SYNTHESIS OF NOVEL PRESSURE SENSITIVE ADHESIVES BY EMULSION POLYMERIZATION TECHNIQUE

by

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To Grandma, Mum,

and my beloved Turgay…

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ABSTRACT

SYNTHESIS OF NOVEL PRESSURE SENSITIVE ADHESIVES BY EMULSION POLYMERIZATION TECHNIQUE

Acrylic based water dispersions are commonly employed in label adhesive industry as pressure sensitive adhesives (PSAs). Although acrylic polymer dispersions have excellent chemical and UV resistance, they cannot fulfill the desired performance requirements of the market. Because of this reason, acrylic polymer dispersions are compounded with tackifier resin dispersions by the PSA producers. However this compounding process requires use of high performance mixers which costs a lot, and use of high amount of surfactant which causes whitening problem in label adhesives when in contact with water. In this study one pot emulsion polymerization technique in the presence of a tackifier was employed to synthesize acrylic based pressure sensitive adhesives for filmic label market which should in principle, eliminate the use of high cost mixers and high amounts of surfactant and thus solve whitening problem of the filmic labels.

ÖZET

YENİ BASINCA DUYARLI YAPIŞTIRICILARIN EMÜLSİYON POLİMERLEŞMESİ TEKNİĞİYLE SENTEZİ

Basınca duyarlı yapıştırıcılar, etiket yapıştırıcıları endüstrisinde genellikle akrilik dispersiyonlar kullanılarak hazırlanmaktadır. Akrilik polimerler kimyasallara ve UV ışımalarına dayanıklı olmalarına rağmen, endüstri tarafından belirlenen hedef yapışma performans değerlerini tek başlarına sağlayamamaktadırlar. Bu sebepten, üreticiler akrilik dispersiyonları yapışkanlık arttırıcı reçine dispersiyonları ile karıştırarak pazara sunmaktadırlar. Bu süreçte enerji tüketimi oldukça fazla olan yüksek performanslı karıştırıcılar ve yüksek miktarda yüzey aktif maddenin kullanımına ihtiyaç duyulmakta, yüzey aktif madde miktarının fazla olması ise etiketlerin su ile teması durumunda beyazlamaya sebep olmaktadır. Bu araştırmada tek adımda emülsiyon polimerleşmesi tekniği kullanarak basınca duyarlı yapıştırıcı sentezlenmesi amaçlanmıştır. Elde edilen su bazlı dispersiyonlar test edilerek uygun özelliktekiler etiket uygulamalarında denenmiştir. Böylelikle yüksek maliyetli karıştıcıların ve yüksek miktarda yüzey aktif maddenin kullanımına gerek duyulmadan, filmik etiketlerde yaşanan beyazlama problemine de bir çözüm getirerek tek basamakta basınca duyarlı yapıştırıcı sentezlemek hedeflenmiştir.

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LIST OF ACRONYMS/ABBREVIATIONS

Mn	Number Average Molar Mass
Mw	Weight Average Molar Mass
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
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
PSA	Pressure Sensitive Adhesive
NMR	Nuclear Magnetic Resonance
RE	Resin Number
SS	Stainless Steel
UV	Ultra Violet
2-EHA	2-Ethyl Hexyl Acrylate

1. INTRODUCTION

1.1. Phenomena of Pressure Sensitivity

Pressure sensitive Adhesives (PSAs) are polymeric materials, which can form a physical bond *via* application of light pressure. Price marking, electronic data processing labels, packaging, diaper, auto/masking tapes, and bandages are examples of applications of PSAs (Figure 1.1) [1].

Pressure sensitive is a term commonly used to designate a distinct category of adhesive tapes and adhesives which are aggressively and permanently tacky at room temperature in dry form. The term pressure sensitive adhesive is self-explanatory. This type of adhesive is an extremely viscous, viscoelastic liquid [1][2].

For pressure sensitive adhesives, typical bonding techniques progress in the following sequence: application of the liquid adhesive, bringing together the adherents or surfaces to be bonded, allowing the adhesive to set by evaporation, cooling or cross linking. However usually pressing the adherents together is sufficient to obtain clean and precise bonds instantly with pressure sensitive adhesives [1].

The first appearance of a pressure sensitive adhesive article was a sticking plaster offered in 1882. Then the application areas extended from the medical to the industrial sector. It provided the impulse for a new technology, dry bonding, which was initiated at some time between the two World Wars. Then self-adhesive articles were produced *via* coating various carriers with pressure sensitive adhesives by this new industry [3].

A feverish advancement had occurred in this novel branch of industry, after the Second World War. The producers of that time had succeeded to convert the raw materials at their disposal, such as natural and synthetic rubber, poly isobutene and polyvinyl ethers, into pressure sensitive adhesives. [3].

Specialization to accommodate discrete applications led, of necessity, to more wide reaching demands on the adhesive compounds. Novel classes of products were sought and revealed in the shape of polyacrylates at last [2].



Figure 1.1. Examples of PSA applications [4].

Initial tack, peel resistance and shear resistance are the common prerequisities for these types of materials. Based on the balance of these properties various PSA products have been designed. All PSA applications include bond formation and debonding steps. Bond formation occurs as a result of a polymeric material being free to flow and wet the substrate under light pressure and by means of that is able to create a contact area with the substrate surface. The debonding step includes deformation of the polymeric material under stress, typically extension, followed by separation from the substrate. Though being at different rates, both the bonding and debonding processes are related to the rheological properties of the PSA materials. Bonding takes place typically in one second whereas debonding, occurs in the range of one-hundredth to one-thousandth of a second. Adhesive performance of PSAs depends on the bulk viscoelastic and mechanical properties of the adhesive such as tensile strength, storage modulus and dissipation of the adhesive polymers. Low plateau modulus, typically G´ measured at the bonding frequency and high energy dissipation at the corresponding debonding frequency, are the main requirements for good PSAs. Some fundamental polymer parameters such as molecular weight, entanglement molecular weight (M_e), glass transition temperature (T_g) and cross linking density can also be related to the performance of commercial PSAs. Usually, the higher the plateau modulus or the more extended the plateau, the better the shear. This is because the more extended or flatter rubbery plateau is characteristic for either a higher degree of entanglement due to higher molecular weight or a higher chemical/physical cross-link density [3].

1.1.1. Bond Formation

Thermodynamically favorable bond formation and establishment of sufficient contact area with substrate surface upon light pressure within a reasonably short time are the prerequisites to be met for a PSA material to form a physical bond. The first requirement is a thermodynamic process at the interface which may be expressed as an intrinsic surface energy, I. Intrinsic surface energy is an outcome of some thermodynamic interactions such as dispersion forces and polar interactions. When the adhesive and the substrate have alike surface energy, maximum adhesion occurs. The second requirement the bonding term, B, is a kinetic process and depends on how easily a PSA material can flow under pressure. If A_0 is the total area available for the adhesive material to make a contact and A is the actual contact area established during time, t, then the bonding term B, is proportional to the ratio A/A_0, which is related to the creep compliance, J(t), given by the following equations:

$$A/A_0 = 1 - e{-}J(t) = J(t)$$

$$J(t) = \{1/G'(\omega)\} \times \{1/(1 + \tan \delta 2(\omega))\} = 1/G'(\omega)$$

When $\tan \delta << 1$.

G´ is the dynamic storage modulus measured at the bonding frequency, ω, and tan δ is the ratio G″/G, where G″ is the dynamic loss modulus measured at the same frequency in the equations above [3].

1.1.2. Debonding

One more essential aspect of PSAs is the energy of separation (debonding). Debonding resistance is a measure of the energy dissipated on deformation. The energy of deformation can be related to the dynamic loss modulus, G″, measured at the debonding frequency, through the following equation:

$$\Delta E = \pi G'' L2$$

Where ΔE is the dissipation energy per cycle of the oscillatory shear deformation and L is the applied strain amplitude of the deformation. An uncomplicated correlation for the PSA adhesive was submitted by combining the effect of bond formation and separation [3].

$$P \sim I \times G''(\omega 1)/G'(\omega 2)$$

Where G″ is measured at the peeling frequency, ω1, and G′ is measured at the bonding frequency, ω2 [3].

This equation supply a base to associate PSA adhesive strength, measured by 180° peel or loop tack, with the linear viscoelastic properties of the adhesives [3].

1.1.3. Parameters Affecting Bonding and Debonding

G′ and G′′ can be correlated with the basic polymer parameters such as molecular weight, molecular weight distribution, T_g, and M_e (entanglement molecular weight) through linear viscoelastic theory. G″ should be increased, and bonding frequency, G′ should be decreased to increase the adhesive strength noticeably. This can be achieved *via* mixing a compatible resin into the polymer. Because tackifying resins normally have higher T_g's (typically 20-50 °C) than the PSA polymers (typically -70 to -30 °C), adding a compatible resin to the polymer will bring about a higher T_g product. As a result, the G″ peak, which is associated with the T_g, will shift to a lower frequency. Therefore, this shift will result in a higher G″ at the debonding region. Another essential result of adding a compatible resin is to lower the modulus in the bonding region. Since resins are low molecular weight materials, adding a compatible resin to the polymer matrix can be considered as diluting a concentrated polymer solution with a solvent. The result is a drop in the plateau modulus, G_n, according to the following equation:

$$G_n \sim= \rho RT/M_e\,(Vp)_2$$

Where Vp is the volume fraction of the polymer in the polymer resin blend, Me is the entanglement molecular weight of the polymer, ρ is the density of the blend, R is the gas constant and T is temperature in Kelvin [3].

M_e of the polymer is closely related to the structure of polymer chain segments and is another important parameter affecting G′. To have good bonding characteristics, we need polymers with low G′ at the bonding region and low G′ associates with the high M_e. For acrylic polymers M_e increases with increasing monomer side chain length. Unfortunately the T_g for these polymers also decreases with increasing side chain length. Therefore it is crucial to employ some higher T_g comonomers, such as methyl methacrylate or methyl acrylate, to counterbalance the low T_g monomers such as butyl acrylate or 2-ethylhexylacrylate [3].

1.2. Evaluation of The Adhesive Performance

The adhesive performances of the PSAs can be evaluated as tack, peel resistance, and shear strength [1].

1.2.1. Peel Resistance

Peel resistance is the is the force required to peel off a pressure sensitive product such as label and tape, from a substrate and is the average load per unit width of bond line needed to successively separate a flexible member from a rigid member or another flexible member (Figure 1.2).

It is very crucial to control peel resistance in PSA products for both manufacturers and customers. The value of peel resistance is one of the criteria used to classify applications in label industry; labels are classified according to their value of peel resistance as permanent or removable. PSAs used for permanent labels possess high peel resistance; such labels are absolutely laminated on the substrate surface. However, PSAs for removable labels have low peel resistance, which allows their slight detachment from

substrates. Chemical structure, tackifier type and content, cross-linking density and viscoelastic properties are some bulk/surface properties that effect peel resistance of PSAs [1].

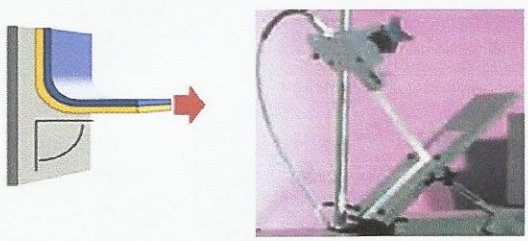

Figure 1.2: Peel resistance test [4]

1.2.2. Shear Resistance

Shear resistance describes a PSA's capacity to resist shearing forces. Shear resistance is also called as holding power and it is one of the most significant characteristics of PSAs (Figure 1.3). Generally, shear resistance enhances progressively with increasing assembly time. It can be connected with both kinetics of the adhesive joint formation and stress relaxation. Because an increase in temperature usually leads to a drop in viscosity, it is understandable that temperature reduces shear resistance and decreases significantly the time to failure. The shear adhesion of PSAs increases with molecular weight, probably due to the increased number of entanglements per molecule and, as a consequence, the growth of viscosity. Polymers with large side groups, such as non-cross linked acrylates, have high molecular weights between the entanglements, thus they are characterized by low holding power. Hydrogen bonding, ionic bonding, acid-base exchange have an effect similar to the decrease in molecular weight between entanglements. These interactions increase the holding power of the PSA. Improving PSAs shear behavior means, an increase in their cohesive strength. Thus there is a permanent risk of sacrificing tack and peel. For cross linking polymers, the improvement of shear resistance is connected with degree of crosslinking density, physical and chemical cross linking increases holding time. The selection of monomers is very important for acrylics: monomers with shorter side chains enable higher cohesive strength. The most evident way of enhancing the cohesive strength is to increase their Mw. This method increases the viscosity of the PSA and does improve

the shear resistance, but higher viscosity can make the processing more difficult. Broad Mw distribution can contribute to the preservation of the good peel and tack performance, while increasing the shear resistance [1] [3].



Figure 1.3: Shear resistance test [4].

1.2.3. Tack

Tack of PSAs is a, physical characteristic and may be defined as separation energy. Tack is a function of T temperature (T) (Tack > 0 if $T > T_g$) and it is inversely proportional to the elasticity modulus; conversely, the modulus depends on the branching, as does the T_g [1].

Tack is the resistance offered by an adhesive film to the detachment from a substrate; it is the measure of the stretchiness of an adhesive, or the capacity to form an instant bond when brought into contact with a substrate surface. Tack is also called as wet tack, quick stick and initial adhesion (Figure 1.4) [1].

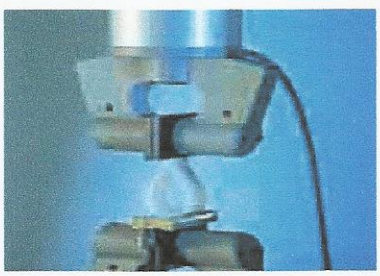

Figure 1.4: Initial tack test

1.3. Raw Materials and Pressure Sensitive Adhesives

Elastomers, which forms the load bearing structure and gives the internal strength, or the cohesion is the most vital component in a PSA. The various groups of adhesives derive their names from the nature of the elastomer used such as rubber and acrylate adhesives in the PSA formulation [2].

Most of the elastomers such as natural rubber and styrene butadiene rubber copolymers are not tacky enough and should be blended with resins to become permanently adhesive. Although poly isobutene and poly vinyl ethers are slightly tacky, the nature of a plasticizing resin depends on the degree of polymerization. The variation of polyacrylate properties from soft to highly cohesive products depends on the monomers used, and the molecular weight of the polymer obtained [2].

1.3.1. Natural Rubber

The classical elastomer for the production of pressure sensitive adhesives is natural rubber. It is obtained in the form of latex by tapping hevea trees and after the necessary treatment; it is placed on the market. Natural rubber gives great cohesion to pressure sensitive adhesives and is handled only in solution. Due to the double bonds present in its structure, it has little resistance to aging and this requires the addition of an antioxidant to the formulations [2][3].

1.3.2. Styrene-Butadiene Rubber

Another type of elastomer that is very commonly used in the production of pressure sensitive adhesives is styrene butadiene rubber, usually with a styrene content of about 23 %. These provide superior adhesion to the pressure sensitive adhesives but have less cohesion than natural rubber. Styrene butadiene rubber is also processed in the form of solutions and has poor resistance to aging [2].

1.3.3. Polyisobutene

Polyisobutenes are aging resistant polymers. They are frequently mixed with natural and styrene butadiene rubbers to accomplish special properties, such as resistance to aging, initial tack at low temperatures, and good peel off. They are used in the form of solution [2].

1.3.4. Poly(vinyl ethers)

Poly(vinyl ethers) are largely saturated polymers that are offered in several molecular mass gradations, too. Since they are prone to oxidation, addition of antioxidants is necessary. They are applied in the solution form. [2][3].

1.3.5. Polyacrylates

Polyacrylates often do not require modification with resins or plasticizers in many applications since they have the desired adhesive properties such as outstanding stability to heat and light, excellent resistance to plasticizers, clarity, good adhesion to PVC, and good resistance to shear even at high temperatures. They are also available in the form of solutions and dispersions [1] [2].

1.4. Processing Pressure Sensitive Adhesives

Flexibility and high viscosity of PSAs cancel out the deformation which is necessary for coating the adhesive onto webs of carrier material. Subsequently, these properties must be temporarily withheld during coating; the flow of the adhesive compound must be enhanced. This can be accomplished by applying the adhesives in the form of solutions, aqueous dispersions of the polymers, and melts [3].

Another ingenious way of application is offered in the shape of liquid polymers, which are solvent free, reactive products that have a low molecular mass and flow easily at room temperature. After they have been applied, they are subjected to heat, ultraviolet, radiation or electron beams. In the chemical reaction that occurs, they are converted into the final pressure sensitive adhesive compounds [3].

1.4.1. Pressure Sensitive Adhesives Applied In The Form of Solutions

Basically, all raw materials can be applied in the form of solutions, and this technique represents the classical means of coating materials with pressure sensitive adhesives. Currently about 60 to 70 % of all pressure sensitive adhesives are still being applied by this means [3].

1.4.2. Dispersion Type Pressure Sensitive Adhesives

Theoretically, all groups of polymers could be processed in the form of dispersions, however, only the acrylic polymer dispersions can be processed in application [3].

1.4.3. Pressure Sensitive Adhesives Applied In The Form of Melts

Application of solvent free coatings in the form of melts dates back to 1953. Solvent free coatings were aided by growing environmental consciousness and increasing prices for solvents [1] [3].

1.4.4. Reactive Systems

Reactive systems are solvent free, polyurethane and acrylic systems which can be applied at room temperature and then cross linked by employing heat or electron beams [3].

1.5. Pressure Sensitive Articles

Many multistage operations become easier thanks to the articles coated with pressure sensitive adhesives. Use of pressure sensitive articles is very helpful in industry, office administration, the household and handicrafts. Therefore they are primarily used in with high labor cost and a high standard of living [2].

Various types of pressure sensitive articles are offered on the market. The main difference between them is the manner in which the carrier materials have been adapted to meet the requirements in the various fields of application [2].

Pressure sensitive articles can be roughly categorized in three classes as tapes, labels and miscellaneous articles [2].

1.5.1. Adhesive Tapes

Adhesives tapes are named according to their application area such as packaging tapes, masking tapes and electrical insulation tapes. They are flexible substrates which have been coated with pressure sensitive adhesive, wound up into rolls, and cut into various widths [2].

1.5.2. Adhesive Labels

Adhesive labels are pieces of paper, plastic film or metal foil coated with pressure sensitive adhesives. Upon removal of a release film, adhesive labels can easily adhere to any desired substrate [2].

1.5.3. Miscellaneous Pressure Sensitive Articles

Decorative films, map covers, bookbinding films, adhesive medicinal articles and protective films are important products that are included in this group. Plasticized PVC is

the carrier material for most of these articles. Acrylic dispersions and acrylic solutions are the most common adhesives for these specialties. They are resistant to plasticizers and ageing [2].

1.6. Acrylic Adhesives

In 1928, acrylic acid esters were firstly used as pressure sensitive adhesive by Walter Bauer working at the Röhm and Haas Company. Bauer's used polymers to bond paper, glass or material to metals and described them simply as an adhesive. His polymers were applied either as a 10 % solution in acetone or as a film placed between the adherents. Use of modern acrylic PSAs has great importance for so many reasons Acrylic PSAs are intrinsically tacky and colorless polymers that have resistance to oxidation. Highly versatile compositions can be obtained *via* copolymerization with a wide variety of additional non-acrylic monomers, capable of being delivered in organic solution, aqueous dispersions or 100 % solid forms. Additionally, they are susceptible to cross-linking via a range of chemical reactions to produce an excellent balance of properties tailored to the particular requirements of the application [1].

1.6.1. Composition

A number of methods can be used for preparation of acrylic PSAs. The desired balance of pressure sensitive adhesives can't be achieved *via* use of a homopolymer not even with one that is inherently tacky. To possess the desired balance it is a must to design a copolymer. Such a copolymer may be prepared from a mixture of acryl or vinyl unsaturated monomers that modify the properties or impart a specific functionality (Figure 1.5) [1].

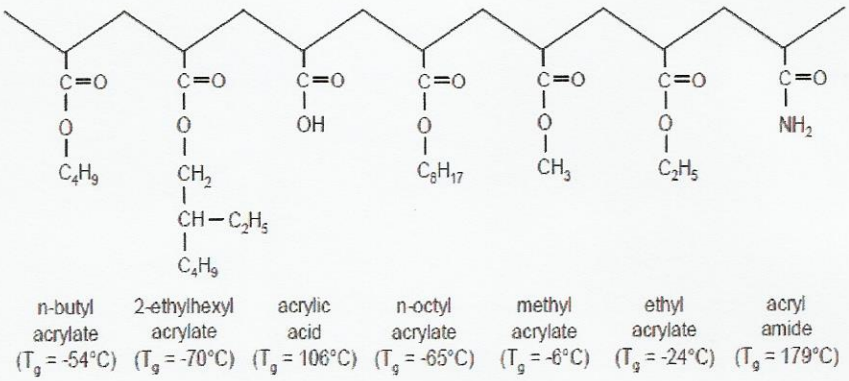

Figure 1.5: Common monomers used in acrylic PSA formulations [1]

1.6.2. Glass Transition

It is very crucial to understand the relationship between glass transition temperature and monomer selection (Table 1.1). Foremost among the physical property requirements is that the polymer glass transition temperature, T_g, should be well below the expected temperature of bond formation [1].

Table 1.1: Glass transition temperatures of homopolymers (°C) [1]

Acrylic and Methacrylic Esters			
Alkyl C_n	Alkyl Group	Poly (Acrylate)	Poly (Methacrylate)
C_1	Methyl	22	105
C_2	Ethyl	−8	67
C_3	*n*-Propyl	−25	
C_4	*n*-Butyl	−43	32
	iso-Butyl	−17	64
	sec-Butyl	−6	
	tert-Butyl	55	102
C_6	*n*-Hexyl	−51	−14
C_8	2-Ethylhexyl	−58	
C_{12}	Lauryl	−17	
Polar and functional acrylic and methacrylic polymers			
Acrylic acid	130	Methacrylic acid	162
Acrylamide	220	Methacrylamide	243
Acrylonitrile	105	Methacrylonitrile	112
Other polymers			
Vinyl acetate	42		
Vinyl propionate	8		
Styrene	107		

At low temperatures the polymer chains have little mobility; therefore, the adhesive is stiff and glass-like and characterized by a high modulus of elasticity, G′. As the temperature is increased, the polymer chains acquire sufficient thermal energy to permit segmental mobility [1].

1.6.3. Primary Monomers

The primary monomeric component has low homopolymer T_g to provide a soft, tacky film and typically constitutes from about 50 to about 98 wt % of the polymer (Figure 1.7). Acrylate monomers with side chains shorter than C4 do not impart sufficiently low T_g to be considered the primary component. Thus in practice, the choice is normally reduced to one of a small group of C4-C8 monomers that are produced at a commercial scale and yield the desired low T_g polymer and obtain desired modulus of elasticity (Figure 1.8) [1].

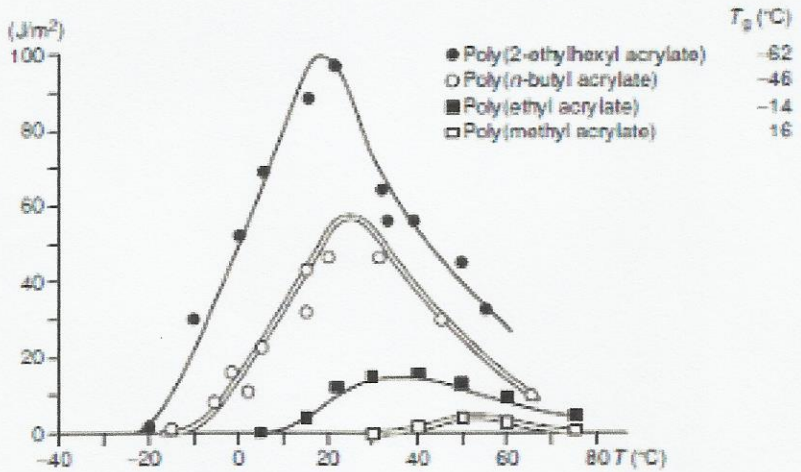

Figure 1.6 : Tack of various acrylic homopolymers as a function of the temperature [1]

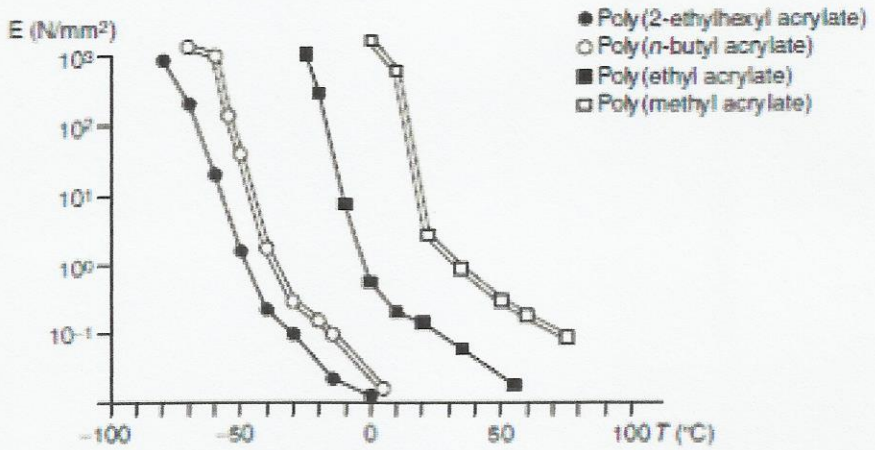

Figure 1.7: Modulus of elasticity of various acrylic homopolymers as fuction of T [1].

1.6.4. Secondary Monomers

Appropriate PSAs are not homopolymers. Usually, even an undoubtedly tacky, polymer would lack a good balance between tackiness and the cohesive strength needed to resist an applied shear stress, to ensure clean removal. Therefore a comonomer is used to increase modulus and T_g, thereby improving cohesion according to the demands of the application. These hardening comonomers have T_g's greater than 0 °C [1].

1.6.5. Polar and Functional Monomers

It is desirable to incorporate some polar monomers, when polar surfaces are the substrates to be bonded. Polar monomers contribute to stronger Van der Waals attractions at the interface, therefore increase the thermodynamic work of adhesion, as well as to an increase in cohesion in the bulk adhesive mass via dipole-dipole interactions [1].

To accomplish the required four-fold balance of adhesion, cohesion, stretchiness and elasticity, it is crucial to include a carboxylic acid co-monomer such as acrylic, methacrylic, or itaconic acid [1].

Hydroxyl functional groups are less polar than the carboxylic acids, thus they have correspondingly less impact on the properties. Their major value comes from their ability to react with certain cross linkers. They may also be used when there is a specific objection to using a carboxylic acid [1].

1.6.6. Molecular Weight and Viscoelasticity

Molecular weight of a pressure sensitive adhesive has a great importance to its mechanical properties. Low molecular weight may improve tack but this is not sufficient for a useful PSA, which must have sufficient cohesion to peel cleanly from a surface and carry the required load. Since the viscoelastic properties are a function of temperature, at low temperatures, where the adhesive is glassy, relaxation times are very long and the local mobility of the polymer chains is affected by the selection of monomers, which determine the glass transition temperature [1][3].

1.6.7. Cross-linking and Physical Interactions

To achieve sufficient cohesive strength in a solvent borne acrylic, cross-linking is an indispensable tool for achieving high cohesive strength due to the restrictions on molecular weight imposed by the requirement for a coatable solution viscosity. Emulsion PSAs are less dependent upon cross-linking to achieve cohesion due to the independence of viscosity on molecular weight [1].

Physical associations whether resulting from van der Waals forces, which may be considered collectively to include interactions resulting from electrostatic charge, dipoles, and hydrogen bonding, or from a microphase separation, are affective as means to increase cohesive strength. Physical interactions are readily reversed with a moderate increase in temperature [1].

Highly polar functional monomers such as AA, interact strongly via hydrogen bonding and dipole-dipole interactions and impart shear strength to PSA. At the bond interface they contribute to adhesive forces [1] [2].

The typical acrylic PSA produced by free radical polymerization has a statistical distribution of monomers determined by the monomer reactivity ratios and further influenced by the timing of addition. The polymers may be regarded as completely random with the same distribution in every chain. Those polymers are characterized by a single glass transition temperature. However when there is a large disparity in monomer reactivity it is possible, even in a simple free radical addition polymerization, to achieve a phase separation into domains rich in one or another of the monomers where two different glass transitions may be observed [1].

Chemical cross-linkings, involving only functional groups attached to the polymer, are sometimes referred to as internal cross-linking, and reactions that require an additional reagent. Some reactions will proceed rapidly under ambient curing conditions, whereas others require heating and perhaps a catalyst. Many of the techniques employed in cross-linking acrylic PSAs have been adapted from the metal and textile coatings industries or from the vulcanization of rubber. The chief differences are that PSAs are only lightly cross-linked to preserve viscoelastic properties and reactions that require consequential heat input are not practical for PSAs coated on a continuous web [5].

The challenge in cross-linking any PSA is to confirm that the process is reproducibly completed within some reasonable time following the coating and that further reaction does not occur during storage of the finished article, resulting in an unwanted change in properties, particularly a loss of tack [5].

Cross-linking may be accomplished during polymerization process by the intended inclusion of a multifunctional monomer or due to the chain transfer processes, which are inherent in emulsion polymerization [1][5].

Cross-linking may occur during polymerization by chain transfer to polymer. In an emulsion polymerization process under the usual conditions of high instantaneous conversion, that is, low monomer and high polymer concentration within the particle, chain transfer to polymer leading to branching is highly privileged. Gel networks appear within the particle when the ends of long chain branches produced by intermolecular chain transfer meet and terminate by combination (Figure 1.8) [1][5].

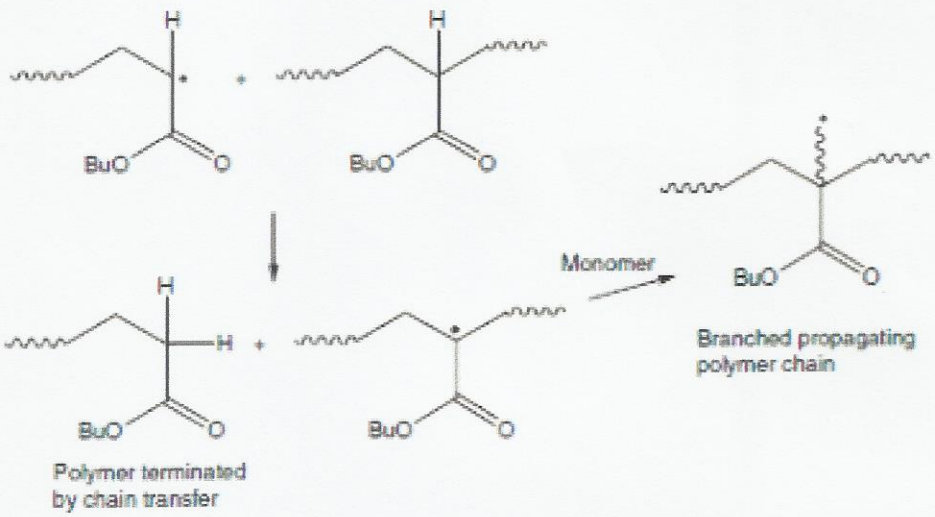

Figure 1.8: Chain transfer to polymer in polymerization of n-butyl acrylate [1][5].

1.6.8. Synthesis

A stirred tank reactor is usually used for the production of PSAs which is equipped with a jacket for heating and cooling, a condenser, and a number of auxiliary tanks equipped with meters for the addition of monomers, initiator, and any other required components for the particular process. The polymerized product is a base polymer emulsion or solution that is then transferred to another stirred tank for formulation with additional components such as a tackifiying resin, cross-linker, or diluents and adjustment of the final solids content and viscosity, as desired for subsequent coating. The final product is then filtered and transferred to bulk containers or packaged into drums [1] [3].

In homogeneous free radical polymerization, initiation is carried out in one of two ways: by hemolytic dissociation, using heat or UV light, or by a redox reaction. To begin the polymerization process the primary radical must further react with a monomer. An important part of primary radicals are often lost to formation of by-products [1] [3].

The consecutive addition of monomer to initiating radicals proceeds immediately to build a high molecular weight polymer, even in the early stages when most of the monomer remains unreacted [1][3].

Termination of growth generally stem from two radical chain ends coming together to combine or to disproportionate (Figure 1.9). Monomers and polymerization conditions determines which reaction path is dominant. Less hindered radicals such as methyl acrylate or acrylonitrile tend to combine, whereas MMA has a greater tendency for disproportionation [3].

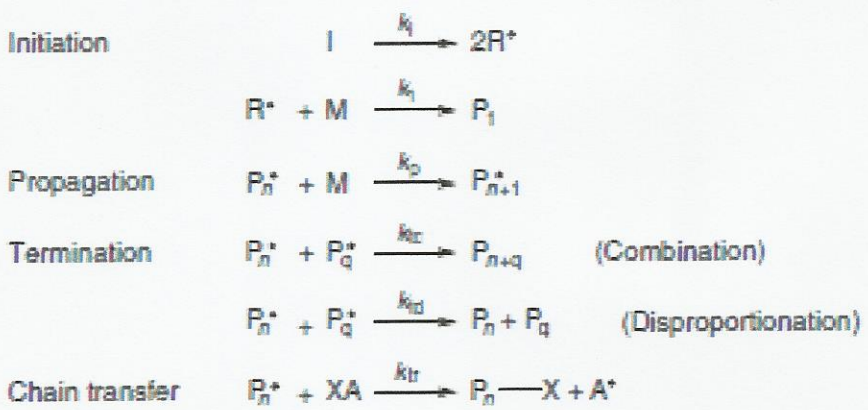

Figure 1.9: Reaction steps involved in free radical polymerization [3].

Chain transfer, also known as radical displacement, alludes to the premature termination of a growing polymer chain by reaction with another molecule to create a dead polymer molecule. A new radical is generated at the end of a chain transfer reaction different from the termination reactions. This respectively, reacts with a monomer to initiate polymerization of a new chain. All of the components present in the reaction are competent of acting as chain transfer agents: initiator, monomer, solvent, and polymer as

well as CTAs, which may be added particularly for this aim. The effect is therefore to decrease the molecular weight while preserving the number of radicals. An exception appears in transfer to a polymer, where the degree of polymerization is not necessarily reduced. As long as the rate of reinitiation can be compared to the rate of propagation, the rate of polymerization remains the same. Although sometimes a problem, in PSA production chain transfer is often used to advantage to arrange molecular weight, especially to improve tack [3].

The first acrylic PSAs were polymerized in organic solution. Although the emulsion process dominates commercial production, solution polymerization continues to be crucial in a number of applications where emulsion polymers have not yet fulfilled all requirements for adhesive performance and coating quality [3].

In a typical production process, a portion of the monomer and solvent, sufficient to cover the agitator is charged to the reactor, oxygen which inhibits polymerization is purged from the headspace with an inert gas such as nitrogen, and jacket heating is begun. At this stage, initiator may or may not be present. Since heating times may be variable, there can be some advantage to delaying the introduction of initiator until the reaction temperature is reached, provided that it can be quickly and uniformly incorporated. Once the mixture begins to reflux and initiator is present, the reaction proceeds rapidly. The reaction is exothermic and the heat of polymerization is removed by the vaporization and condensation of solvent and the more volatile monomers. Jacket heating is modified to obtain a controlled reflux throughout the reaction. By operating under reflux conditions, the reaction temperature is entirely controlled by the boiling point of the mixture in the reactor, which results in a very reproducible process from batch to batch. After a short time, further addition of monomer, solvent, and initiator begins and continue as for several hours at controlled rates until all the reactants and polymerization solvent have been added to the reactor. After an additional period under reflux to complete the reaction, the polymer solution is ready to be diluted, cooled, and discharged from the reaction vessel [3].

Emulsion polymerization is heterogeneous, unlike solution polymerization, which is homogeneous. The reaction occurs within the growing particle, as well as in the continuous

aqueous phase. Therefore, emulsion polymerization is a much more complex process. In addition to water, monomers, and initiator, the starting material include emulsifiers and, optionally, buffers, CTAs, and perhaps seed latex. In a typical process, the emulsifier is dissolved in water at a concentration above the critical micelle concentration (CMC), and then the monomer is introduced into this solution with agitation to from an oil-in-water emulsion. The particle size of these monomer droplets is generally in the range of 1-10 μm.

1.7. Emulsion Polymerization

1.7.1. Emulsion Polymerization Models

A batch reaction process which involves three stages has been proposed by Harkins. According to Harkins, initiation of a polymer particle takes place in micelles formed by the very small amount of monomer, which is dissolved in the continuous aqueous phase and surrounded by a monolayer of anionic surfactant. Frequently, a water soluble initiator is .employed. An initiating free radical diffuses into the monomer swollen micelle and polymerization process starts. The monomer swollen micelles, of size 10-20 nm, have a large collective surface area in contrast to the monomer droplets; so, the probability of a free radical entering a droplet is small. While the monomer is used up in the growing particle, a concentration gradient drives diffusion from the reservoir of monomer droplets and monomer swollen micelles to the particle. The particles are supposed to grow until another free radical enters to terminate the reaction. Growth keeps on when a new free radical enters the particle. This first stage involving particle nucleation is assumed to be completed when uninitiated micelles are no longer present and no new particles are formed. Generally, about 10-15 % of the monomer has been converted at this stage [6].

In the second stage, polymerization proceeds within the swollen particles where all the monomer in the droplets has been used up and the conversion is typically about 40-60 %. During this stage, the particle size increases but the number of particles remains the constant. Since the rate of reaction is proportional to the monomer concentration, the reaction proceeds faster than in a homogeneous solution polymerization [6].

Throughout the third stage, the monomer within the particles is converted to polymer. The rate of reaction decreases as the monomer concentration diminishes. During this stage, chain transfer to polymer causes branching and intraparticle cross-linking becomes increasingly probable. CTAs may be used to minimize this effect if adhesion properties and tack are adversely affected (Figure 1.10) [6].

Prostate cancer cells need androgens to survive and grow. In this respect the aim of the hormone therapy is to reduce the amount of androgens [28]. Hormone therapy can be applied in three ways [29]:

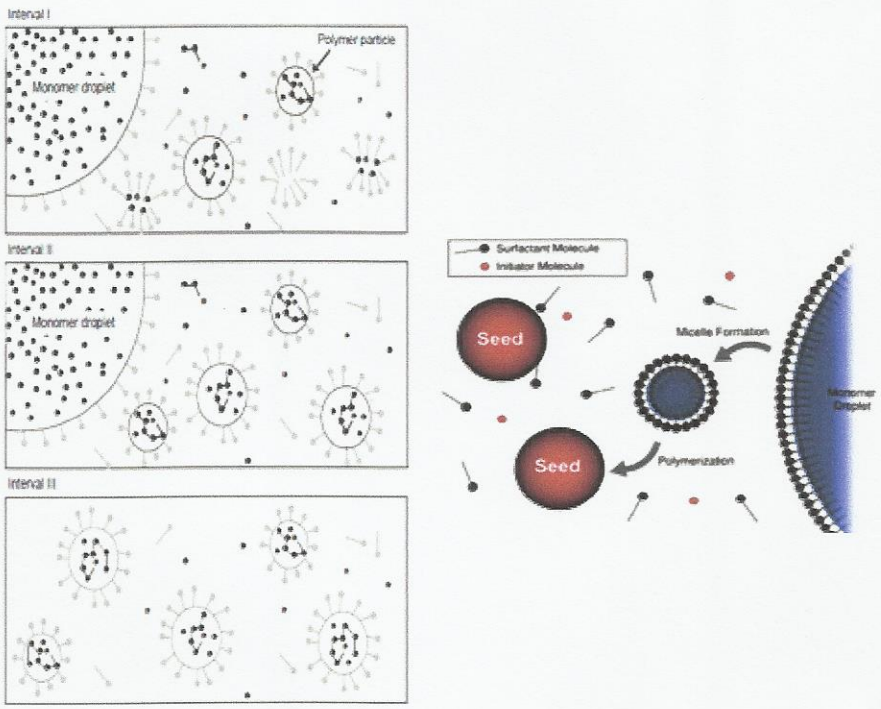

Figure 1.10: Schematic representation of emulsion polymerization intervals [5].

Emulsion polymerization requires a number of additional components in comparison with an organic solution polymerization. Besides water, monomers and an initiator, stabilizers, CTAs, and buffers are typical components [7].

1.7.2. Initiators

Free radicals are generated by thermal decomposition of peroxy compounds or *via* redox. Water soluble initiators are employed in the production of emulsion PSAs whereas oil-soluble initiators are employed in organic solution polymerization. The most commonly employed thermal initiators are sodium, potassium or ammonium persulfates, which dissociate into two sulfate radical anions (Figure 1.11). It is also common to use a buffer such as sodium bicarbonate to prevent acid-catalyzed decomposition of the persulfate, which does not yield free radicals. Typical redox couples include a persulfate used with a reducing agent such as a bisulfite or iron (II) compound, as well as sodium formaldehyde sulfoxilate, together with an oxidizing agent such as t-butyl hydroperoxide. These are useful at low temperatures [7] [8].

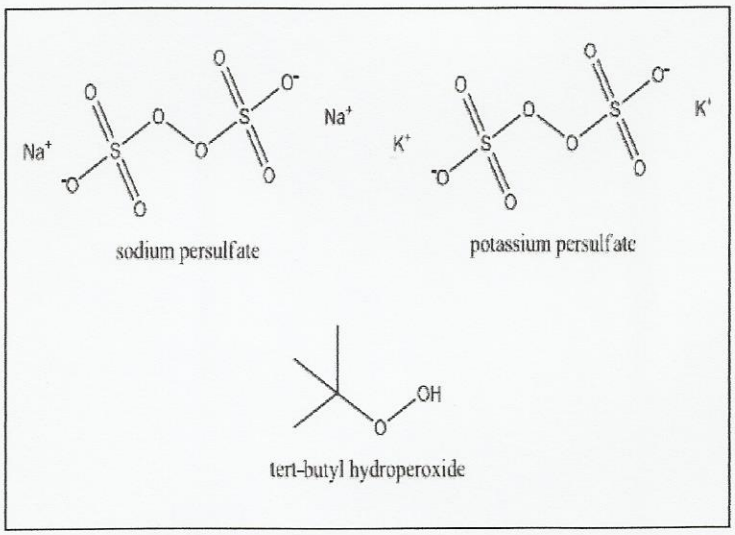

Figure 1.11: Strucutures of commonly used initiators [5].

1.7.3. Stabilizers

The role of the stabilizers is to create particle nucleation and to stabilize the particles against flocculation. Much work has been devoted to countering the general destructive effects of these stabilizers on adhesive properties and particularly on water and humidity resistance. Besides the surfactants and emulsifiers, it should be noted that initiator

contribute to particle stabilization. The acidic monomer is a major component of water-soluble chains adsorbed on the particle surface and provides electrostatic as well as steric stabilization [9].

Anionic surfactants are the most frequently encountered stabilizers. Electrostatic stabilization and pH depended behavior are determined by the hydrophilic head group, whereas the hydrophobic chain affects adsorption and steric stabilization of the latex particle, interfacial tension and the CMC. One important class is the salts of sulfonic and fatty acids, such as, sodium dodecyl sulfate (SDS). Other common ones are sodium dihexyl and dioctyl sulfosuccinate. Ammonium salts are also useful and may promote enhanced water resistance by loss of ammonia upon drying. Phosphate esters, among many other types, are also used (Figure 1.12) [9].

Nonionic surfactants are prone to aggregate at higher temperatures thus they are not such effective stabilizers when used alone unless polymerization is carried out at low temperature. However, they are commonly employed in combination with anionic surfactants [10].

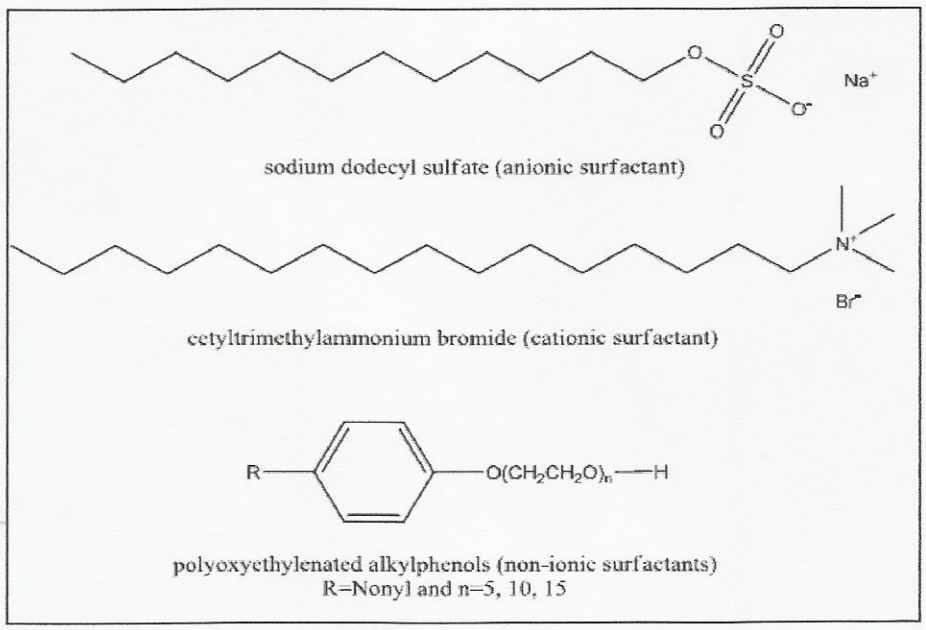

Figure 1.12: Structures of commonly used stabilizers [5].

1.7.4. Chain Transfer Agents

Although many chemicals are able to chain transfer mercaptans such as Dodecyl mercaptan (DDM) are most commonly used ones in emulsion PSA polymerization due to their very high chain transfer constant and thus require only small amounts to be employed, typical about 0.1% w/w of the monomer. DDM has relatively low volatility and can sufficiently diffuse from monomer droplets into the aqueous phase [8].

1.7.5. Reduction of Residual Monomers

A solution of acrylic polymerization will normally proceed to about 95-97% monomer conversion unless special steps are taken. Most displeasings residual unreacted monomers are the low volatility higher acrylates difficult to remove when drying the coated adhesive which remain in the finished product, creating an odor. There may also be concern regarding the potential for sensitization, in skin contacting applications [7] [8]. Therefore techniques to remove the residuals have been developed.

For removal of residual monomers, addition of short life initiator, at the cost of an extended holding time at reflux temperature or extrusion of the polymer solution into a counter current of a solvent in which the polymer precipitates as fiber are effective methods used in organic solutions [3].

Introducing a sparging gas such as steam is a well-known method for devolatilizing polymers. By increasing the partial pressure of the volatile material, the rate of evaporation is raised [3].

Conversion is much higher in emulsion polymers, typically 99% or more, but it is still desirable to decrease residual monomer amount for some applications. This may be achieved by treating the polymerized emulsion with an oil soluble initiator, or using a water soluble redox initiator. Alternatively, to sprinkle the emulsion with steam has been

achieved by treating the polymerized emulsion with an oil soluble initiator, or using a water soluble redox initiator. Alternatively, to sprinkle the emulsion with steam has been used and special columns have been designed for the purpose of increasing the area of the gas/emulsion interface [3].

1.7.6. Compounding

In many cases the polymer will require some additives to modify the adhesive performance, to facilitate the coating process, or to improve stability during storage although acrylic PSAs are sometimes used as polymerized [3].

Tackification is perhaps the most useful formulating tool. The major advantage of the addition of tackifier (Figure 1.13), which increases the entanglement molecular weight, is the advancement in adhesion to low surface energy substrates such as untreated polyolefins. Nevertheless, this benefit in sophistication of adhesion is not without penalties. These low molecular weight materials decrease the modulus at higher temperatures, which negatively impacts cohesive strength. The glass transition temperature is increased, that minimizes low temperature bond formation. Many of the tackifiers used with acrylics are unsaturated; therefore resistance to oxidation and discoloration is compromised. This may be acceptable in a temporary label but not in an application requiring long term constancy. Above all, tackification is the formulation made to enhance tack and peel resistance. In some cases no tack is present without tackification. Tackification can enhance various tack grades; that is, it can enhance the common tack on dry substrate surfaces or the special tack on wet surfaces. The enhanced tack can be constant in time or disappear. As regarding the site of tackification, it can deed on the whole polymer or on preferred segments of the polymer. Compatibility, reactivity, solubility, melting point and absorptivity are the major technical criteria for the usability of the tackifier resins [1] [3].

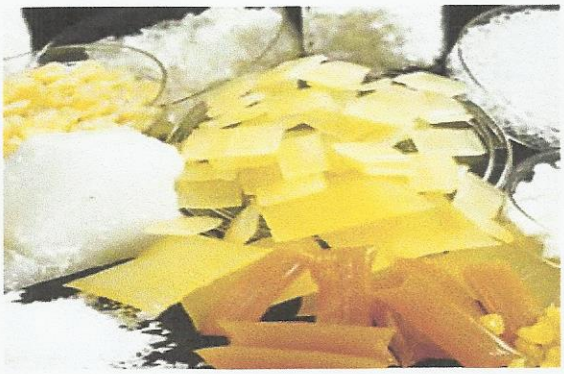

Figure 1.13: Tackifier resins [4].

Enhancing the tack and peel resistance are usually the goal of tackification. This may be quantified by knowing the base performance of the adhesive and the chemical or macromolecular characteristics of the formulating components. Tackification can be correlated with the viscoelastic properties of the polymer. Supposing that the tack is bonding related, to enhance it the adhesive must be softened and its modulus must be decreased. Thus, theoretically each additive that softens the adhesive, that is, decreases the plateau modulus, works as a tackifier. This means that, depending on the viscoelastic characteristic of the base polymer, a wide range of various compounds can act as plasticizers [1] [3].

Compounds employed as tackifier resins are low-molecular weight (400-2000) polymers or monomers that are glassy, amorphous materials in the solid state. In specific cases, these compounds can be low-molecular-weight derivatives of common plastomers such as vinyl aromatic polymers. [3].

While selecting a tackifying resin, compatibility is the first consideration. The selection is bounded because of relatively high solubility parameter of most acrylic PSAs. Rosin acid derivatives, particularly esters, are most commonly used, but a number of other classes are useful, including some phenol modified terpene resins [3].

Tackification must foster bond formation and make bond rupture harder. The major prerequisites for a tackifier are low molecular weight, high T_g, and compatibility. Usually,

and increases the T_g. Lowering of the modulus results in decrease in the shear resistance [1][3].

2. AIM OF THE STUDY

Label adhesive industry commonly prefers to use acrylic water based polymer dispersions which have accomplished UV and chemical resistance. However peel and tack performance values of these polymer dispersions are not sufficient for market requirements. Producers try to solve this problem by mixing the acrylic dispersions with tackifier resins, namely by compounding their polymers.

Investigating a new way of synthesis and preparation of label adhesives is the main objective of this study. The new method proposed is based on carrying out the acrylic emulsion polymerization in the presence of a tackifier which is sometime referred as the the *in-situ* emulsion polymerization technique for the filmic label market.

Seeded semi-continuous *in-situ* emulsion polymerization in the presence of a tackifier comes out as a new advance in the synthesis of ready dispersions for label adhesives. Use of high cost dispersion machines and high level of surfactants employed in the dispersion process of tackifiers can be discarded by this way. Additionally, this new method can be a solution for the whitening of filmic labels in contact with water or moistures.

3. EXPERIMENTAL

3.1. Materials and Method

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

DSC thermograms were measured with a DSC Exstar 7020 (TA Instrument). Each sample was analyzed with a different method of heating and cooling rate. Mass of samples was ~10 mg. The T_g values reports here were obtained from second scans to assure reproducible thermograms free from thermal history effects. 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.

3.3. A General Procedure For The Synthesis of Water Based Acrylic Latexes *via* Seeded Semi-continuous *in-situ* Emulsion Polymerization

The copolymer synthesis was performed in two stages, in the presence of a tackifier as seeded semi-batch emulsion polymerization. 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, surfactants and AA 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.

In the first stage, a computer controlled automatic reactor equipped with a 2000 mL glass reaction pot, a stirring blade, peristaltic feeding pumps and sampling ports was used. DiW was added into the glass reactor and heated. The stirring speed was maintained at 100 rpm in the beginning of the runs. Then, buffer solution, seed and initiator were added to the reactor respectively and the temperature decreases. Then, the initiator and monomer emulsion stock solutions were added slowly to the reactor using two separate peristaltic pumps. 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 time to increase the monomer conversion, at the reaction temperature. In the second stage of the procedure, the temperature was decresaed to finish the polymerization. Sulfate salts dissolved in DiW was added to the reaction media. Then, the temperature was decreased again for the addition of hydroperoxide diluted in DiW. After this step, reaction vessel was cooled down to start the reduction and oxidation. Then, reaction was cooled to the room temperature. During the cooling process, pH was set to 7.0 and finally biocide was added.

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.

3.4. Performance Tests Applied To Polymer Dispersions

After the basic measurements such as pH, solid content and viscosity complete, performance tests are applied to the polymer dispersions. 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, according to the results of these first five tests, the rest are conducted on the polymer dispersions.

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

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

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. ChemInstruments LT 1000 was used to measure tack loop tack performances.

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.

The research was done in two steps. First step was carried out by Sukru Eren which involved the selection of proper tackifier resins and accordingly, modifications of parameters in standard formulation, such as the initial pH, the tackifier amount, reaction temperature, surfactant package and feeding time. All of these modifications were done according to the results of design of experiment (DoE) studies [11].

Throughout the second step of this research modification of double bonds in unsaturated rosin resin via UV, changes in monomer composition and type of resin and investigation of resin-polymer distribution have been done.

Here, the polymerization of acrylate monomers in the presence of a tackifier, the performance analysis of polymer latexes produced, and polymer-resin distribution will be discussed.

4.1. Synthesis of Polymer Latexes

In-situ semi-continuous 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.

4.2. Modification of Double Bonds In Unsaturated Rosin Resins *via* UV Light

Tackifying resins are amorphous and oligomeric materials which are thermoplastic, low molecular weight and high glass transition temperature polymer modifier [10]. The addition of a tackifier makes the PSA products wet the substrate to form adhesive bonds. The role of a tackifier is usually called as anti-plasticizing in the sense that the polymer matrix is diluted with a high T_g compound, increasing the T_g of the blend and reducing the Young's modulus. The lower Young's modulus promotes polymer flow, bond formation, and when coupled with the higher T_g, enhances the resistance to bond rupture [12]. A tackified PSA is stiffer at high strain rates, such as during debonding, however, it flows more easily at low strain rates, such as when wetting a substrate. The most significant effect of addition of a tackifier resin in acrylic PSAs is the enhancement of tack and peel strengths to substrates with a low surface energy, such as polyolefins and carton board [13].

When monomer starved feed strategy is used during semi batch polymerization of acrylic monomers of different reactivity, gel formation can occur due to the predominance of chain transfer to polymer reactions. Intermolecular chain transfer reactions can lead to the formation of long chain branches which results in formation of gel structures when the branch ends meet and terminate each other, namely termination by combination occurs. Control of the molecular weight and gel content is usually achieved by employment of a chain transfer agent [14] [15].

When tackifier rosin resins are employed in the polymerization of acrylates, two important effects should be taken into consideration. Firstly, when the resin is free in the polyacrylate, it has a negative effect as hydrogen abstraction of radical from tertiary carbon atoms. Secondly, the small amount of abietic acid in the resin can consume a part of radical and can make them inactive and then lead to the decrease in monomer conversion (Figure 4.1), (Figure 4.2) [14].

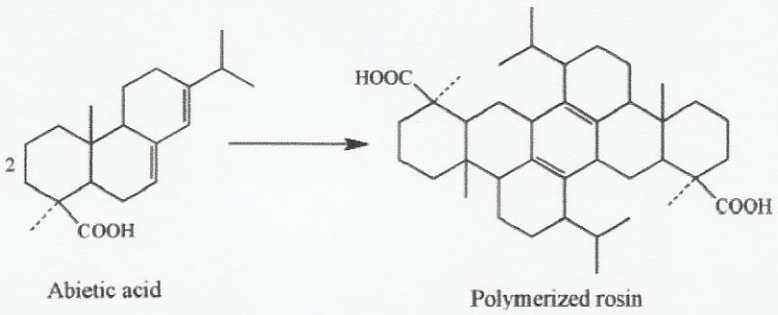

Figure 4.1: Polymerization reaction of abietic acid [14].

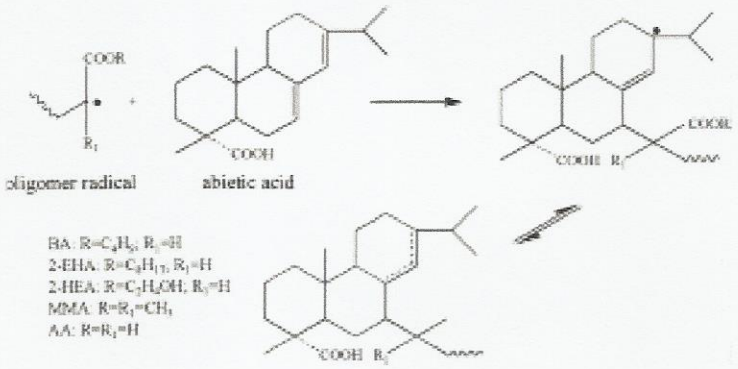

Figure 4.2: A proposed mechanism for chain transfer [14].

According to the results of polymerizations done in first part of this research, it was obviously seen that use of when saturation levels of rosin esters increases such as RE9, RE10 and RE11, higher tack performances were obtained. When unsaturated rosin ester RE3 was used in trials, synthesized polymer cannot fulfill the standard requirements of performance tests (Table 4.1), (Table 4.2).

Table 4.1: Performance test results for polymers tackified with unsaturated resins

POLYMER SPECIFICATIONS	Standard specification	Trial: 61	Trial: 61T4	Trial: 61T5	Trial:D61T6	Trial:D61T7	Trial:D61T10
Solid content, %	60,00	63,10	62,50	62,40	62,80	61,30	60
pH	7.5- 8.5	7,20	8,00	7,10	6,80	7,90	7,50
Viscosity, cps (LVT 3/30)	max 1000	300	180	120	140	140	-
APPLICATION TESTS							
Compound peel on label, on Cardboard, N/25mm, 180°	>8- AF/PT	10.16- 1%FP	5.63- 1%FP&PT	6.46- 1%FP	7.12 1%FP-PT	4.93 1%FP	4.59-1%FP
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	6,08	4,21	3,80	4,24	3,01	4,86
Compound shear on label, at 22°C	>6 hrs	>24 hrs	>24 hrs	99 hrs	37 hrs	8 hrs	7 hrs
Loop tack test of compound, on label, on SS, N/25mm	>14- AF	15,25	10,60	11,49	8,74	8,21	10,66
Loop tack test, on label, on LDPE, N/25mm	>7- AF	5,71	2,45	3,37	2,31	2,62	4,34
Tackifier used in compound		%10 RE3	%10 RE3	%10 RE3	%10 RE3	%10 RE3	%10 RE3

Table 4.2: Performance test results for polymers tackified with saturated resins

POLYMER SPECIFICATIONS	Standard specification	Trial:D9T1	Trial:D10T1	Trial:D10T2
Solid content, %	60,00	63,60	63,70	63,20
pH	7.5- 8.5	6,40	6,40	7,50
Viscosity, cps (LVT 3/30)	max 1000	600	940	1320
APPLICATION TESTS				
Compound peel on label, on Cardboard, N/25mm, 180°	>8- AF/PT	6.76-AT	4.62-AT	8.11-AT
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	12.46-AT	9.37-AT	14.52-AT
Compound shear on label, at 22°C	>6 hrs	6'-6'	5'-7'	5'-6'
Loop tack test of compound, on label, on SS, N/25mm	>14- AF	24.14-AT	22.90-AT	21.08-AT
Loop tack test, on label, on LDPE, N/25mm	>7- AF	8,79	7,50	6,54
Tackifier used in compound		%10 RE-9	%10 RE 10	%10 RE 10

However, due to high cost of saturated rosin ester, manufacturers tend to use unsaturated ones. To solve this problem, UV light was employed to disperse double bonds of unsaturated rosin resins. A thin layer of powdered unsaturated rosin resin RE 3 was exposed to 35 watt 254 nm UV light for six hours. However this method hasn't succeeded. There is no significant decrease in intensity of shifts between 4.0 and 5.5 which are characteristic for vinyl structure (Figure 4.3), (Figure 4.4).

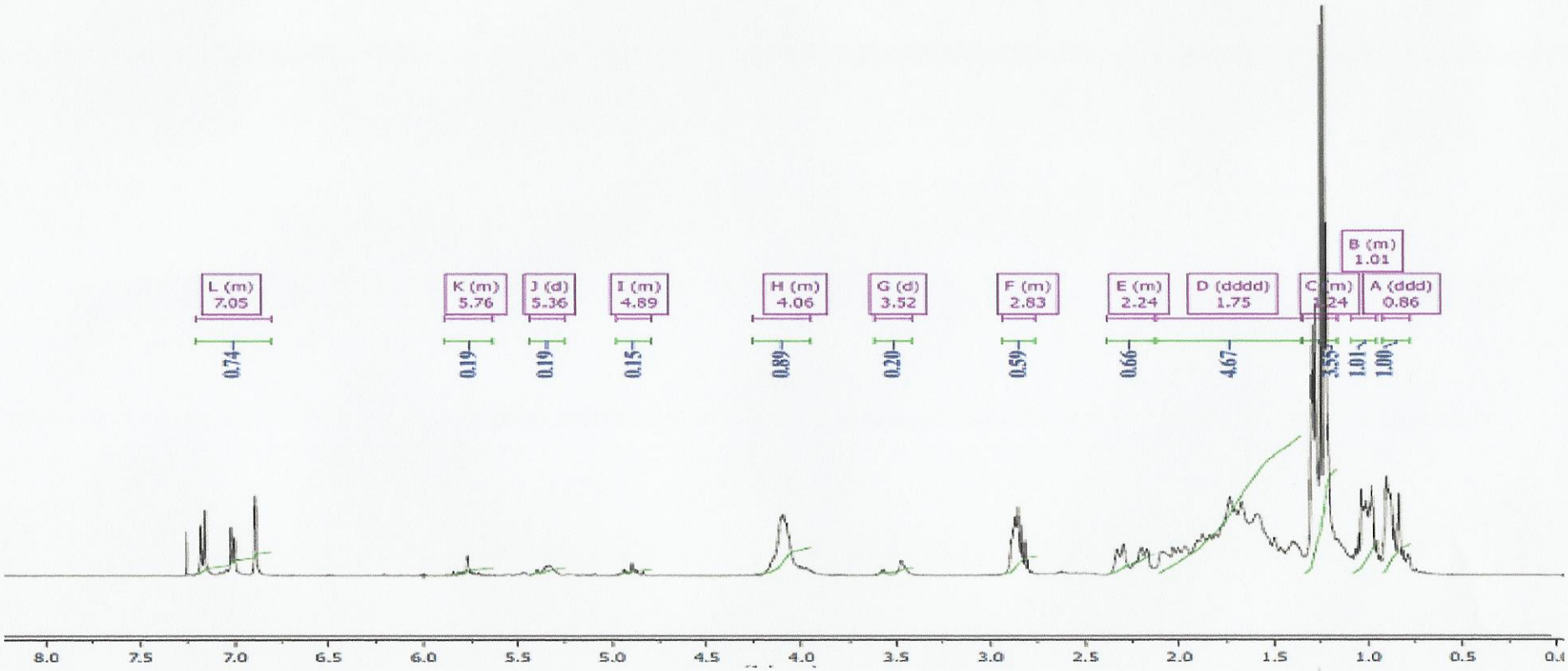

Figure 4.3: ^{1}H NMR spectra of unsaturated resin RE-3

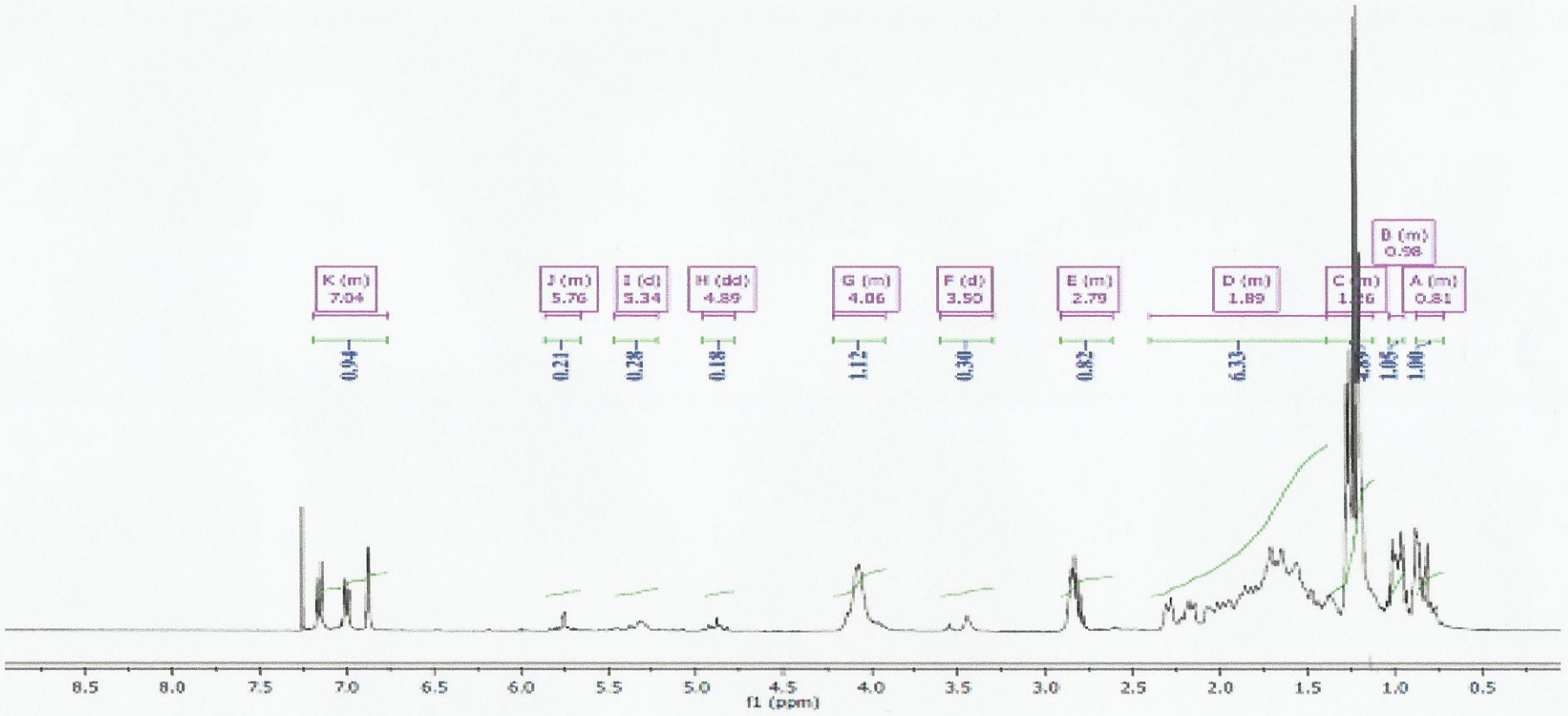

Figure 4.4: ^{1}H NMR spectra of unsaturated resin RE-3 after exposion to UV

4.3. Investigation of Resin Dispersion In Polymer Matrix

Resin can be present in polymer matrix in different places. It can be bonded to the polymer chain, act as a chain transfer agent, can be present in the matrix unbonded, can be encapsulated with polymer chains or can be bonded to polymer chains and form micelle-like structures.

To understand the exact place of resin in polymer matrix, firstly soxhlet extraction was used to see whether resin can be extracted from polymer matrix or not. Secondly glass transition temperatures of synthesized polymers were investigated with Differential Scanning Calorimeter.

A soxhlet extraction can be carried out when a compound of high solubility needs to be extracted from a solid mixture. A specialized piece of glassware is employed between a flask and a condenser. A solid sample is placed in porous container and the refluxing solvent continuously washes the solid extracting the desired compound into the flask (Figure 4.5).

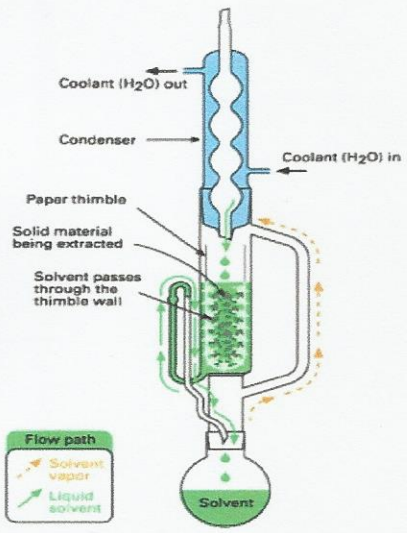

Figure 4.5: Schematic representation of soxhlet extraction [16].

Differential Scanning Calorimetry (DSC) , is a technique in which the heat flow rate difference into a substance and a reference is measured as a function of temperature while the substance and the reference is measured as a function of temperature while the substance and the reference subjected to a controlled temperature program [18].

Polymers or polymer blends are miscible when they form a single phase. Generally, the components of a polymer blend are not miscible unless there is an attractive interaction between them. Use of glass transition is the most widely use way to determine miscibility. The observation of a single glass transition with T_g somewhere between the T_g values of the individual components polymers, indicates a miscible system. A nonmiscible blend shows two glass transitions with T_g values corresponding to those of individual components, adversely. In case of partial miscibility, the lower T_g in the blend is shifted toward the higher T_g when compared to the pure component, while the higher T_g is lowered with respect to its pure component's T_g (Figure 4.6) [17].

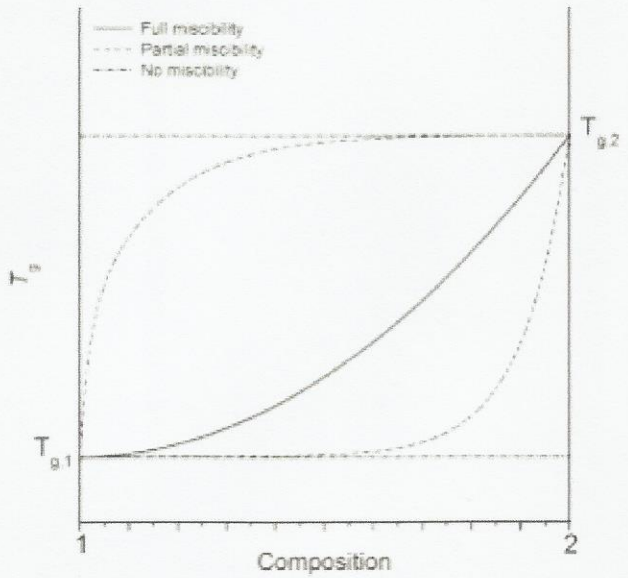

Figure 4.6: A schematic representation of the dependence of T_g on composition in binary polymer blends, fully miscible systems, compatible systems and immiscible systems [12].

One of the most important performances for PSAs is tack and it is affected by T_g of the materials, the miscibility of the tackifier and rate of separation [20]. The miscibility between the polymer and the tackifier resin affects the phase structure in the solid state, the mechanical properties and the practical performance of the PSA [21]. A good miscibility of the tackifier resin with the elastomer part of the polymer is crucial to produce adhesives with good tack [22][23].

In our study the miscibility between water borne acrylic emulsions and 4 different tackifier resins were investigated using DSC. As tackifier resins, 4 different rosin resin were used which have different hydrogenation level. Unsaturation levels were determined using NMR spectroscopy (Figure 4.7), (Figure 4.12), (Figure 4.15), (Figure 4.18).

Soxhlet extraction was applied to the product obtained from the *in-situ* polymerization of acrylates with unsaturated resin RE-3, (Trial 61T5). Resin amount is 10% (w/w) of total monomers used in formulation. However, the amount of resin extracted is 6.6 % (w/w). If the resin was miscible with base elastomer, acrylic part, the product was supposed to have one single glass transition temperature, between the glass transition of base elastomer (Figure 4.10) and of tackifier resin (Figure 4.9). Besides this, the shift in glass transition temperature of base elastomer would be directly proportional to the amount of resin incorporated to the base elastomer. It can be clearly seen from the DSC thermogram of Trial 61T5, there is one glass transition temperature which is -46°C (Figure 4.11). Second glass transition temperature which belongs to resin RE3 (Figure 4.9) could not be observed. Additionally, according to the NMR spectra of soxhlet extract, there is a significant decrease in unsaturation level (Figure 4.7), (Figure 4.8).

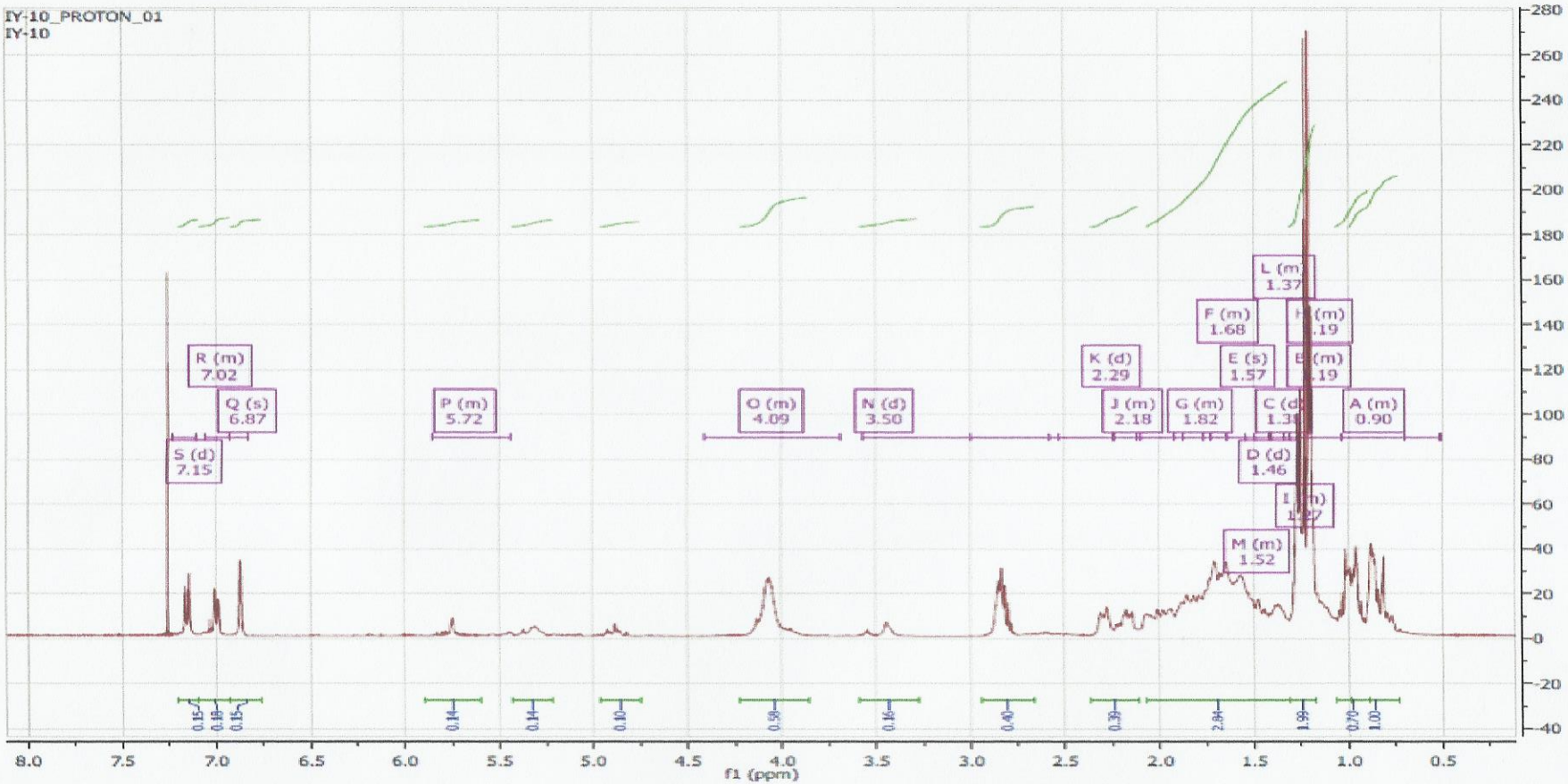

Figure 4.7: ^{1}H NMR spectra of of unsaturated resin RE-3



Figure 4.8: ^{1}H NMR spectra of soxhlet extract of Trial 61T5, polymerization done with unsaturated resin, RE3

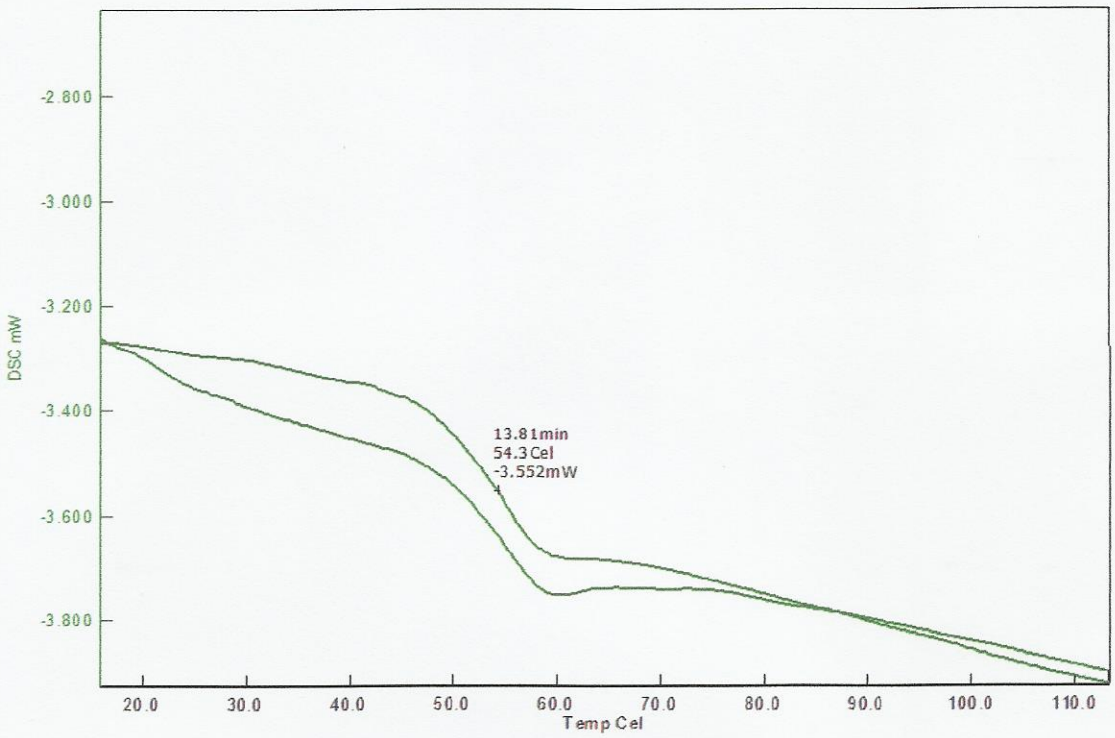

Figure 4.9 : DSC thermogram of unsaturated resin RE-3

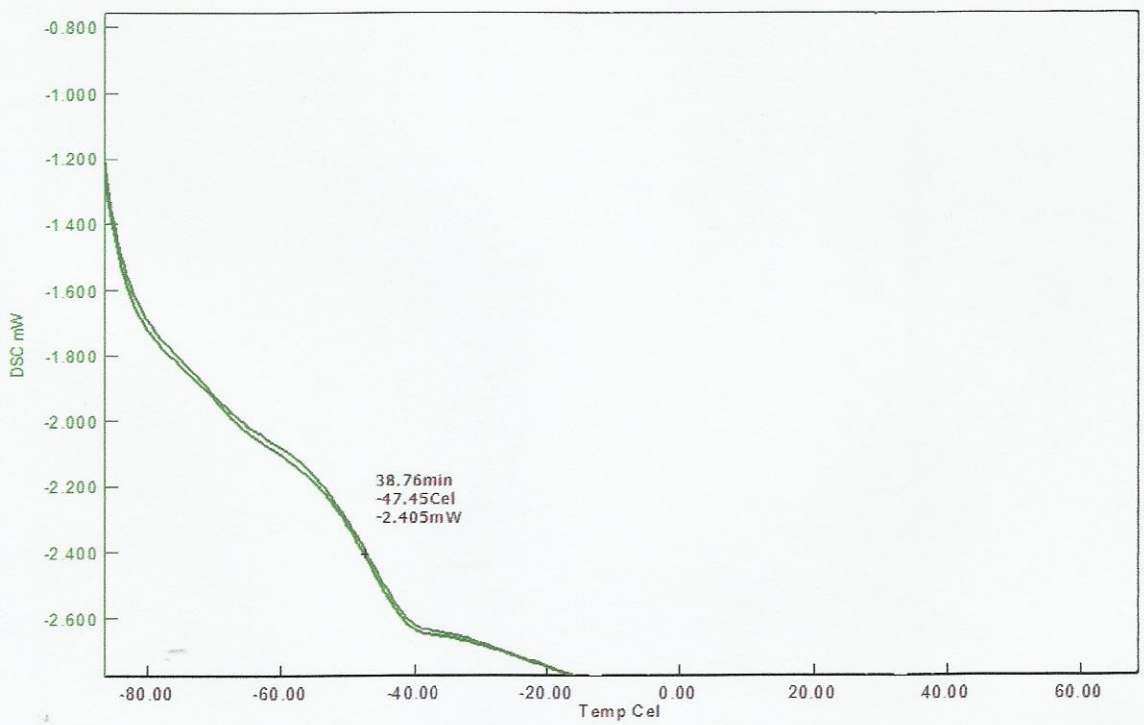

Figure 4.10 : DSC thermogram of polymer synthesized without tackifier, base elastomer

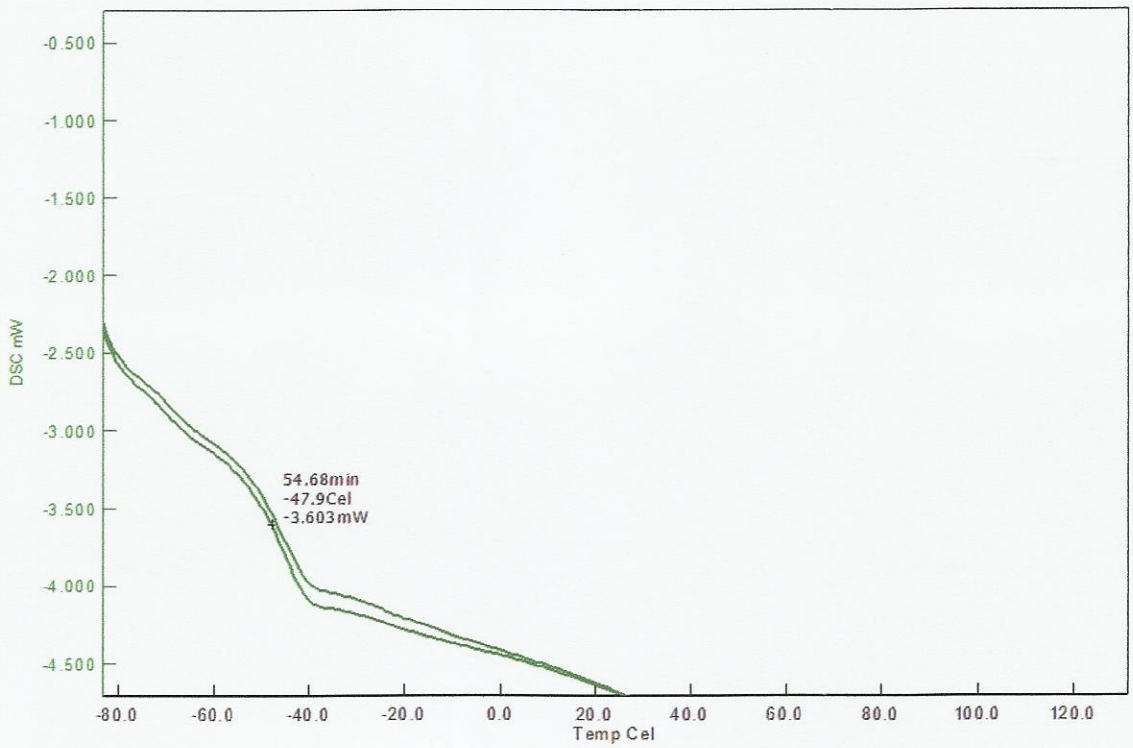

Figure 4.11 : DSC thermogram of Trial 61T5

Single glass transition temperatures were observed when saturation levels of rosin resins increase, too. Glass transition temperatures of these polymers were higher than the glass transition temperature of the polymer synthesized without tackifier, base elastomer (Figure 4.10). It can be concluded that saturated rosin resins are miscible with base elastomer. Besides incorporation of saturated resins enhances tack properties. Additionally, soxhlet extraction could not be applied to Trials 117, 118, 119 and resins RE9, RE10, RE11 cannot be extracted from base polymer with soxhlet extraction since appropriate solvent cannot be found in which the resin is soluble and the polymer is not.

Glass transition temperature of rosin resin RE 10 is 56°C (Figure 4.13). It has resulted a 2.8°C increase in T_g of base elastomer (Figure 26), since the glass transition of polymer synthesized is -45.8°C (Figure 4.14).

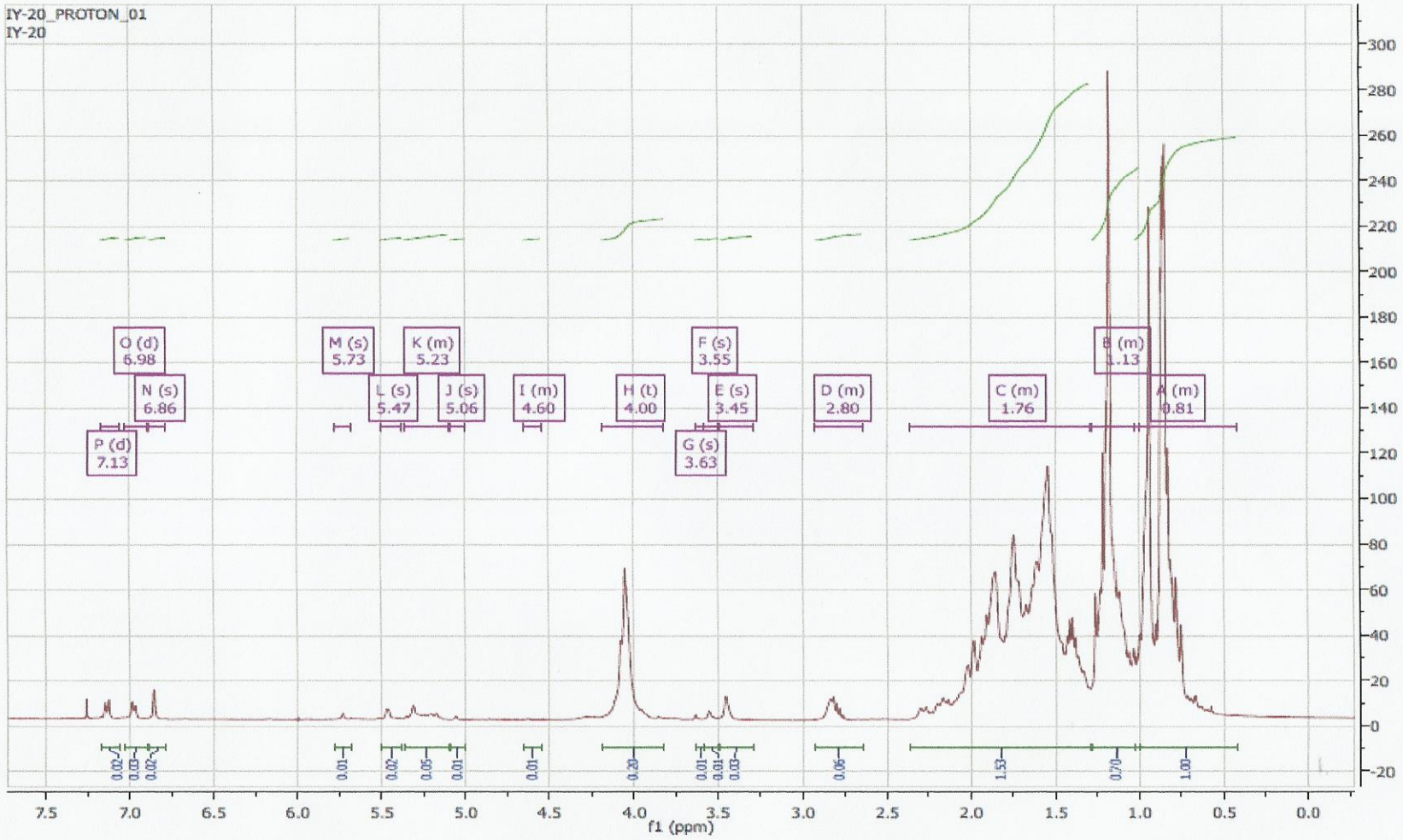

Figure 4.12 : ^{1}H NMR spectra of saturated resin, RE-10

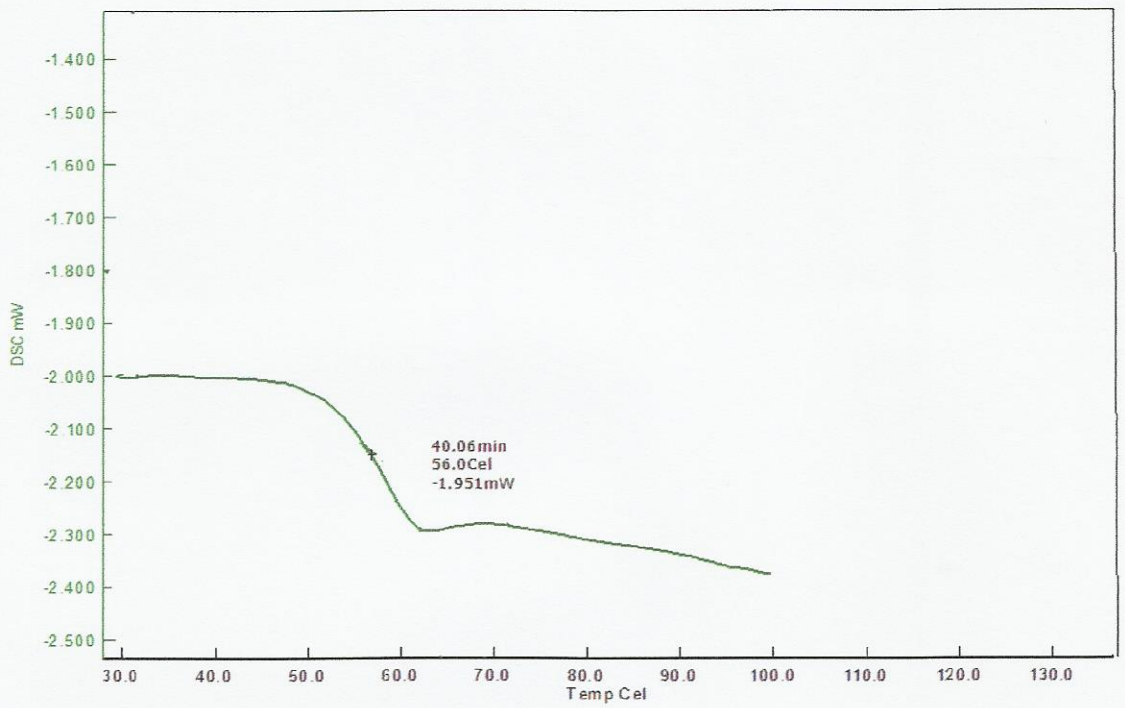

Figure 4.13 : DSC thermogram of unsaturated resin, RE-10

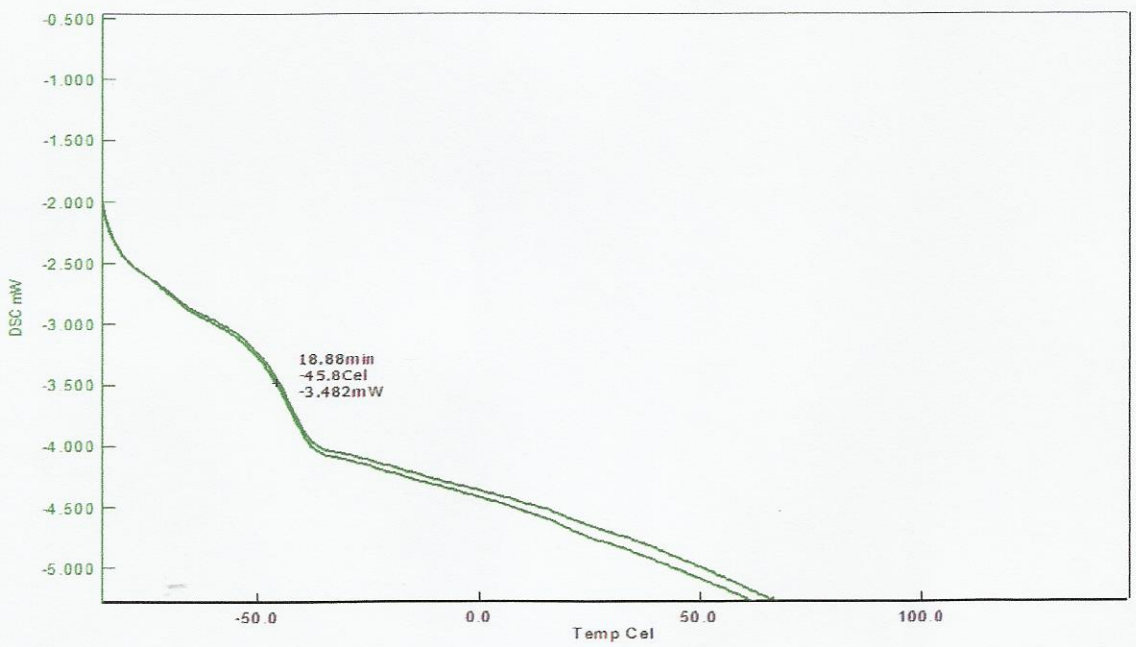

Figure 4.14: DSC thermogram of Trial 117

The glass transition temperature of rosin resin RE 9 (Figure 4.15) is 52.26°C (Figure 4.16). When this resin was used during *in-situ* emulsion polymerization, it has caused a 2°C increase in the glass transition temperature of base elastomer (Figure 4.10). The glass transition temperature of the polymer synthesized which is Trial 119, is -45°C (Figure 4.17).



Figure 4.15: ^{1}H NMR spectra of rosin resin, RE-9

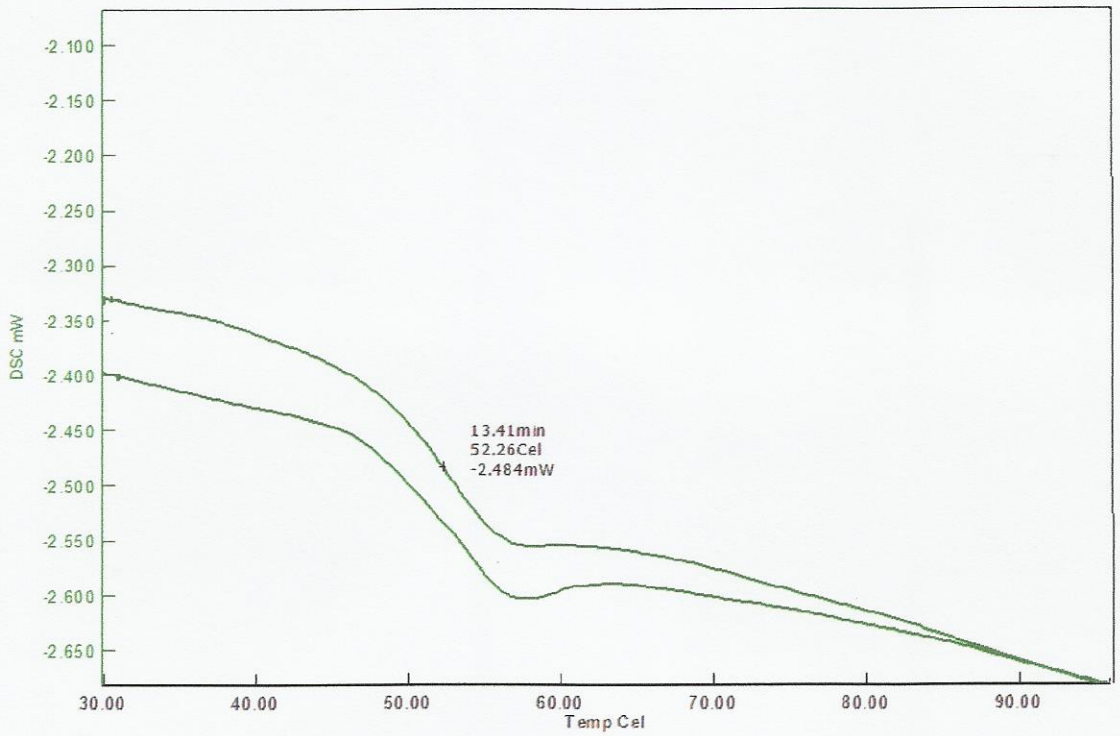

Figure 4.16 : DSC thermogram of saturated resin, RE-9

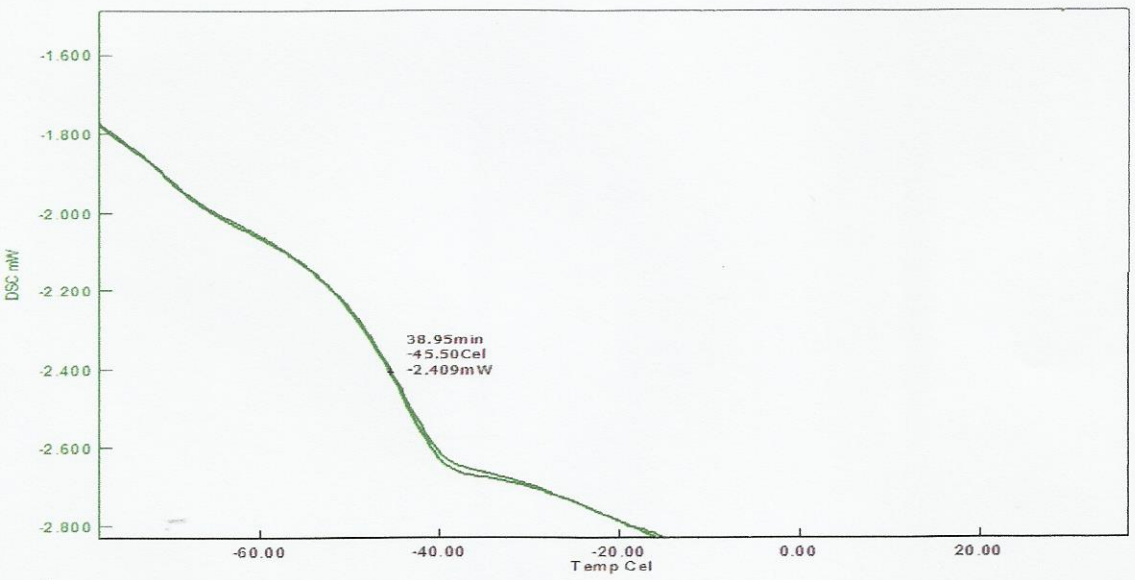

Figure 4.17: DSC thermogram of Trial 119

When rosin resin RE 11 (Figure 4.18), was used in polymerization, a polymer obtained with a single glass transition which is -47.3°C (Figure 4.19). Use of resin RE 11 has resulted in a 2.7°C increase in T_g of base elastomer (Figure 4.10), (Figure 4.20)

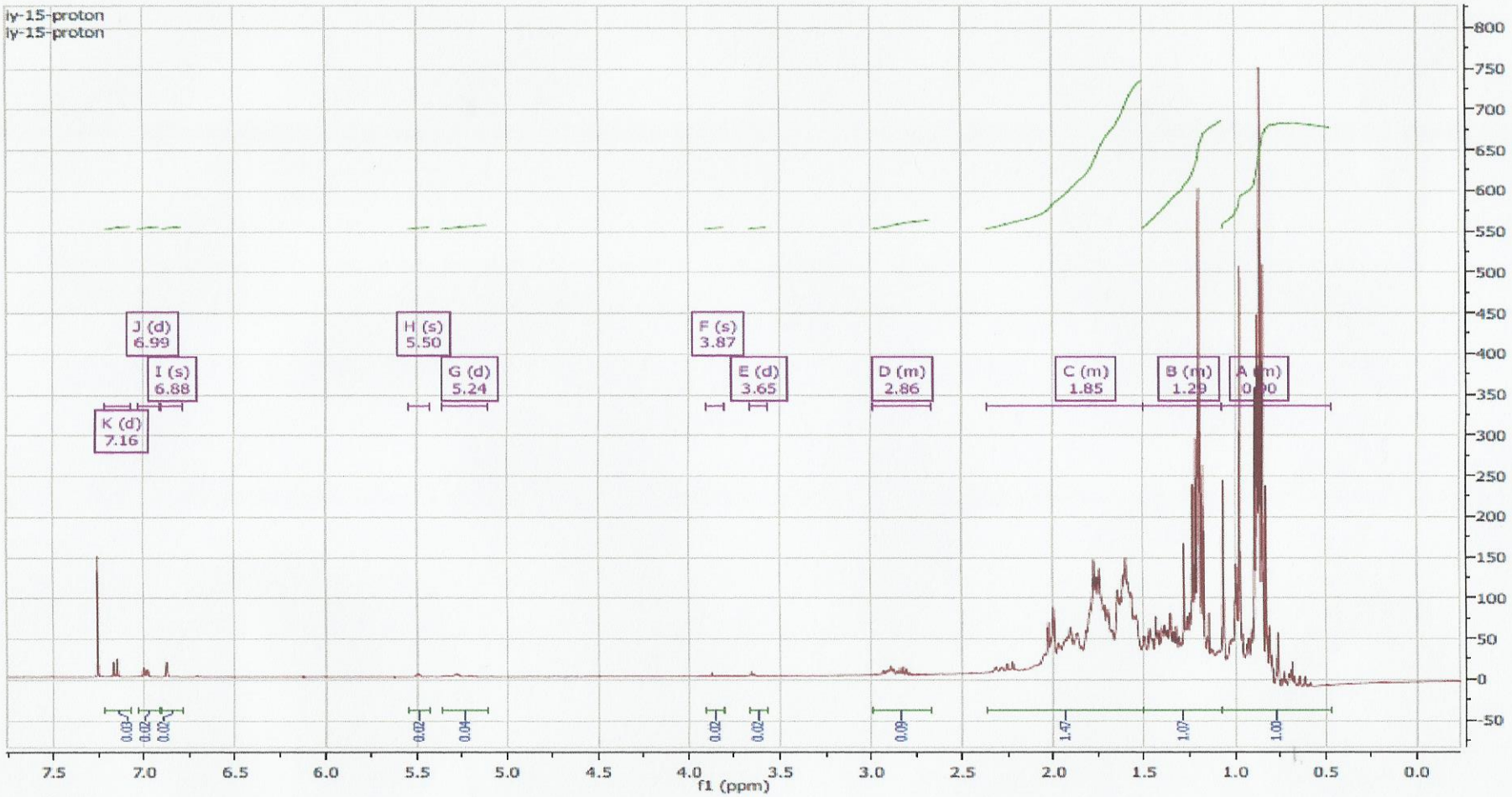

Figure 4.18 : ^{1}H NMR spectra of rosin resin, RE-11

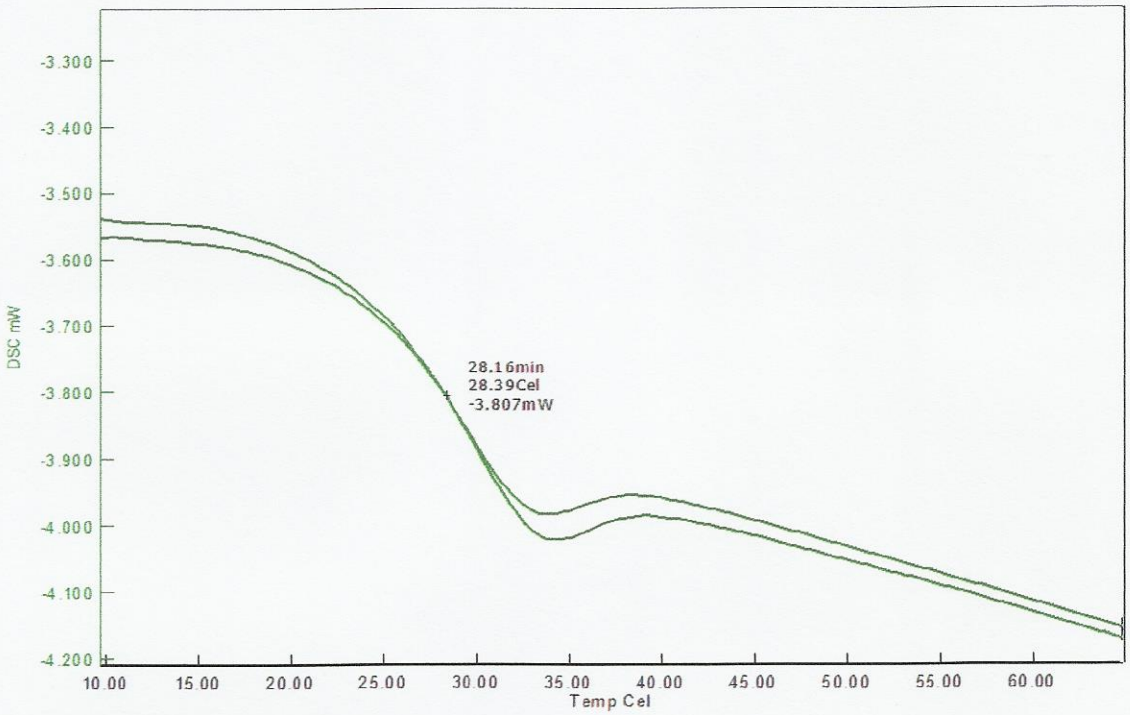

Figure 4.19: DSC thermogram of saturated resin, RE-11

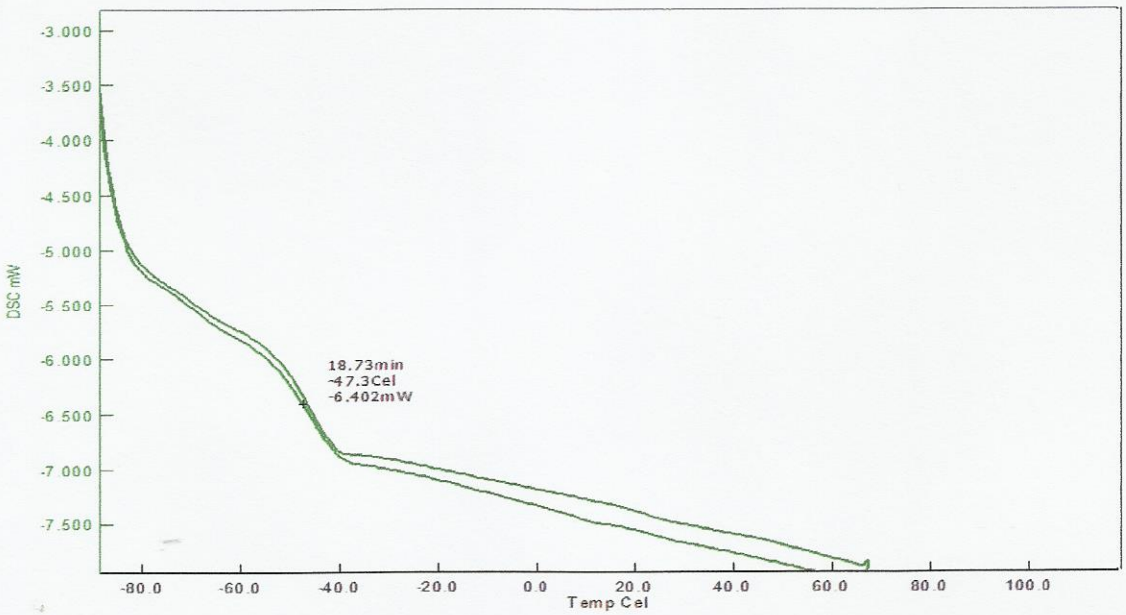

Figure 4.20: DSC thermogram of Trial 118

Table 4.3: Performace test results of some selected trials

POLYMER SPECIFICATIONS	Standard specification	Trial: 61T5	Trial:D117	Trial:D118	Trial:D119
Solid content, %	60,00	62,40	60	60	61.70
pH	7.5- 8.5	7,10	7,50	6,70	7,10
Viscosity, cps (LVT 3/30)	max 1000	120	-	-	120
APPLICATION TESTS					
Compound peel on label, on Cardboard, N/25mm, 180°	>8- AF/PT	6.46- 1%FP	8.79-AT	0.30-AT	9.51-AT-PT
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	3,80	5,15	4,10	6,09
Compound shear on label, at 22°C	>6 hrs	99 hrs	13-'10'	1'-2'	1.8 hrs
Loop tack test of compound, on label, on SS, N/25mm	>14- AF	11,49	13,88	10.38-AT	13,41
Loop tack test, on label, on LDPE, N/25mm	>7- AF	3,37	6,36	8.81-AT	5,27
Tackifier used in compound		10 % RE-3	10 % RE-10	10 % RE-11	10 % RE-9

Since when tack is improved, peel and shear resistances are decreased, some additional trials were attempts to improve shear and peel resistances. To achieve these mole percentages of monomer were changed. However, the desired results cannot be obtained (Table 4.3).

Table 4.4: Performance tests results of some additional trials

POLYMER SPECIFICATIONS	Standard specification	Trial: 120	Trial: 121	Trial: 122	Trial: 123	Trial:124
Solid content, %	60	60	60,9	60,9		
pH	7.5- 8.5	7,5	7,2	7,2		
Viscosity, cps (LVT 3/30)	max 1000	100	680	700		
APPLICATION TESTS						
Compound peel on label, on Cardboard, N/25mm, 180°	>8- AF/PT	4.71-1%FP	0.70-AT	0.43-AT	3.85-1%FP	5.29-AT
Compound peel on label, on LDPE, N/25mm, 180°	>6.5	2,42	3.48-AT	2.41-AT	10.27-AT	0.65-AT
Compound shear on label, at 22°C	>6 hrs	18 hrs	3'-4'	5'-4'	5'-11'	6'-8'
Loop tack test of compound, on label, on SS, N/25mm	>14- AF	9,64	7.83-AT	6.46-AT	6,72	23.05-AT
Loop tack test, on label, on LDPE, N/25mm	>7- AF	3,03	7.65-AT	6.81-AT	2,74	0.50-AT
Tackifier used in compound		no tackifier	10% RE-11	10% RE-11	10% RE-11	10% RE-11

5. CONCLUSION

Seeded semi-continuous *in-situ* emulsion polymerization has been employed to synthesize water borne acrylic adhesives in presence of various tackifier resins to achieve enhanced cohesion and adhesion performances.

This study is composed of two steps, during the first step standard formulations were modified according to the results of design of experiment study and appropriate surfactant package, initiator amount, reaction temperature were determined by Sukru Eren [11].

During the second step of this study, 4 different tackifier resins were chosen, which have yielded enhanced tack performances and employed during polymerization reactions. Miscibility of these tackifier resins were studied with Differential Scanning Calorimeter. It was observed all of these resin have unsaturations in different levels and they are miscible with base elastomer. DSC thermograms show that, polymers have one glass transition temperature. Besides, saturated resins have caused an increase in the glass transition temperature of base elastomer. Finally some additional trials were done to enhance both peel and shear resistances by modifying mole percentages of monomers used.

All in all, as a result of 124 laboratory trials and two pilot scale experiments a standard formulation is obtained and four tackifier rosin resins were chosen as the most compatible ones with the base acrylic elastomer.

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