomers and Comonomers
- Crosslinkers
- Surfactants
- Initiators
- Buffer agents
- Water
- Chain Transfer Agents (CTAs)
- Antioxidants and UV Stabilizers

- Biocides

The basic component of emulsion polymerization is monomers and comonomers shown in Figure 1.3. The selection of the monomers is done according to the application and performance requirements. Monomers used in emulsion polymerization generally are styrenics, acrylics, methacrylics, vinyl acetate, vinyl chloride, acrylonitrile, butadiene and some special functional monomers [8].


methyl acrylate

methyl methacrylate

acrylic acid

butyl acrylate

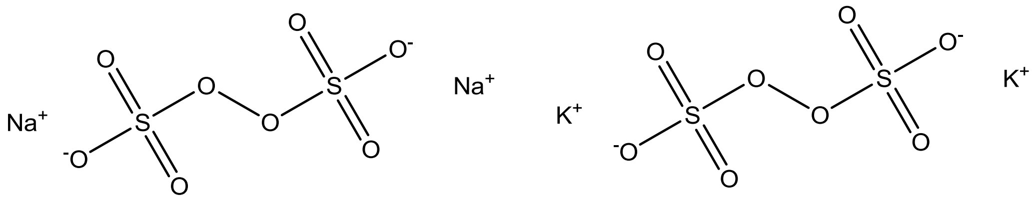
methacrylic acid

ethylhexyl acrylate

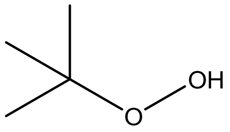
styrene

Figure 1.3. Structures of acrylic monomers.

Initiators used in emulsion polymerization are water soluble persulfates such as sodium persulfate, ammonium persulfate and potassium persulfate and hydroperoxides like *tert*-butyl hydroperoxide as shown in Figure 1.4. Selection of initiators is done according to reaction temperature. In general, hydroperoxides are used in reduction-oxidation systems to generate radicals at lower temperatures [8].



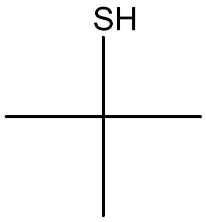
sodium persulfate potassium persulfate



tert-butyl hydroperoxide

Figure 1.4. Common initiators used in acrylic systems.

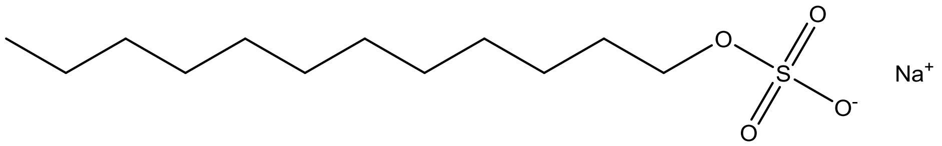
Chain transfer agent such as *tert*-butyl mercaptan as shown in Figure 1.5 is dissolved in oil phase to reduce the molecular weight of the final polymers *via* abstraction of radicals from growing chains. On the other hand, to improve the chemical and physical properties of latexes, crosslinker monomers are used. Acrylamide and divinyl benzene are two examples of such crosslinker monomers. In emulsion polymerization, pH plays an important role and buffer reagents such as sodium bicarbonate are used to set pH [8].



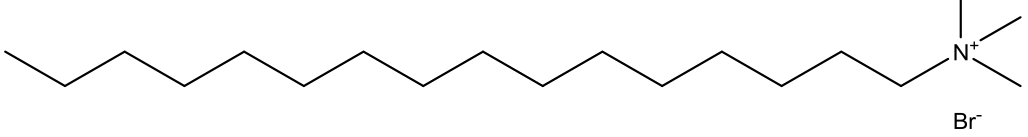
tert-butyl mercaptan

Figure 1.5. Structure of commercial chain transfer agent.

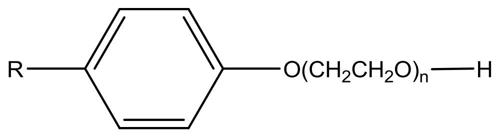
Another important component of emulsion polymerization is the surface active agents, surfactants. Surfactants, often named as emulsifiers by the industry, have an essential role in the preparation of the emulsion and the polymerization process. Surfactants control the particle size and they promote colloidal stability. Anionic surfactants such as sodium dodecyl sulfate, cationic surfactants such cetyltrimethylammonium bromide and non-ionic surfactants such as polyoxyethylenated alkylphenols are the most common surfactants; sometimes used together to improve the stability of emulsions used in the polymerization processes (Figure 1.6). Selection and the amount of surfactants is done by considering variables such as hydrophilic/lipophilic balance (HLB) values, the type of polymerization process and the target particle size. In general, surfactants with HLB values bigger than 7 are used in the conventional emulsion polymerization which is oil in water type. On the other hand, ones with HLB values smaller than 7 are used in the inverse emulsion polymerization which is water in oil type. As mentioned before, sometimes surfactants are used together to improve the stability of emulsion. In industry, anionic and non-ionic surfactants including formulations are common. In these formulations, anionic surfactant controls the nucleation stage in the emulsion polymerization; on the other hand, non-ionic surfactant contributes to the additional electrolyte tolerance, mechanical shear stability and freeze-thaw stability. In addition to all these surfactants, there are specially modified surfactants such as surfmers which have unsaturation on their structure to react with radicals, inisurfs having reactive groups behaving as an initiator, transurfs that contain reactive groups acting as chain transfer agents [8].



sodium dodecyl sulfate (anionic surfactant)



cetyltrimethylammonium bromide (cationic surfactant)



polyoxyethylenated alkylphenols (non-ionic surfactants)
R=Nonyl and n=5, 10, 15

Figure 1.6. Structures of surfactants.

From the most general point of view, emulsions can be categorized in two classes; oil in water and water in oil emulsions (Figure 1.7). By using a certain HLB value surfactants, oil in water emulsions (HLB value >7) and water in oil emulsions (HLB value <7) can be prepared. In conventional emulsion polymerization, oil in water type emulsions is used, water in oil emulsions are used for inverse emulsion polymerization processes [8].

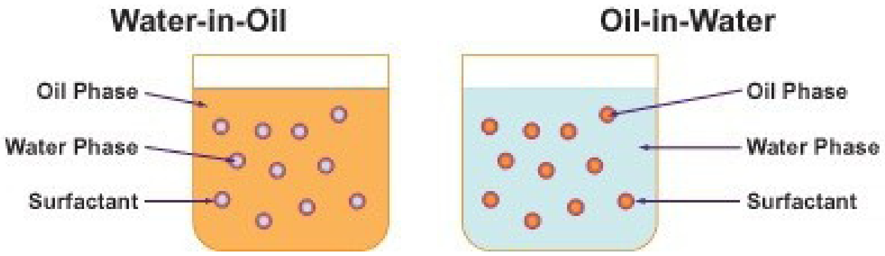


Figure 1.7. Water-in-Oil and Oil-in-Water emulsions [9].

Emulsion polymers can be produced with different kinds of processes. Mechanical and physical properties of polymer latexes are affected by the type of the process. The major types of emulsion polymerization conducted both in industry and in scientific world are listed below [7].

- Conventional emulsion polymerization
- Inverse emulsion polymerization
- Miniemulsion polymerization
- Dispersion polymerization
- Microemulsion polymerization

The most common type of emulsion polymerization process used in the production of commercial water-born emulsion polymers is the conventional one [7].

1.2.1. Conventional Emulsion Polymerization

In this method, generally, mixtures of monomers are dispersed in aqueous phase with the help of an appropriate emulsifier. There are two types of conventional emulsion polymerization according to how the monomers are fed to the polymerization; batch emulsion polymerization and semi-continuous emulsion polymerization [7].

In batch emulsion polymerization all components of an emulsion polymerization are loaded in a reactor prior to the reduction and oxidation (redox) initiator systems. Once the redox initiator is introduced, there are three basic intervals in a batch polymerization as described by Smith and Ewart, and Harkins in early 20th century [10, 11]. In particle nucleation interval which is Interval I, a water soluble initiator is introduced to aqueous phase and hydrophobic oligoradicals are formed. In Interval II which is polymer particle growth, monomer droplets become smaller and smaller due to the migration of monomer to the propagation reactions. In this interval, growing hydrophobic polymer chains in water are surrounded by the surface active agents to form polymer particles. In Interval III, all monomer droplets in the beginning are disappeared and all free monomers go into the polymer particles (Figure 1.8) [7].

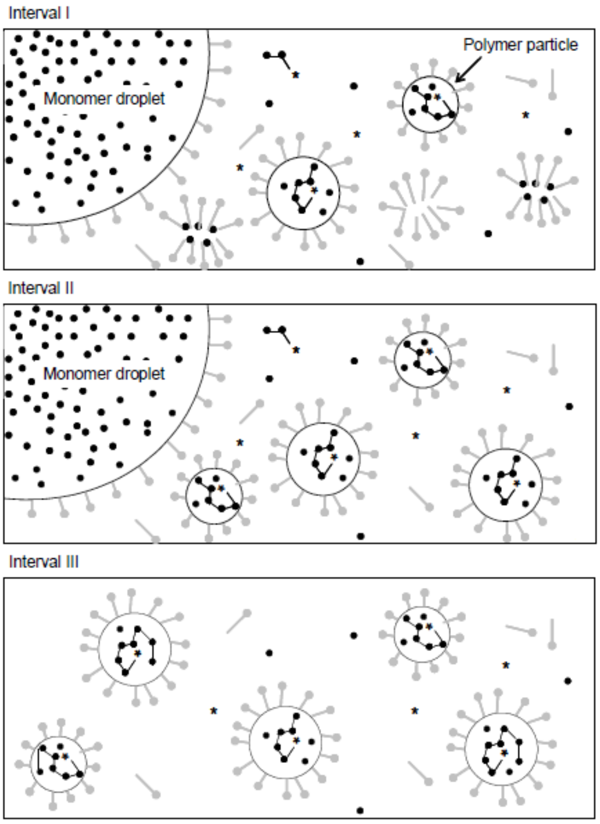


Figure 1.8. Intervals of batch emulsion polymerization [7].

In addition to all these, it is important to indicate that manufacturers use seeded version of batch polymerization as shown in Figure 1.9 in order to start their production from Interval II. Seed is often a short length polymer used to control the particle size [7].

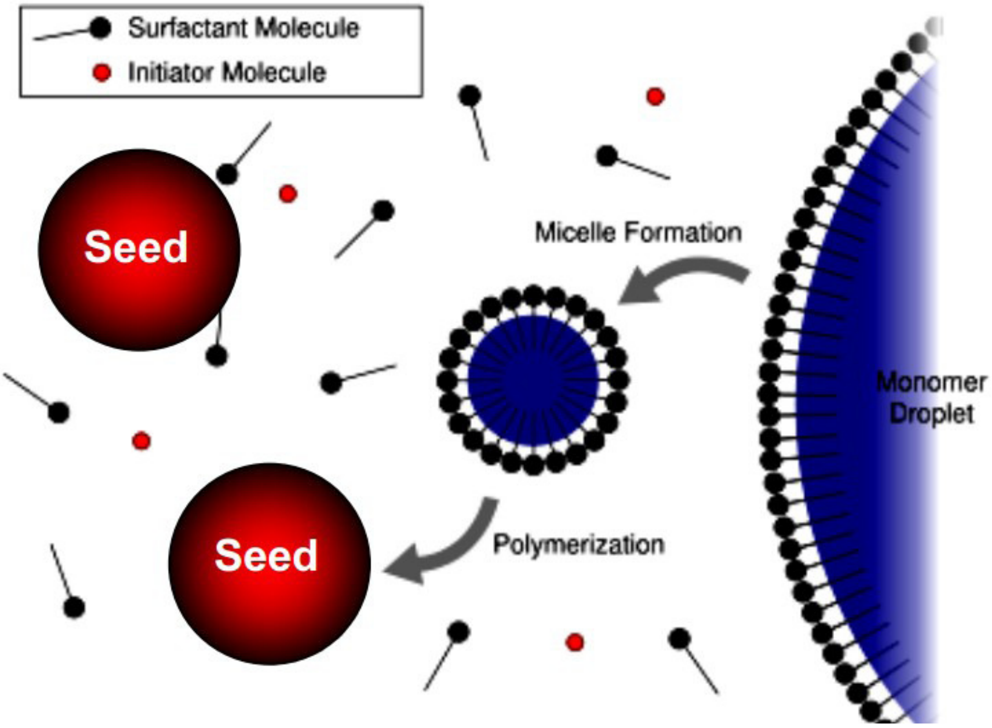


Figure 1.9. Seeded batch emulsion polymerization [12].

In a semi-continuous process, unlike the batch one, monomer emulsion, initiator and buffer solutions are fed into the reactor during the polymerization [7].

Semi-continuous method has some advantages over the batch polymerization. It is the most feasible process for manufacturers because semi-continuous process enables both the molecular weight control and the particle size control. Thus, size distribution and particle morphologies become similar due to this type of process [7].

Similar to the seeded batch polymerization, latex producers often use the seeding techniques in the semi-continuous process [7].

1.2.2. Miniemulsion Polymerization

Another important process type for emulsion polymerization is miniemulsion polymerization process (Figure 1.10). Miniemulsion process is not used in the industry extensively. However, there are some commercial products synthesized *via* miniemulsion process [8].

Small monomer droplets with high stability in the aqueous phase which are obtained with high shear mixers forms the miniemulsion systems. Miniemulsions are kinetically stable. In other words, they are more stable than the one used in conventional emulsion polymerization. Primary differences between conventional emulsion polymerization and miniemulsion process are the droplet nucleation. In miniemulsion polymerization, water soluble radicals enter the stabilized small monomer droplets and polymerization occurs there [8].

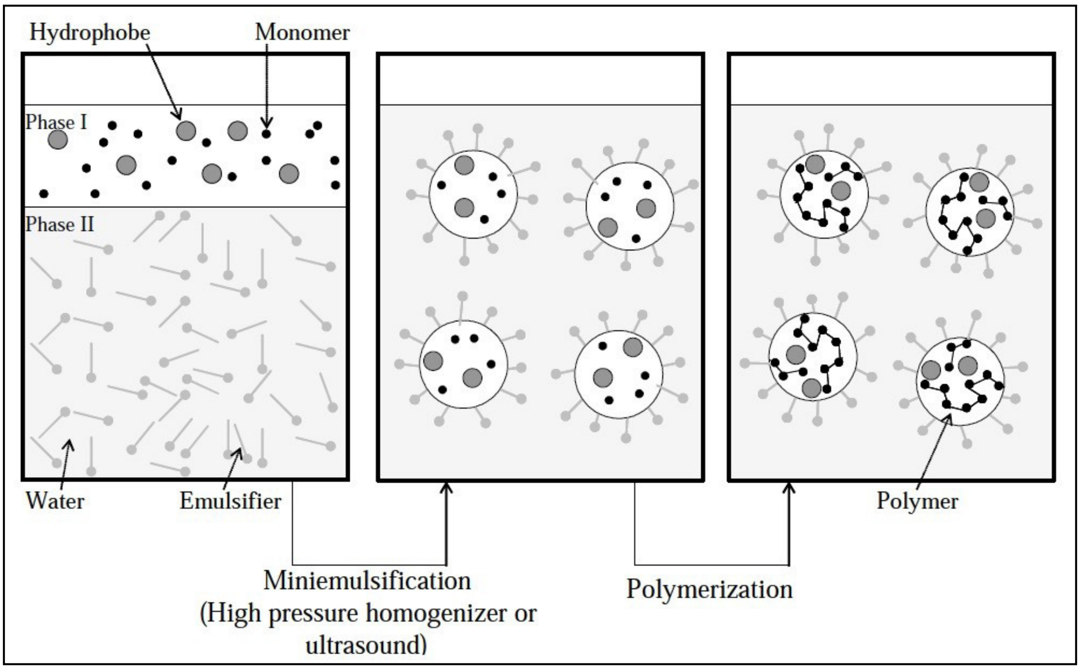


Figure 1.10. Miniemulsion polymerization [7].

Furthermore, water insoluble components like tackifying resins can be added to polymerization thanks to miniemulsion polymerization process. In 1996, Wang and Schork disclosed that acrylic monomers in the presence of alkyd resins can be polymerized [13]. Studies conducted with miniemulsion polymerization technique in the presence of unsaturated resins demonstrated that such resins behaved as chain transfer agents [14].

1.3. Tackifying Resin Chemistry

Resins are usually low molecular weight chemicals. Their major applications are in adhesives, inks and chewing gum. In adhesive application, resins are used to attain high tack and adhesion values. Manufacturers use resins to create the best balance between adhesion and cohesion. On the market, there are various commercial resins used in adhesive applications [15].

Tackifying resins can be classified into three groups: hydrocarbon resins, rosin resins and terpene resins. Hydrocarbon resins are originally coming from petroleum feedstock. Rosin resins are often collected from pine trees. Terpene resins are synthesized from natural sources, wood turpentine or from the kraft sulphate pulping process [15].

1.3.1. Rosin Resins

One of the oldest raw materials for the adhesives industry is rosin or converted version rosin ester. Three types of rosin are used by the resin manufacturers, gum rosin, wood rosin and tall oil rosin, all generated from the pine trees. Rosin resins are not polymers. They are a mixture of different molecules (Figure 1.11). These molecules have poor stability due to the unsaturation. Stability can be enhanced *via* different techniques just as hydrogenation or esterification (Figure 1.12) [15].

Abietic acid and alcohols are used to generate various types of rosin esters. The molecular weight of the alcohol determines the softening point of the rosin ester. In rosin ester production, glycerol and pentaerythritol are the most frequently used alcohols. On the other hand, methanol and triethylene glycol are also used to produce rosin esters, but they have lower softening points [15].

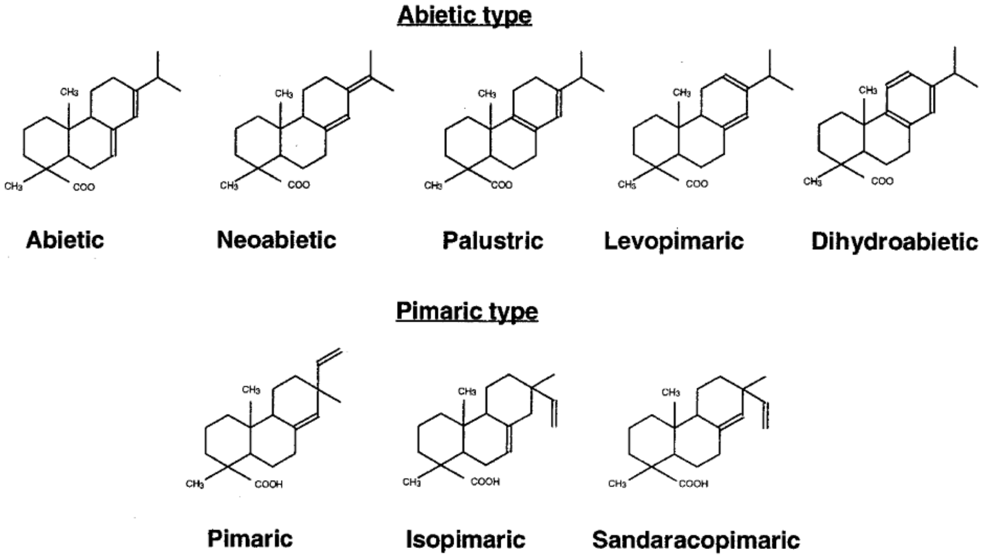


Figure 1.11. Rosin Molecules [15].

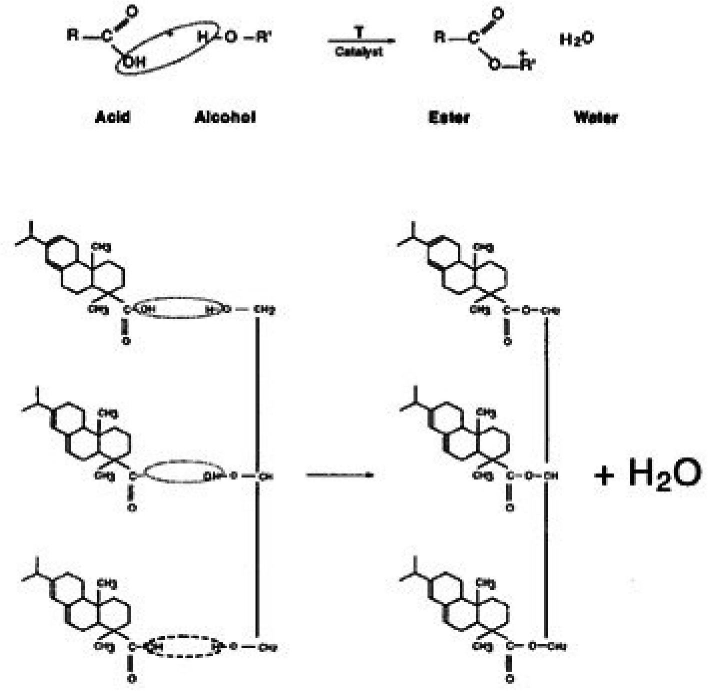


Figure 1.12. Esterification of glycerol with rosin molecules [15].

The esterification reaction is an equilibrium reaction. Thus, there are always some unreacted acid and hydroxyl groups. Acid number of a pure rosin acid is generally around 170. A glycerol ester typically has an acid value below 20. This indicates that the there are unreacted acids in a glycerol ester. Softening points for glycerol esters are around 85°C. On the other hand, esters of pentaerythritol are around 105°C. Softening points and acid values affect the resin compatibility [15].

Rosin resins are compatible with almost all polymers. They contribute to peel and tack performances of adhesives but they partially decrease the cohesive strength of latexes [15].

1.3.2. Terpene Resins

Terpene resins are generally polymers of α-pinene, β-pinene and d-limonene whose structures are shown in Figure 1.13. Advantages of these resins are as follows; excellent initial color and availability of resins with different softening points. Furthermore, there are other resins originated from these terpene resins such as styrenated terpenes, terpene phenolics and hydrogenated terpenes [15].

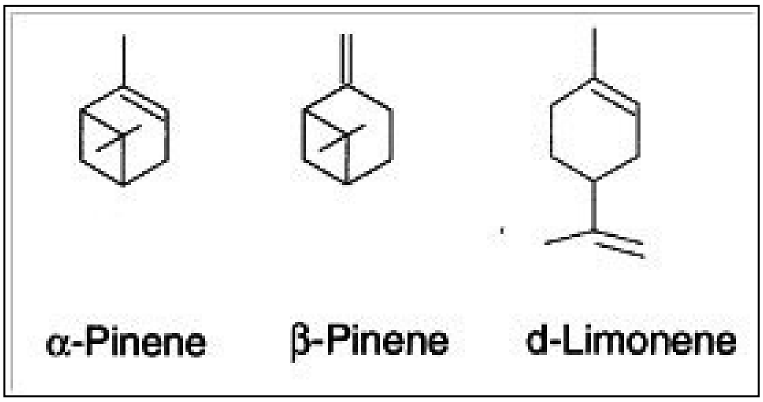


Figure 1.13. Structures of α-pinene, β-pinene and d-limonene [15].

1.3.3. Hydrocarbons Resins

Hydrocarbons resins are another type of commercial resins. Their origin is petroleum stocks. There are four essential classes of hydrocarbon resins: aliphatic resins with 5 carbon atom, aromatic resins with 9 carbon atoms, cycloaliphatic resins dicyclopentadiene (DCPD) and hydrogenated hydrocarbon resins [15].

1.4. Production Process of Pressure Sensitive Adhesives

Pressure sensitive adhesives are produced using various processes such as solvent based, water based and hot melt. There are some advantages and disadvantages of each process. Solvent based adhesives have better tack performances than water based acrylic adhesives. However, water based acrylic adhesives are environmentally more friendly. Thus, water based acrylic adhesive manufacturers and label producers use tackifier resins to reach tack performances of solvent based adhesives.

In the production of labels, manufacturers mix the acrylic emulsions with tackifier dispersions (Figure 1.14). They use tackifier dispersions because tackifiers are not soluble in aqueous acrylic emulsions. With the help of tackifier dispersion, water based acrylic adhesives reach the intended tack performances. However, there are some difficulties in this process. The essential difficulty is the use of high speed mixers which consume a considerable amount of energy in the preparation of the tackifier dispersion. Moreover, this process has an important disadvantage which is the excessive use of surfactants in the preparation of tackifier dispersion. Use of excess amount of surfactant creates whitening problems, in labels in contact with water.

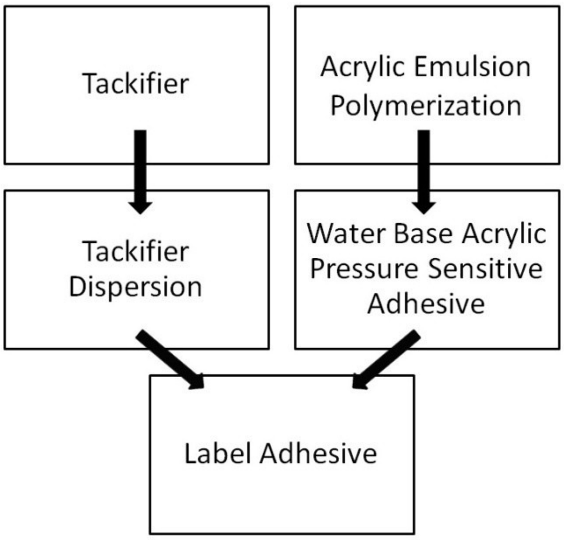


Figure 1.14. Production process of water borne label adhesive.

Water based acrylic polymers are mainly composed of three type of monomers. One of them is acrylic or methacrylic esters such as 2-ethyl hexyl acrylate (2-EHA) and butyl acrylate (BA) with 4-17 carbon atoms with low glass transition temperature (T_g). They are soft monomers and they trigger the adhesion. Another type of monomer used is acrylic acid (AA) or methacrylic acid (MAA). They increase bonding to the applied surface through hydrogen bondings. The final monomer type is T_g modifier monomers like metyl methacrylate (MMA) and styrene (STY) (Figure 1.15) [16].

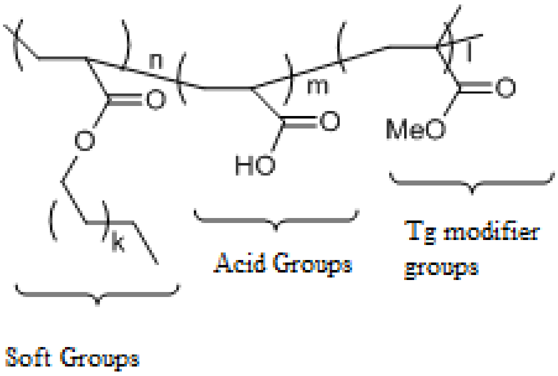


Figure 1.15. Basic components of water borne acrylic adhesives [16].

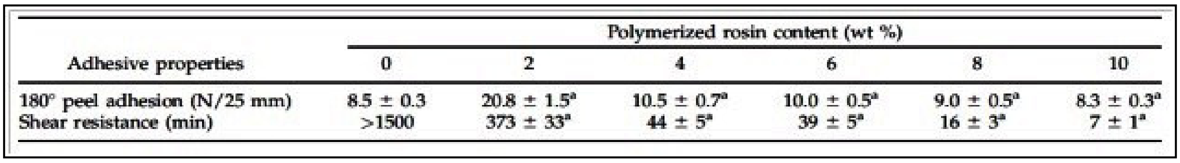
1.5. Synthesis of Water Based Acrylic Adhesives in The Presence of Tackifiers

The adhesives industry tried different approaches to overcome the difficulties of preparation of water based acrylic label adhesives. One of the techniques employed is running the emulsion polymerization in the presence of tackifiers. This is known as the *in-situ* polymerization technique.

In the Exxon 1993 patent, polymerization in the presence of a tackifier and a crosslinker having multiple functions is disclosed. The novelty in this patent is to dissolve solid tackifier and crosslinker in monomer prior to the preparation of the emulsion. In this patent, tackifiers which includes at least 10% aromatic structure are protected and ready to use crosslinked acrylic adhesives are claimed [17]. In the Sony Chemicals patent (2001), a different process was undertaken to overcome the dispersion issues. In this patent, emulsion polymerization was conducted with two unlike emulsions. These emulsions consisted of at most 6% tackifier content. Performance results of polymers synthesized with these emulsions were sufficient [18]. Eastman Chemical Company in 2004 disclosed the miniemulsion process where the polymerization was carried out in the presence of a tackifier. In this patent, 50-500 nm scale miniemulsions are protected [19]. One of the recent patents related to this topic belongs to Cyctec Company. According to this patent (2010), emulsion polymerization in the presence of a tackifier can be achieved *via* miniemulsion process. Only difference of this patent from one of Eastman is the particle size of the miniemulsion [20].

Pingxu and Xingrong recently have disclosed that water based acrylic adhesive can be successfully synthesized with an emulsion containing rosin resin by seeded semi-continuous process. In this study, it is concluded that with the increase of the rosin content, the monomer conversion, gel fraction of polymer and sol molecular weight decreased due to the chain transfer and inhibition reactions caused by the abietic acid. 2% weight rosin gives improved wetting of the adhesive on substrate which means an increase of peel adhesion. The peel adhesion and shear resistance decreased with the increase of rosin content (Table 1.1) [21].

Table 1.1. Pingxu and Xingrong peel and shear performance analysis to polymerized rosin containing emulsion polymers [21].



Adhesive properties	Polymerized rosin content (wt %)					
	0	2	4	6	8	10
180° peel adhesion (N/25 mm)	8.5 ± 0.3	20.8 ± 1.5[a]	10.5 ± 0.7[a]	10.0 ± 0.5[a]	9.0 ± 0.5[a]	8.3 ± 0.3[a]
Shear resistance (min)	>1500	373 ± 33[a]	44 ± 5[a]	39 ± 5[a]	16 ± 3[a]	7 ± 1[a]

1.6. Various Parameters Affecting Emulsion and *In-situ* Polymerizations

As mentioned before, emulsion polymerization is the most common polymerization technique used in paint, adhesive and construction industries. One of the essential reasons why emulsion polymerization process is so common lies on the fact that manufacturers can change the chemical and physical properties of their products by changing different parameters in polymerization. These factors are monomer and comonomers compositions, feeding time of monomer emulsions to the reactor, amount of seed and initiator, type and amount of surface active agents. In addition to these, for *in-situ* polymerization, tackifier amount plays an essential role for the final performances of the adhesive emulsion [7].

1.6.1. Effects of Monomer and Comonomer Compositions

The most important variable in emulsion polymerization is monomers. Most of the time, soft monomers such as 2-EHA and BA that generate low T_g homopolymers are used in the production of PSAs. However, cohesion performances of latexes which are coming from merely soft monomers are not adequate. Thus, T_g of polymers is tuned with hard monomers such as MMA since homopolymers of MMA have high T_g. Cohesion performances of latexes, in other words shear resistance, are affected positively with the increasing amount of MMA. On the other hand, high amount soft monomer compositions give rise to better adhesion performance. Thus, monomer compositions should be well-tailored for PSA formulations because it is important to have a balance between adhesion and cohesion properties. Furthermore, AA amount affects the connection between substrate and polymer latex thanks to hydrogen bonds. Another crucial role of AA is to increase interconnection between polymer chains *via* hydrogen bonding [22, 23].

1.6.2. Effects of Initiator Concentration and Emulsion Feeding Time

Two other parameters which influence the final performances of polymer latexes are initiator concentration and emulsion feeding time. According to Plessic and Arzemendi, gel content is independent of these two variables. However, it is important to note that increasing initiator concentration and increasing emulsion feeding time results in a decrease of the molecular weights obtained. In other words, it can be concluded that it is possible to control the molecular weight with the amount of initiator and feeding time. Molecular weight plays a significant role in performances of latexes because low molecular weight polymers triggers high peel and tack performances while high molecular weight polymers increases shear performances of the latexes [24].

1.6.3. Effects of Other Variables

As before, amount of seed is another parameter that affects the chemical and physical properties of the polymer latexes. The seed nuclei are small particles which grow to give the final latex particles. If all the propagating oligomer radicals can pass into the seed particles the final latex will be monodispersed. The number of seed particles added determines the number and the size of the final latex particles [25].

In emulsion polymerization, the emulsified monomer droplets dispersed in the continuous aqueous phase with the help of a surfactant characterize the reaction system. As known, there are three types of surfactants anionic, non-ionic and ionic. In industry, non-ionic and anionic surfactants are widely used to manufacture latex polymers. Anionic surfactants provide repulsive force between two similarly charged electric double layers to the latex particles. On the other hand, non-ionic surfactants impart two approaching particles with the steric stabilization mechanism and improve the chemical and freeze–thaw stability of the latex products [26].

1.6.4. Effects of Tackifier in *In-situ* Polymerization

As discussed above, there are three basic type of tackifier resins used in pressure sensitive adhesives. These adhesives have different chemical structures and various functional groups. Thus, all of them apparently behave differently during the emulsion polymerization. That is the reason why the type of the tackifier is crucial during the *in-situ* emulsion polymerization. Unsaturated rosin esters behave as chain transfer agents. On the other hand, hydrocarbons having unsaturation on their structure react with acrylic monomers and get grafted onto the backbone of the polymers [27, 28].

2. OBJECTIVES

Acrylic water based polymer emulsions are widely used in the label adhesives industry. These acrylic polymer emulsions have excellent UV and chemical resistance whereas their peel and tack performance values alone are not adequate for market requirements. To solve this problem, producers prepare compounded polymer dispersions by mixing the acrylic emulsions and tackifier resin dispersions especially for paper labels.

In this study, the major goal is to introduce a new approach to the synthesis and preparation of label adhesives. The goal is to carry out the emulsion polymerization in the presence of a tackifier, in other words to employ the *in-situ* emulsion polymerization technique for the filmic label market (Figure 2.1). The technical difficulty is the right choice of resins which should be economic and compatible with the latexes. However, available economic resins such as rosin esters include high unsaturation levels and the effects of unsaturation on performances are not known.

Seeded semi-continuous *in-situ* emulsion polymerization in the presence of a tackifier provides a new approach to the synthesis of ready dispersions for label adhesives. With the help of this new approach, elimination of high cost dispersing machines and high level of surfactant used in the dispersion process of tackifier resin may be possible. In addition, elimination of surfactants coming from tackifier resin dispersions is a solution for whitening problem of filmic labels.

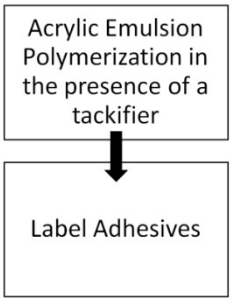


Figure 2.1. *In-situ* emulsion polymerization process for label adhesive.

3. EXPERIMENTAL

3.1. Methods and Materials

Acrylic monomers (Organik Kimya, Industrial Grade), AA or MAA (Organik Kimya, Industrial Grade), persulfates (Organik Kimya, Industrial Grade), carbonates (Organik Kimya, Industrial Grade), seed (Organik Kimya, Industrial Grade), pyrophosphates (Organik Kimya, Industrial Grade), sulfate salts (Organik Kimya, Industrial Grade), hydroperoxides (Organik Kimya, Industrial Grade), surfactants (Organik Kimya, Industrial Grade), sodium hydroxide (Organik Kimya, Industrial Grade), disodium salts of 2-hydroxy-2-sufinatoacetic acid (Organik Kimya, Industrial Grade), deionized water (DiW) (Organik Kimya, Industrial Grade), biocides (Organik Kimya, Industrial Grade) and 28 different hydrocarbon, saturated hydrocarbon, rosin ester and saturated rosin ester resins with various softening temperatures (Organik Kimya, Industrial Grade) were used without purification.

3.2. Instrumentation

T_g values were determined with a TA Instruments Differential Scanning Calorimeter (DSC Q100). Peel performance tests for polymer latexes were conducted with a Chem Instruments Peel Tester. Shear performance tests for polymer latexes were done with a Chem Instruments Shear Tester. In addition, loop tack tests were done with a Chem Instrument LT 1000. Particle size distributions of polymer latexes were measured with Malvern Instruments Particle Size Analyzer. Size exclusion chromatography (SEC) analyses were done using a Viscotek GPCmax VE-2001 Analysis System with a PL Gel 5 µm MIXED-C Column that was calibrated against polystyrene standards.

3.3. Polymer Synthesis

3.3.1. A general procedure for the synthesis of water based acrylic latexes *via* seeded semi-continuous *in-situ* emulsion polymerization

The copolymer synthesis in the presence of a tackifier was performed as seeded semi-batch emulsion polymerizations in two stages. The first stage was a continuous stage involving feeding a pre-emulsion and initiator stock solution, and the second stage was a batch finishing.

In the preparation of pre-emulsion, selected tackifiers with changing amounts 10%-30% with respect to the monomer composition were dissolved in a mixture of acrylic monomers in a 1-L beaker with the help of a mechanical stirrer. This phase is called as the oil phase. In another 1-L beaker, emulsifiers and AA or MAA were dissolved in DiW. This phase is called as the aqueous phase. Oil phase was added slowly to aqueous phase while aqueous phase was stirred with a mechanical stirrer. White or yellowish pre-emulsions were obtained at the end of 10-15 minutes mixing.

On the other hand, as pre-additives; persulfate, carbonate or pyrophosphate and seed was dissolved in DiW. In the preparation of initiator stock solution, persulfate was dissolved in DiW.

In the first stage, a 2000 mL four neck round bottom flask equipped with an anchor stirring blade and various feed and sampling ports was used. DiW was added into the glass reactor and heated till the temperature was 86 °C. The stirring speed was maintained at 120 rpm in the beginning of the runs. Then, buffer solution, seed and initiator were added to the reactor respectively and the temperature decreased to 82-83 °C. After 3 minutes, the initiator and monomer emulsion stock solutions were added slowly to the reactor using two separate metering pumps and the temperature was kept constant between 82-84 °C. The feeding times for the initiator and the monomer emulsion stock solutions were 4 and 3.5 h, respectively. During polymerization, the stirring speed was raised due to the increasing viscosity. After the feed was complete, the reaction was allowed to proceed for an additional 30 min to increase the monomer conversion.

In the second stage of the procedure, the temperature was set down to 78 °C to finish the polymerization. Sulfate salts dissolved in DiW was added to the reaction media at that temperature. Then, the temperature was decreased to 75 °C for the addition of hydroperoxide diluted in DiW. After this step, reaction vessel was cooled down to 70 °C to start the reduction and oxidation reaction with the help of disodium salts of 2-hydroxy-2-sufinatoacetic acid and 2-hydroxy-2-sufonatoacetic acid dissolved in DiW. Addition of these chemical were done with the aid of a peristaltic pump in 15 minutes. Temperature changes were observed and recorded to estimate the amount of unreacted monomers. Then, reaction was cooled to the room temperature. During the cooling process, pH was set above 7.0 around 50 °C by the addition of adequate amount of NaOH solution and finally biocide was added at below 40 °C.

Solid content which is defined as the weight ratio of the monomers and tackifiers to the obtained polymer/tackifier emulsions was determined gravimetrically. The viscosity of polymers was measured with a Brookfield Viscometer.

3.3.2. Performance Tests Applied to *In-Situ* Polymer Latexes

After the basic tests such as pH, solid content and viscosity measurement are complete, performance tests are conducted on the polymer latexes. Performance tests are as follows:

- Biaxially-oriented polypropylene (BOPP) film appearance
- Gel formation
- Peel test, on BOPP, N/cm, 180°
- Shear test, on BOPP, 22°C, min
- Compound peel on label, on Cardboard, N/25mm, 180°
- After humidity, compound peel on label, on Cardboard, N/25mm, 180°
- Compound peel on label, on Low density polyethylene (LDPE), N/25mm, 180°
- Compound shear on label, at 22°C
- After humidity, compound shear on label, at 22°C
- Loop tack test of compound, on label, on Stainless Steel (SS), N/25mm

- Loop tack test, on label, on LDPE, N/25mm
- After humidity, loop tack test, on label, on LDPE, N/25mm
- Mandrel test, on LDPE, cm

Most important performance tests for PSAs are shear on label at 22 °C, peel on label and on LDPE at 180° angle and loop tack test on label and on LDPE. Thus, first these tests are conducted with the polymer latexes and other follow when the results coming from these essential tests are adequate.

Shear test is applied to measure the cohesion performances of polymer latexes. As it is mentioned before, ChemInstruments Shear Tester having standards accredited by the European Association for the Self Adhesive Tape Industry (AFERA) was used (Figure 3.1). In the measurement of cohesion performance, 5012- International Harmonized Test Method- AFERA Test Method was used.

Figure 3.1. Shear performance test.

Peel test is applied to measure the adhesion performances of polymer latexes to different surfaces. As mentioned before, ChemInstruments Peel Tester having standards accredited by the AFERA was used (Figure 3.2). In the measurement of adhesion performance, 5001-International Harmonized Test Method (single coated tapes, peel adhesion at 180° angle) was used.

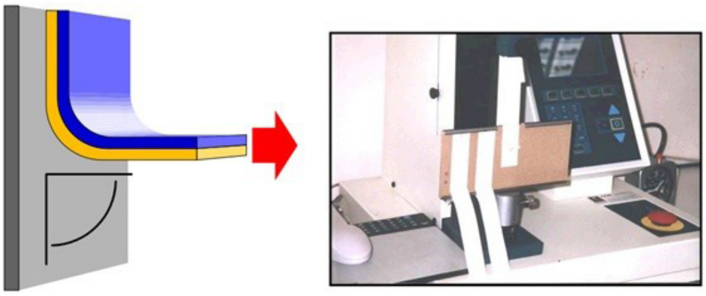


Figure 3.2. Peel performance test.

Loop tack test is applied to measure the instantaneous adhesion performances of polymer latexes to different surfaces such as LPDE, SS and high density polyethylene (HDPE). For tack, a strip of 2.5 cm *versus* 15 cm was cut from the film and was formed into a loop with the adhesive side facing outward. The instrument moved the upper grip downward at a constant speed until a specific surface area came into contact with the substrate mounted into the lower grip. Next, the tester moved the upper grip upwards at the same speed while recording the force needed to de-bond the loop from the substrate. The maximum force per meter necessary to remove the adhesive was called as the loop tack. As it is mentioned before, Chem Instruments LT 1000 was used to measure tack loop tack performances (Figure 3.3).

Figure 3.3. Loop tack performance test.

4. RESULTS AND DISCUSSION

The goal of the study was to develop a new method for the production of the water based acrylic latexes in the presence of a tackifier resin and to investigate the effects of various tackifiers to the polymerization process. In this study, acrylic monomers are polymerized in the presence of different tackifiers such as saturated and unsaturated types of rosin esters, saturated and unsaturated kinds of hydrocarbon resins and terpene resins. In literature, seeded semi continuous emulsion polymerization technique in the presence of a tackifier is not reported yet.

Here, the polymerization of acrylate monomers in the presence of a tackifier and the performance analysis of polymer latexes produced with new emulsion process will be discussed.

4.1. Synthesis of Polymer Latexes

Emulsion polymerization of acrylate monomers in the presence of a tackifier was preferred throughout this study. The components of the system were chosen to obtain polymer latexes with intended chemical and physical properties and also with desirable shear, peel and tack performances mentioned above.

4.2. Selection of Tackifier Resins

A standard formulation procedure, various amount and type of tackifier resins was used to synthesize pressure sensitive adhesive polymer latexes with a seeded semi-continuous *in-situ* emulsion polymerization process. It is important to mention that this formulation included a specific surfactant package having three different emulsifiers. Prior to our work, 24 different resins were tested with the standard formulation by Organik Kimya. Among the 24 different resins, resin number 5 (RE5) and resin number 11 (RE11) were selected as the best suitable resins for the new process. RE5 is a very light color and stable pentaerythritol rosin ester with high softening point. On the other hand, RE11 is a unique partially hydrogenated water-white inert thermoplastic hydrocarbon resin derived from petrochemical feedstock. In short, rosin resins and hydrocarbon resins were used as tackifiers to improve the performance of the final PSA emulsion. However, RE11 is an expensive commercial resin.

4.3. Modifications of Parameters in Standard Formulation for RE5 and RE11

As mentioned before, there are many variables which play an essential role in the new process. Amount of initiator, pH, type and amount of surface active agents, monomer and comonomers compositions, and amount of tackifier, feeding time and reaction temperature are some essential parameters for *in-situ* polymerization technique.

4.3.1. Initial pH, Tackifier Amount and Reaction Temperature Modifications

After the selection of two best performing resins, RE5 and RE11, reaction parameters were changed especially one by one for RE5. Less attention was paid to RE11, later since it was found to be expensive. For trials 38, 39, 40, 41, 42, 43 and 44 in which three surfactant package was used, variables such as the initial pH of the polymerization, tackifier amount and reaction temperature were changed and performance analyses were done. According to results, trials 38 and 40 gave adequate shear, peel and tack performance values (Table 4.1). On the other hand, performances of trials 39,41,42,43 and 44 were not enough. In trials 40, 41 and 42, tackifier amount were slowly increased from 10% to 16.6% and it was found that shear performance decreased with the increasing amount of RE5. However, peel and tack performances were approximately similar. Reaction temperature was increased and initial pH was changed in trials 43 and 44 to enhance performances of polymer latexes but these modifications did not improve application performances.

4.3.2. Surfactant Package and Feeding Time Modifications

Instead of three different emulsifiers contained in the surfactant package, two different emulsifiers were used in all trials after trial 47. The best performance polymer latex synthesized was trial 40 till this change. The same recipe rather than surfactant package was used in trial 47. Since the performance values for trial 47 was not as good as

Table 4.1. Performance analysis results of trials 38-44 with RE5.

	Standard specification	**Trial38**	**Trial38-R**	**Trial39**	**Trial40**	**Trial41**	**Trial42**	**Trial43**	**Trial44**
Solid content, %		61.10	61.40	60.30	60.60	60.30	59.30	60.00	60.80
pH		7.10	4.96	7.00	6.80	6.80	7.10	6.00	7.00
Viscosity, cps	max 1000	300	340	220	180	180	100	140	160
APPLICATION TESTS									
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	6.67	5.12	4.96	7.24	4.25	4.05	5.92	6.45
Compound shear on label , at 22°C	>6 hours	>24 hours	16 hours	19 hours	25 hours	23 hours	6 hours	6.6 hours	6.2 hours
Loop tack test, on label, on LDPE, N/25mm	>7	7.10	7.59	5.80	7.51	6.17	4.68	9.42	9.70
Tackifier % used	Tackifiered	10% RE5	10% RE5	10% RE5	10% RE5	13.3% RE5	16.6% RE5	16.6% RE5	16.6% RE5
Application Comments		Sufficient Results.	Very low peel.	Very low peel.	Sufficient Results.	Very low peel.	Very low peel.	Low peel.	Low Shear.
Changes on formulation			Reproduciblity was checked.	Initial pH was increased.	Initial pH was increased.	Resin amount was increased.	Resin amount was increased. Solid content was changed.	Reaction temperature was increased.	Reaction temperature was increased and pH increased.

the one for trail 40, a similar experiment with longer feeding time of initiator stock solution 49. Peel performance for trial 49 was below intended value. Thus, it was decided that the problem was not about surfactant package. In trial 50, seed amount was decreased and shear performance jumped to more than 50 hours (Table.4.2).

4.3.3. Monomer Composition Modifications

In trials 52 and 53, in order to observe the effect of hard monomer on performance values, amount of hard monomer was reduced step by step and removed from formulation in trial 56. Decreasing hard monomer amount affected shear performance of polymer latexes dramatically. Shear performance of trial 56 was measured as 6 hours in the absence of hard monomer (Table.4.2). Glass transition temperatures of the resulting polymers for trials 40, 52, 53 and 56 were respectively measured as -41 °C, -46 °C, -47 °C and -50 °C. T_g analysis showed that increasing hard monomer amount increased T_g of the polymer latexes.

4.4. Testing of New Rosin Ester Resins

New rosin resins RE24, RE22, RE25 and RE26 with different chemical properties and softening points were tried in polymerization due to the supply problem of RE5. RE24 is a low softening point glycerol rosin ester with high unsaturation. RE22 is s a very light and stable glycerol ester with a medium softening point. RE25 and RE26 are very light color and stable pentaerythritol rosin esters with a moderately high softening point. Performance analyses for trials 51, 55, 57, 58 in which these new resins were correspondingly used showed that cohesion performance of the polymer latex with RE24 was too low. Furthermore, these analyses showed that RE22 could be a meaningful tackifier for high tack performance polymer latexes but low in peel performance. Moreover, peel and tack performances of polymer latexes including RE25 were worse than the ones of polymer latexes of RE26 (Table 4.3). After this point, it was decided that main focus would be on RE26 which was similar to RE5 in terms of free hydroxyl values, unsaturation levels, molecular weight and acid number.

Table 4.2. Performance analysis results of trials 47-56 with RE5.

POLYMER SPECIFICATIONS	**Standard specification**	**Trial47**	**Trial49**	**Trial50**	**Trial52**	**Trial53**	**Trial56**
Solid content, %		63.00	61.50	60.00	64.00	64.00	62.30
pH		7.50	7.00	7.30	6.50	6.60	8.20
Viscosity, cps	max 1000	1540	420	120	640	540	220
APPLICATION TESTS							
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	5.29	4.50	5.24	4.09	4.54	4.20
Compound shear on label , at 22°C	>6 hours	45 hours	22 hours	>50 hours	>50 hours	15.5 hours	6 hours
Loop tack test, on label, on LDPE, N/25mm	>7	6.05	7.42	4.80	6.74	5.38	6.50
Tackifier % used	Tackifiered	10% RE5	10% RE5	10% RE5	10% RE5	10% RE5	10% RE5
Application Comments		Low Tack.	Very low peel.	Very low peel.	Very low peel.	Very low peel.	Low peel.
Changes on formulation		Surfactant package was changed.	Feeding time for Trial 40 was increased.	Seed amount decreased.	Hard monomer amount decreased.	Hard monomer amount decreased.	Hard monomer amount decreased.

Table 4.3. Performance analysis results of trials 51, 55, 57 and 59 with different tackifiers.

POLYMER SPECIFICATIONS	**Standard specification**	**Trial51**	**Trial55**	**Trial57**	**Trial58**
Solid content, %		60.80	60.00	63.30	62.80
pH		7.30	7.10	8.30	7.60
Viscosity, cps	max 1000	260	80	1860	320
APPLICATION TESTS					
Compound peel on label, on LDPE, N/25mm, 180°	>6.5		5.00	1.86	4.73
Compound shear on label , at 22°C	>6 Hours	<1 hours	>24 hours	>24 Hours	>24 hours
Loop tack test, on label, on LDPE, N/25mm	>7		6.18	3.14	4.33
Tackifier % used	Tackifiered	10% RE24	10% RE22	10% RE25	10% RE26
Application Comments		Low Shear.	Low peel.	Low peel.	
Changes on formulation		Different tackifiers were tried.	Different tackifiers were tried.	Different tackifiers were tried.	Different tackifiers were tried.

4.4.1. Modifications of Parameters in Formulations with RE26

First trial with resin RE26 is trial 58. After this trial, different modifications were done to the polymerization procedure. Firstly, as peel and tack values are related to the low molecular weight polymer chains, initiator amount was increased gradually. These changes were done in the recipes of trials 59, 60 and 61. In these three experiments, application results showed that there was not a big change in shear performance. However, there were small improvements in adhesion properties. In addition, in the formulations of trials 62 and 63, percentages of RE26 were raised to 15% and 20% respectively to increase the peel and tack performances. Unfortunately, shear performances of polymer latexes gained in trials 62 and 63 decreased sharply to 2 hours from more than 24 hours. In contrast, peel and tack performance were not enhanced (Table 4.4).

4.4.2. Particle Size Distributions Analysis of Polymer Latexes

Particle size distribution analysis of compounded polymer dispersion with a tackifier and polymer dispersion obtained in Trial 61 are shown in Figure 4.1 and Figure 4.2. The analysis showed that, there are two peaks corresponding to the two different sizes of polymer particles in both dispersions.

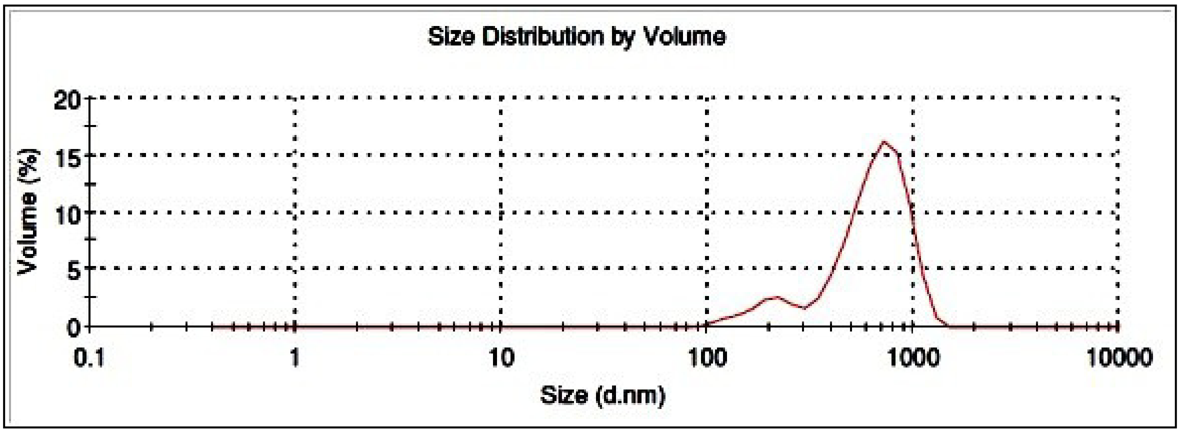


Figure 4.1. Particle size distribution analysis of compounded polymer dispersion with a tackifier.

Table 4.4. Performance analysis results of trials 59,60,61,62 and 63 with RE26.

POLYMER SPECIFICATIONS	**Standard specification**	**Trial59**	**Trial60**	**Trial61**	**Trial62**	**Trial63**
Solid content, %		62.60	63.20	63.10	61.70	61.90
pH		6.90	6.90	7.20	6.90	6.80
Viscosity, cps	max 1000	280	540	300	100	100
APPLICATION TESTS						
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	5.85	5.60	6.08	6.19	6.60
Compound shear on label , at 22°C	>6 hours	>24 hours	>24 hours	>24 hours	3 hours	2 hours
Loop tack test, on label, on LDPE, N/25mm	>7	4.32	6.43	5.71	4.40	6.81
Tackifier % used	Tackifiered	10% RE26	10% RE26	10% RE26	15% RE26	20% RE26
Application Comments		Low peel.		Low Tack.	Low Tack.	Very low shear.
Changes on formulation		Total initiator amount was increased.	Total initiator amount was increased.	Total initiator amount was increased.	Tackifier amount was increased.	Tackifier amount was increased.

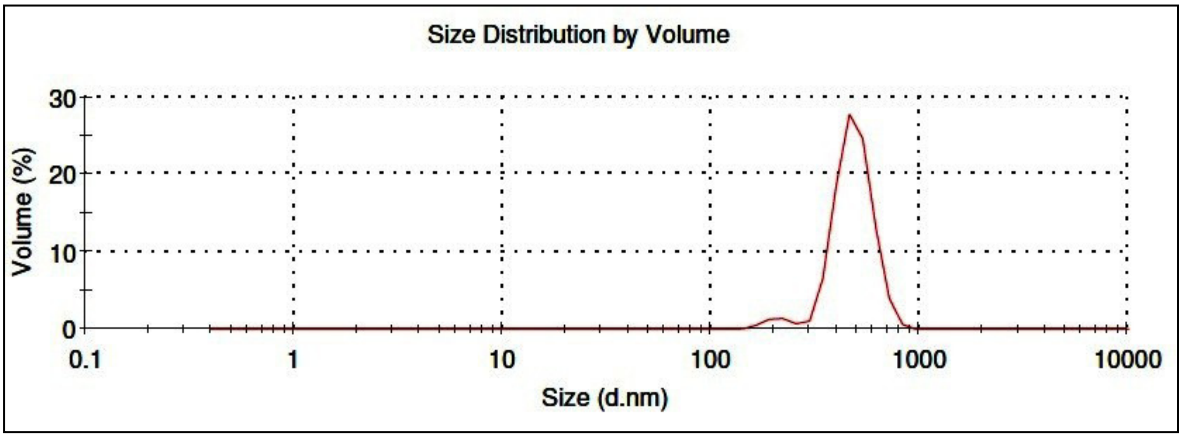


Figure 4.2. Particle size distribution analysis of Trial 61.

4.4.3. Design of Experiment (DOE) Study

A systematic study on emulsion polymerization to decide polymerization conditions that can produce latexes with predetermined properties is of greater industrial importance [29]. The statistical method would be very useful to design the experimental conditions to achieve this. DOE is one of the quality management tools and methods used to get more information from fewer experiments and collect only the information that is really needed.

In this part of the study, it is aimed to figure out whether design of experiment is a useful process improvement method for the preparation of water borne polymer emulsions with *in-situ* emulsion polymerization process.

As a part of the DOE, nine trials 64, 65, 66, 67, 68, 69, 70, 71 and 72 were done at two levels with three factors including temperature, initiator concentration and tackifier content (additive) together with a mid-point run (Figure 4.3). Trails 64 and 68 were repeated two more times to obtain replicates and measure standard deviations. In trial 64, initiator amount was increased and the intended shear, peel and tack performance values were obtained. Then, it was decided to use a statistical method, DOE, to optimize variables for *in-situ* emulsion polymerization. Trial 64 was chosen as the reference starting point and formulations of other trials were modified accordingly (Table 4.5).

Table 4.5. Performance analysis results of trials conducted DOE study.

POLYMER SPECIFICATIONS	**Standard specification**	**Trial64**	**Trial65**	**Trial66**	**Trial67**	**Trial68**	**Trial69**	**Trial70**	**Trial71**	**Trial72**
Solid content, %		61.80	62.00	62.00	61.30	62.00	62.50	62.60	62.90	63.30
pH		7.20	6.80	7.70	8.00	7.50	7.10	6.90	6.70	6.50
Viscosity, cps	max 1000	130	120	340	240	140	220	240	170	140
APPLICATION TESTS										
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	7.10	5.36	6.66	5.27	4.61	5.17	5.36	6.94	6.55
Compound shear on label , at 22°C	>6 hours	>24 hours	9 hours	7.3 hours	22.5 hours	7.5 hours	<1 hours	<2 hours	<2 hours	7.7 hours
Loop tack test, on label, on LDPE, N/25mm	>7	7.00	6.96	6.06	6.66	6.53	6.06	6.53	8.39	7.42
Tackifier % used	Tackified	%10 RE26	%10 RE26	%10 RE26	%10 RE26	%15 RE26	%20 RE26	%20 RE26	%20 RE26	%20 RE26
Application Comments		Sufficient Results.	Low peel.	Low Shear.	Low peel.	Low peel.	Low Shear.	Low Shear.	Low Shear.	Low Shear.

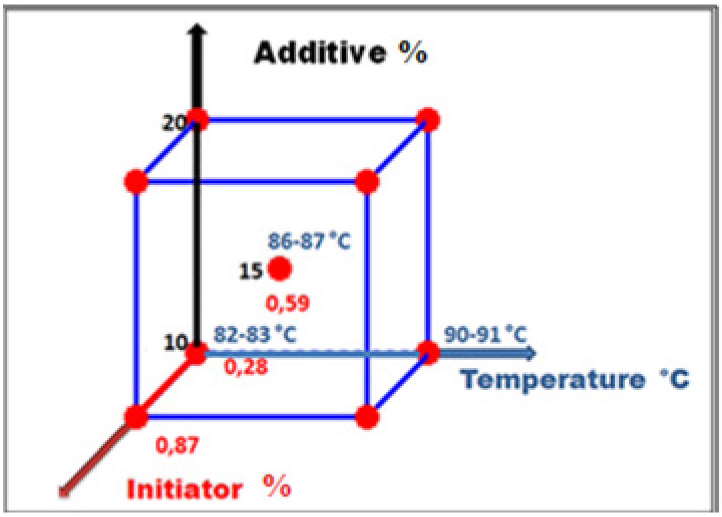


Figure 4.3. Nine experiments with two levels and three factors.

DOE analysis were done by Design-Expert® 6 for Windows—Software. Standard deviations of peel and tack performance results for these trials were too high which rendered the statistical analysis impossible. On the other hand, shear performance results could be used for such an analysis.

The effect of resin percentage on the shear performances at the given initial initiator concentrations and temperatures were evaluated. The data at 82 °C or at 90 °C showed a significant decrease when the amount of tackifier was increased from 10.00% to 20.00% (Figure 4.4).

It can be concluded that temperature played an important role in shear performances of water borne polymers synthesized with high initiator content. Shear decreased significantly with higher tackifier amounts at 82°C but, stayed constant at 90°C (Figure 4.5).

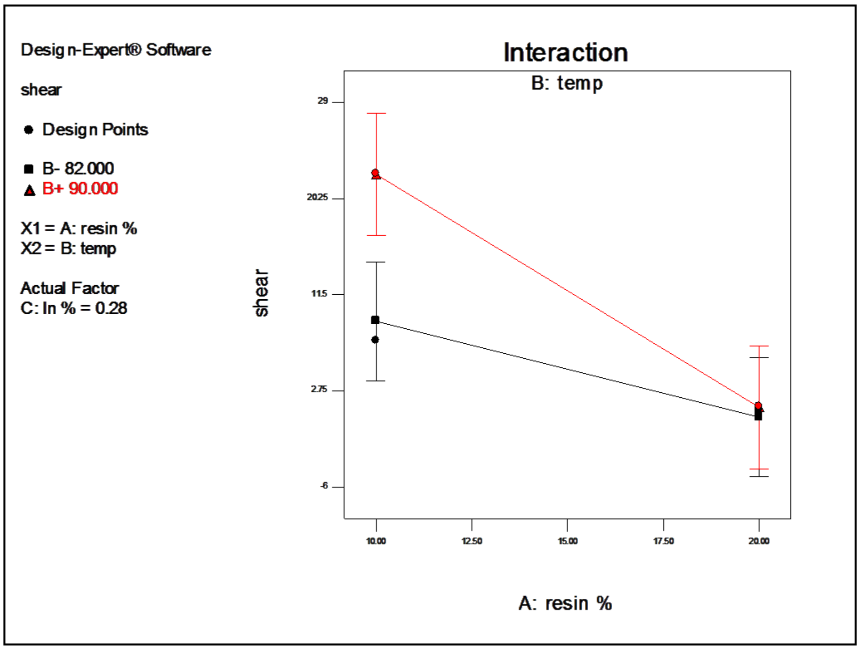


Figure 4.4. Shear *vs* tackifier % analysis with 0.28% initiator.

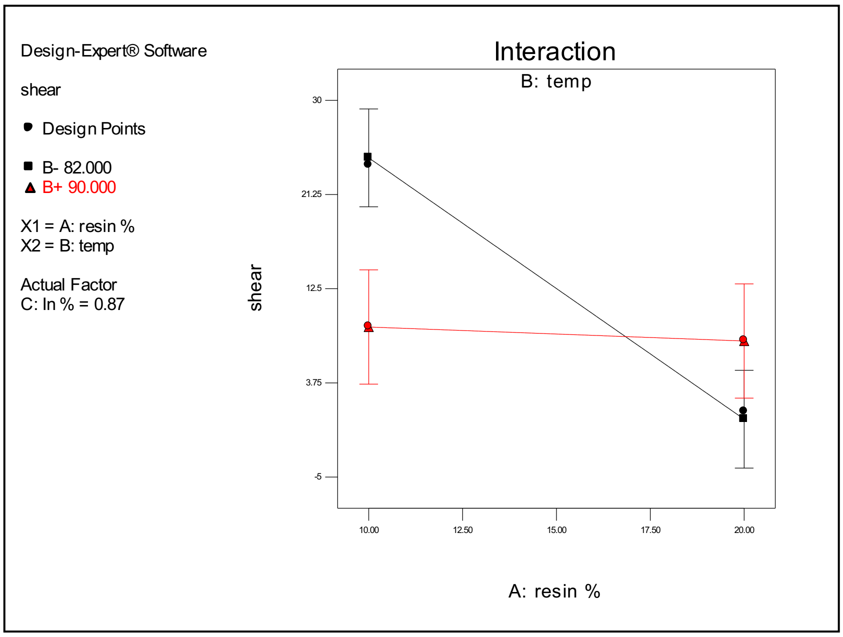


Figure 4.5. Shear *vs* tackifier % analysis with 0.87% initiator.

In this situation where the tackifier content kept constant at 10.00% the shear performances of emulsions with 0.28% and 0.87% initiator contents were analyzed with increasing temperature. DOE showed that shear values got lower at higher temperatures with high initiator amounts. On the other side, shear performances with lower initiator content behaved oppositely (Figure 4.6). Similar analyses were carried out at tackifier content kept constant at 20.00% and behaviors were evaluated. Emulsions coming from high initiator content showed better cohesion with increasing temperature (Figure 4.7).

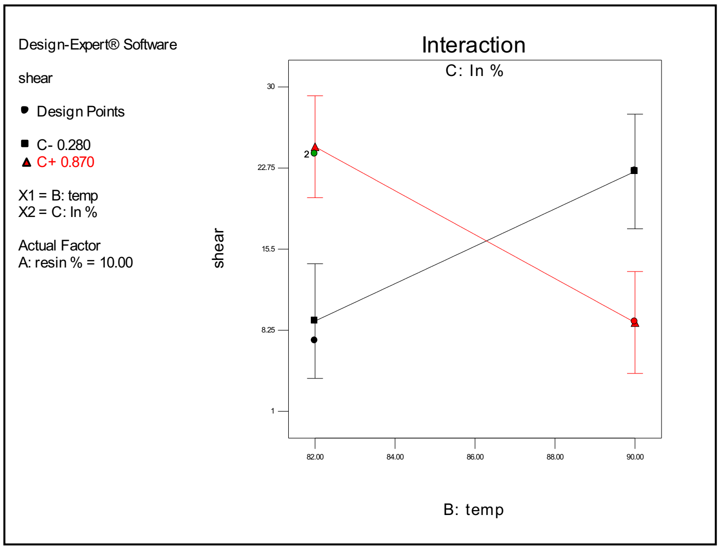


Figure 4.6. Shear *vs* temperature analysis with 10.00% tackifier, 0.28% and 0.87% initiator contents.

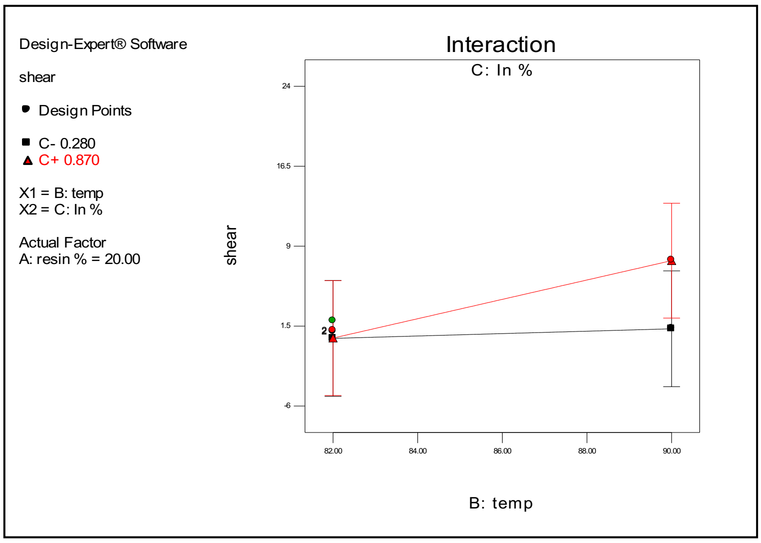


Figure 4.7. Shear *vs* temperature analysis with 20.00% tackifier, 0.28% and 0.87% initiator contents.

In short, to acheive the best shear perfromance with 10.00% tackifier content, temperature should be low when initiator amount is high or temperature should be high when one is low (Figure 4.8).

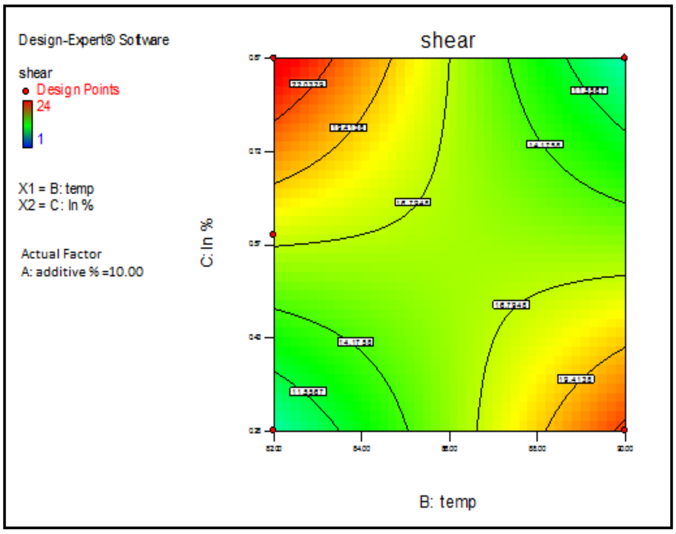


Figure 4.8. Initiator % *vs* temperature analysis with 10.00% tackifier content.

4.4.4. Formulation Modifications under the Enlightment of DOE Study

After the DOE study of *in-situ* emulsion polymerization, additional experiments were conducted by using RE26. In trials 76, 77, 78, 79, 82 and 83, reaction conditions such as decrease in reaction temperature, increase in amount of initiator and change in surfactant content were alternated. Performance analysis were presented that these modifications in formulations did not seriously influence shear performances of polymer latexes which were above 24 hours. These changes were not remedies for low performance peel and tack values (Table 4.6).

4.4.5. Testing of A New Rosin Ester and A New Approach to Formulation

In addition to runs with RE26, a new resin with a low softening point glycerol rosin ester with high unsaturation, RE27, was tried in run 77 to achieve predetermined performances for ready to use polymer latexes for label applications. Performance tests for RE27 showed that it caused serious decrease in cohesion, 15 minutes, but intended

Table 4.6. Performance analysis results of trials 75-83 with RE26 and RE27.

POLYMER SPECIFICATIONS	**Standard specification**	**Trial75**	**Trial76**	**Trial77**	**Trial78**	**Trial79**	**Trial80**	**Trial81**	**Trial82**	**Trial83**
Solid content, %		63.00	62.50	62.60	62.50	62.70	62.70	62.60	62.80	62.70
pH		7.4	6.90	6.60	7.60	7.10	7.50	7.50	7.50	7.20
Viscosity, cps	max 1000	290	240	160	230	340	160	160	200	150
APPLICATION TESTS										
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	6.40	5.71	6.37	5.51	6.04	6.21	6.08	5.74	5.30
Compound shear on label , at 22°C	>6 hours	<1 hours	>24 hours	>24 hours	>24 hours	>24 hours	9.5 hours	<1 hours	71 hours	30 hours
Loop tack test, on label, on LDPE, N/25mm	>7	10.24	6.90	6.90	6.56	5.47	8.92	9.99	5.62	5.09
Tackifier % used	Tackifiered	10% RE27	10% RE26	10% RE26	10% RE26	10% RE26	RE26 / RE27=2/1 10%	RE26 / RE27=1/1 10%	10% RE26	10% RE26
Application Comments		Low Shear.	Low peel.	Low Tack.	Low Tack.	Low Tack.	Low peel.	Low Shear.	Low Tack.	Low Tack.
Changes on formulation		Tackifier changed.	Based on 64, reaction temperature was decreased.	Based on 64, initiator amount increased.	Based 77, reaction temperature was decreased.	Based 77, surfactants was decreased.	Two tackifiers	Two tackifiers	Based 64, initiator amount was increased.	Based 64, initiator amount was decreased.

increase in adhesion; peel on label was 6.37 and loop tack on label was 10.24. At this point of study, it was suggested to use two different resins in emulsion polymerization. Experiments conducted with this innovation were trials 80 and 81. 6.66% RE26 and 3.33% RE27 in run 80 and 5% RE26 and 5% RE27 in run 81, total amount of resins 10%, were used to increase cohesion with RE26 for recipe 77. Cohesion forces in trial 80 were increased to approximately 10 hours. On the other hand, adhesion forces regressed to 6.2 and tack performances decreased to 8.92. Performance analyses were illustrated that shear performance decreased with the increasing amount of RE27 to 10 minutes while tack performance enhanced to 9.99 (Table 4.6).

4.4.6. Effect of Unsaturated Rosin Ester RE26 on Molecular Weight of Polymers

Molecular weight of polymers play a substantial role in performances of water based acrylic emulsion polymers. Thus, analyses of polymer latexes produced with *in-situ* emulsion polymerization technique came to our agenda. The unsaturated rosin ester tackifiers used in the polymerization as mentioned earlier could behave as chain transfer agents. Thus, if they behaved in this way, molecular weight of polymers should have decreased with the increasing amount of resin content. Low molecular weight polymers influence the peel performances of polymer latexes positively and shear performances is enhanced by high molecular weight polymers.

Table 4.7. SEC analyses.

	Trial64	**Trial84**	**Trial85**	**Trial86**	**Trial87**
Mn (Daltons)	479.617	736.843	256.981	465.395	963.498
Mw/Mn	4.586	3.149	7.942	5.195	3.363
RE26	10%	11%	12%	13%	14%

The best performance results obtained from trial 64. It was decided to increase amount of RE26 by 1% based on run 64 to verify this influence of resin amount (trials 84, 85, 86 and 87). SEC analyses of these trials showed that molecular weight of polymer latexes did not decreased with increasing amount of tackifier (Table 4.7). In addition to these measurements, expectation was to obtain small increases in peel performances and small decreases in shear performances as amount of tackifier was increased. Unfortunately, performance analyses showed that there was not such a trend in peel performances and they decreased as increasing amount of tackifier (Table 4.8).

4.5. Synthesis of Polymer Latexes by Using Two Different Tackifiers

Performance results of trials 80 and 81 including two unlike tackifiers directed this study to use a tackifier package which consisted of at least two different resins with different softening points. After the examination of performance results of all trials, it was decided to use a tackifier package 1 (TP1) including RE26 and RE22.

4.5.1. Performance Results for Polymer Latexes including TP1

Trials 92, 93, 94, 96 and 97 were conducted with this tackifier package. In these runs, amount of tackifiers were altered between 20% and 30%. Performance results of trial 93, in which 20% tackifier was used, and 96, in which 25% tackifier was used, had sufficient shear, peel and tack values for PSAs. Also in these cases, as tackifier content increased shear performance decreased (Table 4.9). From these results, it was concluded that two types of resins should be used to achieve intended performance values. Reason for this conclusion is the fact that lower softening point tackifier controls peel and tack performances of polymer latexes and on the other hand, higher softening point resin determines shear performance of water based adhesives.

4.5.2. Performance Results for Polymer Latexes Containing Different Tackifier Packages

In addition to this TP1, other tackifier packages were also tried. These packages were TP2 including RE25 and RE28, TP3 consisting RE26 and RE2, TP4 including RE6 and RE7, TP5 with RE26 and RE28, TP6 consisting RE26 and RE6 and TP7 with RE26 and RE7. At this point, it is really important to state that RE26 and RE 25 are unsaturated pentaerythritol rosin ester resins with different softening points and chemical properties,

Table 4.8. Performance analysis results of trials conducted for SEC analyses.

POLYMER SPECIFICATIONS	**Standard specification**	**Trial64**	**Trial84**	**Trial85**	**Trial86**	**Trial87**	**Trial88**
Solid content, %		61.80	63.50	63.50	62.90	63.40	63.60
pH		7.20	6.50	6.50	7.60	7.70	7.20
Viscosity, cps	max 1000	130	230	220	180	180	180
APPLICATION TESTS							
Compound peel on label,on LDPE, N/25mm, 180°	>6.5	7.10	6.09	6.05	5.75	5.27	5.08
Compound shear on label, at 22°C	>6 Hours	>24 hours	19 hours	21.5 Hours	26 Hours	31 hours	32 hours
Loop tack test, on label, on LDPE, N/25mm	>7	7.00	6.73	7.23	6.08	6.00	5.27
Tackifier % used	Tackifiered	10% RE26	11% RE26	12% RE26	13% RE26	14% RE26	15% RE26
Application Comments			Low Tack.	Low peel.	Low Tack.	Low Tack.	Low Tack.
Changes on formulation		Initiator amount has been increased.	Tackifier amounts were increased 1% in each experiment.				

Table 4.9. Performance analysis results of trials conducted with different tackifier amounts.

POLYMER SPECIFICATIONS	**Standard specification**	**Trial92**	**Trial93**	**Trial94**	**Trial96**	**Trial97**
Solid content, %		62.00	63.70	63.80	63.70	63.50
pH		6.90	6.70	6.90	6.50	6.90
Viscosity, cps	max 1000	150	160	130	150	120
APPLICATION TESTS						
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	5.31	7.96	7.34	6.50	7.65
Compound shear on label , at 22°C	>6 hours	38 hours	39 hours	20 Hours	13 hours	4 hours
Loop tack test, on label, on LDPE, N/25mm	>7	4.74	8.00	5.67	8.38	8.67
Tackifier % used	Tackifiered	RE26/RE28 =3/1 20%	RE26/RE22 =1/1 20%	RE26/RE22 =1/1 20%	RE26/RE22 =1/1 25%	RE26/RE22 =1/1 30%
Application Comments		Low Tack.	Sufficient Results	Low Tack.	Sufficient Results	Low Shear
Changes on formulation		2 resins Trial 68	2 resins Trial 68	Different initiator origin Trial93	2 resins Trial 68	2 resins Trial 68

RE7 and RE6 are saturated rosin ester resins with unlike softening points and chemical properties and RE2 and RE28 are glycerol rosin ester resins with different softening points and chemical properties. In trials 98 and 99, TP2 was used but results showed that polymer latexes produced in the presence of TP2 had poor cohesion forces between polymer chains. In trial 101, TP3 was used and the total tackifier amount was 20%. Performance analyses showed that it is possible to reach intended cohesion and adhesion force with package but shear performance was in borderline. TP4 was used in the formulation of trial 102. As it was mentioned above, this trial was conducted in the presence of two different saturated rosin esters Peel and tack performance values were high, but shear performance was too low. Furthermore, performance results of runs 104, 105 and 106 with TP5, TP6 and TP7 respectively was not sufficient in terms of cohesion strength (Table 4.10).

4.6. Detailed Performance Analyses of Best Resulting Trials 38, 40, 61 and 93

Detailed performance analyses were conducted to the polymer latexes from trials 38, 40, 61 and 93. The main reason for the selection of these trials was the fact that basic performance analyses of mentioned trials were sufficient for market requirements. Peel and shear analyses on different surfaces such as cupboard, LDPE and label at various conditions were measured. In addition, loop tack performance values on label and SS were analyzed (Table 4.11). According to results, it is possible to produce water based acrylic pressure sensitive adhesives with the processes and formulations used in these runs at 1 kg scale.

Table 4.10. Performance analysis results of trials with different tackifier packages.

POLYMER SPECIFICATIONS	**Standard specification**	**Trial98**	**Trial99**	**Trial101**	**Trial102**	**Trial104**	**Trial105**	**Trial106**
Solid content, %		63.30	63.10	63.50	63.10	63.70	63.30	62.60
pH		6.10	6.10	7.20	7.20	6.70	7.20	7.20
Viscosity, cps	max 1000	120	120	120	140	140	140	140
APPLICATION TESTS								
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	8.23	7.23	7.11	4.09	6.22	8.10	19.57
Compound shear on label , at 22°C	>6 hours	<1 hours	<1 hours	10 hrs	<1 Hours	3.3 Hours	<1 hours	<1 hours
Loop tack test, on label, on LDPE, N/25mm	>7	6.03	6.21	7.76	8.59	6.33	8.43	8.20
Tackifier % used	Tackifiered	RE25/RE28 =2/3 25%	RE25/RE28 =1/1 25%	RE26/RE2 =1/1 20%	RE7/RE6 =1/1 20%	RE26/RE28 =3/1 20%	RE26/RE6 =3/1 20%	RE26/RE7 =1/1 20%
Application Comments		Shear Low	Shear Low	Sufficient Results	Shear Low	Shear Low	Shear Low	Shear Low
Changes on formulation		Tackifier package was changed.	Tackifier package was changed.	Tackifier package was changed.	Tackifier package was changed.	Tackifier package was changed.	Tackifier package was changed.	Tackifier package was changed.

Table 4.11. Detailed performance analysis results of best trials.

POLYMER SPECIFICATIONS	**Standard specification**	**Trial38**	**Trial40**	**Trial61**	**Traial93**
Solid content, %		61.10	60.60	61.80	63.70
pH		7.10	6.80	7.20	6.70
Viscosity, cps	max 1000	300	180	130	160
APPLICATION TESTS					
Compound peel on label, on Cardboard, N/25mm, 180°	>8	9.00	16.29	9.42	7.93
After humidity, compound peel on label, on Cardboard, N/25mm, 180°	>4	4.57	3.77	7.55	4.67
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	7.01	7.24	6.33	7.96
Compound shear on label , at 22°C	>6 hours	23.5 hours	25 hours	>24 hours	39 Hours
After humidity, compound shear on label, at 22°C	>24 hours	>24 hours	>24 hours	>24 hours	13 hours
Loop tack test of compound, on label, on SS, N/25mm	>14	14.24	16.65	16.27	14.63
Loop tack test, on label, on LDPE, N/25mm	>7	8.09	7.51	6.74	8.0
After humidity, loop tack test, on label, on LDPE, N/25mm	>3.5	2.58	2.79	4.35	2.12
tackifier % used	Tackifiered	10% RE5	10% RE5	10% RE26	RE26/RE22 =1/1 20%

5. CONCLUSION

In summary, the new emulsion polymerization technique which is a seeded semi-continuous *in-situ* emulsion polymerization in the presence of various tackifiers have been tried to achieve predetermined cohesion and adhesion performances of water based acrylic pressure sensitive adhesives. These tackifiers were mainly unsaturated and saturated rosin ester rosins.

The cohesion and adhesion performances of the synthesized polymer latexes were measured on different surfaces such as label, SS, LDPE and cupboard.

RE5 or RE26 containing polymer latexes showed a sharp decrease in shear performance with increasing amount of tackifier. Optimum amount of tackifier for these polymer latexes was 10% of total monomer amount in accordance with DOE analyses.

SEC analyses were not sufficient to disclose the influences of unsaturated tackifiers on performances of water borne polymers produced with new process.

In addition, RE26 and RE22 tackifier package, named as TP1 in this study, was selected as the most suitable resin package for *in-situ* polymerization with 20% amount of tackifier. RE22 with lower softening point was responsible for adhesion strength. One the other hand, cohesion strength of polymers was depended on RE26.

As a result, two different suitable formulations for pilot scale production have been gained at the end of laboratory trials.

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