SYNTHESIS AND CHARACTERIZATION OF WATERBORNE SILANE COUPLING AGENT CONTAINING SILICONE-ACRYLIC RESIN

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF WATERBORNE SILANE COUPLING AGENT CONTAINING SILICONE-ACRYLIC RESIN

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In this study, waterborne silicone-acrylic resin was produced by incorporating silane coupling agent onto the acrylic main chain by emulsion polymerization. After applying different emulsion polymerization processes, batch polymerization was selected to obtain the resultant resin. Thus finding the optimum conditions by investigating the parameters of monomer ratios, initiators, concentrations of initiators, temperature and time, the novel resin was synthesized. Water-dispersed silicone-acrylic resin was produced using butyl acrylate, butyl methacrylate, methyl methacrylate, 3-

methacryloxypropyltrimethoxysilane and acrylic acid as a hydrophilic monomer. 2,2'-azobis[2-(2-imidazolin-2yl)propane]dihydrogen chloride as thermal initiator and t-butyl hydroperoxide / sodiummetabisulfite as redox couple initiator were selected as the best effective initiators for the production of silicone-acrylic resin. The reaction temperature of the preparation of silicone-acrylic resin was taken as 50°C maximum to prevent gelation and agglomeration. To understand the effect of silane coupling agent on the properties of the resin, a new resin was synthesized which did not contain any silane coupling agent and the properties of both resins were determined by FTIR spectroscopy, thermal analysis and mechanical tests.

Their physical properties were also determined. The addition of 3-methacryloxypropyltrimethoxysilane to the main chain increased the hardness and the gloss values but slightly decreased the abrasion resistance value of the silicone-acrylic resin. All the samples showed superior flexibility. The produced polymer which contains silane coupling agent showed excellent adhesion properties on glass and metal plates.

Key words: Paint, waterborne, silicone-acrylic resin, emulsion polymerization, silane coupling agent.

ÖZ

SİLAN BAĞLAYICI İÇEREN SUDA YAYINIK SİLİKON-AKRİLİK REÇİNE SENTEZİ VE KARAKTERİZASYONU

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Bu çalışmada, silan bağlayıcının akrilik ana zincire bağlanması sağlanarak emulsiyon polimerizasyonu ile su esaslı silikon-akrilik reçine üretilmiştir. Farklı emülsiyon polimerizasyon prosesleri uygulanarak istenen reçineyi elde etmek için kütle polimerizasyonu uygun görülmüştür. Reçine, monomer oranları, başlatıcılar, başlatıcı konsantrasyonları, sıcaklık ve zaman parametreleri incelenerek uygun koşullar bulunduktan sonra sentezlenmiştir. Suda yayınık silikon-akrilik reçine, butil akrilat, butil metakrilat, metil metakrilat, 3-metakriloksipropiltrimetoksilan ve hidrofilik monomer olarak da akrilik asit kullanılarak üretilmiştir.

Silikon-akrilik reçine üretimi için en etkili başlatıcılar; termal başlatıcı olarak 2,2'-azobis[2-(2-imidazolin-2yl)propan]dihidrojen klorür ve redoks başlatıcı çifti olarak t-butil hidroperoksit / sodyummetabisulfit seçilmiştir. Reaksiyon sıcaklığı jelleşme ve topaklanmayı önlemesi açısından silikon-akrilik reçine hazırlanması sırasında en fazla 50°C olmalıdır. Sentezlenen silikon-akrilik reçine ve silan bağlayıcı içermeyen akrilik reçinelerin yapı özellikleri FTIR spektrometreleri ile belirlenmiş olup, polimerlerin ısıl davranışları DSC ile saptanmıştır. Ayrıca, silan bağlayıcı ilavesiyle silikon-akrilik reçinenin fiziksel, mekanik ve ısıl özelliklere etkisi incelenmiştir.

3-metakriloksipropiltrimetoksilanın ana zincire bağlanmasıyla silikon-akrilik reçinenin sertlik ve parlaklık değerlerinin arttığı, ancak aşınma değerinin düştüğü gözlenmiştir. Bütün boya örnekleri üstün esneklik göstermişlerdir. Ayrıca silan bağlayıcı içeren polimer cam ve metal yüzeye üstün yapışma özelliği göstermiştir.

Anahtar sözcükler: Boya, su esaslı, emülsiyon polimerizasyonu,
silikon-akrilik reçine, silan bağlayıcı

To my parents…

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I am dedicating this work to my mother and my father due to their endless love, unlimited support and care throughout my life.

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ABBREVIATION

SCA : Silane Coupling Agents
BA : Butylacrylate
BMA : Butylmethacrylate
MMA : Methylmethacrylate
AA : Acrylic Acid
3-MPTS : 3-Methacryloxypropyltrimethoxysilane
AIBN : 2,2'Azobisisobutyronitrile
t-BHP : t-Butylhydroperoxide
SMBS : Sodiummetabisulfite
DSC : Differential Scanning Calorimeter
FTIR : Fourier Transform Infrared Spectra Photometer

CHAPTER 1

INTRODUCTION

1.1 General Aspects of Paints

Generally, paint is dispersion of a finely divided pigment in a liquid composed of resin or binder and a volatile solvent and it also contains some additives such as driers, stabilizers, plasticizer, flame retardants, etc. The term paint is used when the primary consideration is the decorative purposes, on the other hand when the primary consideration is the protection of the materials the term coating is used; the protective function includes, resistance to water, organic liquids and chemicals, together with improved superficial mechanical properties such as greater hardness and abrasion resistance. The decorative effect may be obtained through color, gloss or combinations of these properties.

The primitive paintings of prehistoric times were done with quite different end in view. Certain objects were colored in order to ensure good fortune in hunting, to hold evil spirits at bay or to honor the dead in their graves. The Egyptians, starting very early, developed the art of painting and discovered the protective functions of the paints. However, it is only at the higher level of cultural development that the purely artistic motive becomes dominant, and it was very late in history, with the birth of industrialism, that painting came to be used extensively to protect objects and extend their useful lives. In our own technical era the protective use of paint is at least as important as its decorative function [1].

1.2. Paint Components

A paint contains three major ingredients together with small quantities of additives. The major ingredients are pigments, binders or resins and solvents.

1.2.1 Pigments

Pigments are the constituents of the paint that provide a colored surface as well as they protect the substrate from corrosion.

Pigments can be inorganic or organic. Inorganic ones are usually metallic oxides, such as cobalt blue, lead oxide, chromium oxide, cadmium yellow etc. on the other hand, organic types generally not found in nature, and they are synthesized from the coal tar and petroleum distillates.

Functions of pigments are to:

- decorate or obscure the underlying surface
- protect the substrate and resin against degradation
- enhance the durability of resin and binders
- improve chemical and corrosion resistance of the paint.

In addition to pigments, extenders which are supplementary pigments, are usually added to the paints to alter the rheological properties of paint by increasing the viscosity, to reduce the tendency of other pigments to settle and to flatten film appearance. Commonly used extenders are calcium carbonate, silica, kaolin and mica.

1.2.2 Resins or binders

Resins are film forming materials which are essential in paint formulation, since without a film forming material the pigments would not cling to the surface.

The function of the resin is to provide the forces which hold the film together (cohesive forces) and which hold the film and the substrate together (adhesive forces). It is the most important components of paints and many of the properties of the paints such as their mode of drying, adhesive and mechanical properties of the films, are determined by the nature of the binder.

Film forming processes in these resins occur in three ways; physical drying, chemical drying, and oxidative drying.

In physical drying, the film formation occurs solely by the evaporation of the solvent. As the solvent evaporates the resin and the pigments are brought close and closer together until they coalesce and form a coherent film. There is no firm chemical bonding in this process so that the film can be redissolved.

In chemical drying, the resin undergoes a change in chemical characteristics. A crosslinking agent is added to resin which enters into polymerization reaction and becomes a part of the final product. Once polymerized the materials cannot be redissolved.

In the oxidative air drying process, the absorption of the oxygen from the air takes place. The oxidation process causes the double bond to become saturated, which crosslinks the molecules [1].

The commonly employed film forming polymers or resins are polyesters, amino resins, phenolic resins, epoxide resins, silicone resins, polyurethane resins, long oil alkyds and acrylic resins.

1.2.3 Solvents

Solvents are volatile liquids that are used to dissolve highly viscous resins to produce a homogeneous phase. It plays no part in film formation and is used only in conveying the pigment-binder mixture to the surface as a thin uniform film.

The proper selection of the solvent is very important in paint industry because solvents differ in flash point, flammability, volatility, solvent power, and toxicity.

The most commonly used organic solvents as hydrocarbons, chlorinated hydrocarbons, esters, ketones, and ethers. Since organic solvents are volatile, flammable, toxic, and do not qualify in low volatile organic compound (VOC) applications, there is an increased interest in water borne coatings.

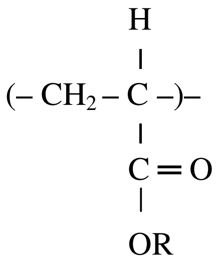
The properties of water are very different from those of organic solvents; this leads to distinct differences in characteristics of water-borne coatings as compared to solvent-borne coatings. Some of these differences are advantageous. For example, water presents no toxic hazard and it is odor-free. Water is not flammable; this reduces risks and thus insurance costs. There are no emission or disposal problems directly attributable to the use of water. With some formulations cleanup of personnel equipment is easy and the cost of water-borne coatings is usually low.

On the other hand, there are some disadvantages of the use of water. For example, the heat capacity and heat of vaporization of water are high, resulting in high energy requirements for evaporation. A problem, unique of water, is that the surface tension of water is higher than that of any organic solvent. In latex paints surfactants must be used to reduce surface tension so as to wet pigments so that a coating can wet many kinds of surfaces.

A further problem with water-borne coatings is that the water tends to increase corrosion of storage tanks, paint lines, ovens, and so forth. This requires that corrosion resistant equipment be used in water-borne coatings, increasing the capital cost [2].

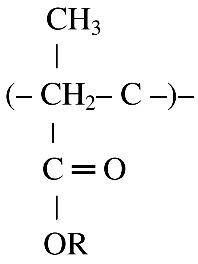
1.3 Acrylic Polymers as Coating Binders

Acrylic polymers, which are used as coating binders, are comprised chiefly of esters of acrylic and methacrylic acid that are polymerized by additional polymerization, usually using a free radical mechanism;



$$(-CH_2-\overset{\overset{H}{|}}{\underset{\underset{\underset{\underset{OR}{|}}{C=O}}{|}}{C}}-)-$$

An acrylate



$$(-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{\underset{OR}{|}}{C=O}}{|}}{C}}-)-$$

A methacrylate

Acrylic technology expanded into the coatings industry in the form of acrylic solution polymers, followed later by acrylic emulsions.

1.3.1 Acrylic Solution Polymers

Acrylic solution polymers are generally copolymers of acrylate and methacrylate esters prepared by direct solution polymerization in a solvent that has a solubility parameter similar to that of the polymer. Typical solvents include aromatics, as well as ketones and esters. Acrylic resins are usually supplied in solvents such as toluene, xylene or methyl ethyl ketone. They are clear, colorless solutions and, if left unpigmented, will also dry down to clear, colorless films [3].

There are two types of acrylic solution polymers: (i) Thermoplastic polymers, (ii) Thermosetting polymers.

Thermoplastic acrylic resins are polymerized directly in a suitable solvent and form a film solely by evaporation of the solvent. They do not need to be oxidized or crosslinked to form a hard, resistant finish.

Thermosetting acrylic resins are compositionally very similar to the thermoplastic-type acrylics, with the exception that they contain functional groups, such as carboxyl or hydroxyl, that are capable of reacting with another polymeric or monomeric multifunctional material (i.e. melamine, epoxy, isocyanate, etc.) to produce a cross-linked network. This crosslinking reaction takes place after the coating has been applied to the substrate, often by the application of heat, hence the term is “thermosetting” [3, 4].

1.3.2 Acrylic Emulsion Polymers

Acrylic emulsion polymers have become one of the major binder types in use in the coating industry today. The acrylic monomers are emulsified to form an emulsion polymer and then polymerized as small droplets in a continuous water phase. The droplets are typically stabilized by surfactants, and usually no solvent is present. While acrylic emulsions are generally associated with quality architectural coatings, they are also used to formulate industrial coatings. In fact, the use of acrylic emulsions in industrial applications is expanding at the expense of solvent-based systems because of the industry's need to control organic emulsions. Over the past 20 years, acrylic emulsion manufacturers have made great strides in improving the properties of acrylic emulsions so that they now offer performance similar to the solvent-based coatings that they are replacing [3].

1.4 Emulsion Polymerization

Emulsion Polymerization has developed into a widely used process for the production of synthetic latexes since its first introduction on an industrial scale in the mid-1930s. Today, millions of tons of synthetic polymer latexes are prepared by the emulsion polymerization process for use as commodity polymers in a wide variety of applications, such as: synthetic rubber, high-impact polymer latexes, latex foam, latex paints, paper coatings, carpet backing, adhesives, binders for non-woven fabrics, barrier coatings additives for construction materials such as portland cement, mortar and concrete, and sealants and adhesives.

Emulsion polymerization is a free-radical-initiated chain polymerization in which a monomer or a mixture of monomers is polymerized in the presence of an aqueous solution of a surfactant to form a product, known as latex. The latex is defined as a colloidal dispersion of polymer particles in an aqueous medium [5].

Emulsion polymerization is one of several alternative methods for effecting free-radical polymerization. In order to set emulsion polymerization into the same perspective, it is necessary to consider briefly the characteristics of each of the methods. The characteristics of various polymerization methods are illustrated in Table 1.1 [6, 7].

Table 1.1 Characteristics of Various Polymerization Methods

					Polymerization			
Method	Medium	Catalyst[a]	Monomer Conc.	Temperature Control	Rate	Degree	Solution viscosity	Remarks
Bulk	--	OS	--	Difficult	Slightly High	High	High	inflammability
Solution	Organic Solvent	OS	Low	Easy	Low	Low	Slightly High	inflammability
	Water	WS	Low	Easy	Low	High	High	
Emulsion	Organic Solvent	OS	High	Very Easy	High	High	Low	Locus of polymerization small; particle size <1 μ
	Water	WS	High	Very Easy	High	High	Low	
Suspension	Water	OS	High	Very Easy	High	High	Low	Locus relatively small; particle size >1 μ

[a] Abbreviations: OS, oil soluble ; WS, water soluble.

The great advantage of emulsion polymerization is not only that it provides a film-forming polymer dispersed in a cheap, odorless and inflammable medium which does not damage the substrate and is readily applied, but also enables the preparation of a polymer which cannot otherwise be made. In an emulsion polymerization the reaction can occur at high speed and yet large molecular weights maybe obtained and, further, although the polymerization of a monomer is highly exothermic, it is easy to maintain an isothermal reaction because of efficient heat transfer through the aqueous phase. Another convenience is that as in remaining monomers after the reaction may be readily removed by steam distillation [8].

1.4.1 Components Used in Emulsion Polymerization

The four basic components of an emulsion polymer system are

1. Monomers - usually a mixture of co-monomers
2. Surfactant-normally a mixture is used which frequently consists of non-ionic and ionic surfactants
3. Initiator-frequently more than one is used
4. Water

The other components normally present include:

a) Colloids
b) Buffers
c) Often post additions of the following are made when the coating is prepared to improve film formation and film performance characteristics such as plasticizers and coalescing solvents.

1.4.1.1. Monomers

Monomers are the building blocks in making polymers. The monomers in the latex manufacture not only has to satisfy polymer end-use needs, but also has to assure latex compatibility with pigments and fillers, and the latex of course must also be processable, i.e., stable during pumping, blending, monomer stripping, etc [5].

1.4.1.1.1 Monomer Selection

There are a wide range of monomers available for use in the formulation of acrylic resins. The selection of monomers is normally dictated by the performance, requirements and cost of the resulting product.

The following tables give general guidelines for monomer selection. When selecting mixtures of monomers, T_g, residual odor, viscosity and many other properties of the resulting polymeric film also have to be considered.

Table1.2 Film Property of Some Monomers

MONOMER	FILM PROPERTY
Methyl methacrylate	Exterior durability Hardness Stain and water resistance
Butyl and higher acrylates	Flexibility Water resistance
Hydroxy methacrylates	Functional groups for cross-linking
Acrylic and methacrylic acids	Functional groups Hardness

In addition to this table, acid monomers such as acrylic and methacrylic acid may be included to improve freeze-thaw stability.

The exterior durability of acrylic homopolymers is illustrated in the Table 1.3 below:

Table 1.3 Durability of Acrylates and Methacrylates

Methyl acrylate	Poor	Increasing durability ↓
Ethyl acrylate	Fair	
Butyl acrylate	Very good	
Methyl methacrylate	Very good	
Ethyl methacrylate	Excellent	
Butyl methacrylate	Excellent	

Acrylic resins usually contain a considerable variety of monomers; the following table 1.4 gives a general classification of monomers and helps to indicate which ones are most suitable for a particular application [9].

Table 1.4 Classifications of Monomers

Monomer	Hardness	Flexibility	Resistance (Alkali)	UV / Gloss retention	Solubility
Methyl methacrylate	Increase in hardness ↑	Increase in flexiblity ↓	Very good	Very Good	Increase in solubility ↓
Ethyl methacrylate			Excellent	Excellent	
Butyl methacrylate			Excellent	Excellent	
Methyl acrylate			Very good	Poor	
Ethyl acrylate			Very good	Fair/Good	
Butyl acrylate			Very good	Very good	

1.4.1.2 Surfactants

The surfactant controls many of the properties of emulsion polymers. Any molecule containing a water-soluble (hydrophilic or lipophobic) group chemically bound to a large water insoluble (hydrophobic or lipophilic) group will act as a surfactant. When a surfactant is dissolved in water, individual molecules concentrate at the water air interface where the hydrophilic groups are lying in the water and hydrophobic groups are sticking into the air. The concentration of individual surfactant molecules in water is limited and at a relatively low value surfactant molecules cluster together to form micelles. There is a critical concentration level below which a surfactant will not form micelles. The minimum level required for micelle formation is known as the ‘critical micelle concentration’ (C.M.C.) and varies with surfactant type.

The role of a surfactant in emulsion polymerization may vary during the course of the polymerization.

Initially they contribute to the rate of polymerization and particle formation. Once polymer is present the surfactant has to solubilise the polymer preventing precipitation, and when polymerization is complete the surfactant is required to stabilize the emulsion preventing flocculation of the polymer and formation of aggregates. Where the product is utilized in latex form the surfactant plays a major part in the performance characteristics and in particular: (1) freeze thaw stability, (2) water sensitivity, (3) mechanical stability, (4) corrosion resistance, (5) gloss.

Surfactants primarily determine the size and size distribution of the particles formed during emulsion polymerization.

Surfactants are generally categorized into four major classes: anionic, cationic, nonionic and amphoteric (zwitterionic) [9].

1.4.1.2.1 Anionic Surfactants

The negatively charged hydrophilic head group of the anionic surfactants may comprise soap, sulfate, sulfonate, sulfosuccinate or phosphate groups attached to an extended hydrophobic backbone [10].

The most common types are the alkali metal salts of straight chain carboxylic or sulphonic acids of 11 to 17 carbon atoms. Sodium laureate is a typical example. When dissolved in water it ionizes:

$$CH_3(CH_2)_{10}COONa \leftrightarrow CH_3(CH_2)_{10}COO^- + Na^+$$

The surface activity is due to the polar nature of the anion which consists of the hydrophilic (water-attracting) COO^- group and the hydrophobic or lipophilic (water-repelling) hydrocarbon chain. Except at very low concentrations the anions from micelles in which the hydrocarbon ends are directed inwards and the carboxyl groups outwards into the water.

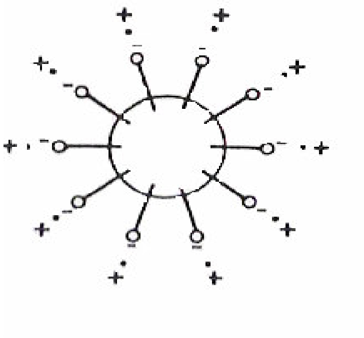
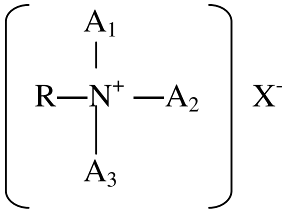


Figure 1.1 Representation of anionic surfactants (where the anions are represented as —O) [11].

1.4.1.2.2 Cationic Surfactants

The cationic surfactants are used infrequently in emulsion polymerization applications since they are not compatible with the anionic surfactants and with the negatively charged latex particles.

These are used very little in latex paints since they would neutralize the charges of an anionic surfactant which might be present and cause a break in the emulsion. Cationic surfactants possess germicidal anticorrosive, antistatic properties. The following is the structure of a cationic surfactant.



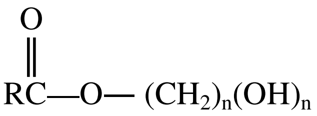
$$\left[R-\overset{\displaystyle A_1}{\underset{\displaystyle A_3}{\overset{|}{\underset{|}{N^+}}}}-A_2 \right] X^-$$

R represents a hydrophobic group such as long-chain aliphatic or aromatic group. X represents a negative ion such as Cl, Br, I, or other monovalent ion, and A_1, A_2 and A_3 represent hydrogen, alkyl, aryl or heterocyclic groups [4, 5].

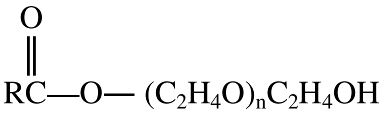
These surfactants are usually of the following types: salts of long chain amines, polyamines and their salts, quaternary ammonium salts (e.g., hexadecyltrimethyl ammonium bromide), polyoxyethylenated long-chain amines and their quaternaized derivatives, and amine oxides [12].

1.4.1.2.3 Non-ionic Surfactants:

Non-ionic surfactants depend chiefly upon hydroxyl groups and ether groups to create hydrophilic action [4].



$$\mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\text{—O— }(\mathrm{CH_2})_n(\mathrm{OH})_n$$



$$\mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\text{—O— }(\mathrm{C_2H_4O})_n\mathrm{C_2H_4OH}$$

The use of non-ionic surfactants may sometimes lead to the formation of small aggregates or grainy emulsions. This tendency is due to the weaker surface activity and the relative difficulty with which non-ionic surfactants form micelles. As a result of these deficiencies non-ionic, anionic surfactant mixtures are normally employed in emulsion polymerization. The ionic component allows easy solubilising of the monomer whilst the non-ionic component confers emulsion polymer stability [9].

Non-ionic surfactants may be separated into the following classes; polyoxyethylenated alkylphenols, polyoxyethylenated straight-chain alcohols, polyoxyethylenated polyoxypropylene glycols (i.e., block copolymers formed from ethylene oxide and propylene oxide), polyoxyethylenated mercaptans, long-chain carboxylic acid esters, alkanolamine ‘condensates’, tertiary acetylenic glycols, polyoxyethylenated silicones, N-alkylpyrrolidones and alkylpolyglycosides. The first three classes of non-ionic surfactants are the most commonly utilized for emulsion polymerization formulations [13].

1.4.1.2.4 Amphoteric (Zwitterionic) Surfactants

These types of surfactants exhibit anionic properties at high pH and cationic properties at low pH and may be categorized as : *β-N*-alkylaminopropionic acids, *N*-alkyl-*β*-iminodipropionic acids, imidazoline carboxylates, N-alkylbetaines and amine oxides. The sulfobetaines are amphoteric at all values of pH. These surfactants are not commonly used in emulsion polymerization formulations [5, 13].

1.4.1.3 Initiators

Initiators decompose into free radicals under suitable conditions; the free radicals are needed for water-borne emulsion polymerization [5, 8].

The free radicals can be produced by thermal decomposition of peroxy compounds like persulfate [14] or by redox reactions like persulfate-bisulfite couple [15] or by γ-radiation [16, 17].

1.4.1.3.1 Thermal Initiators

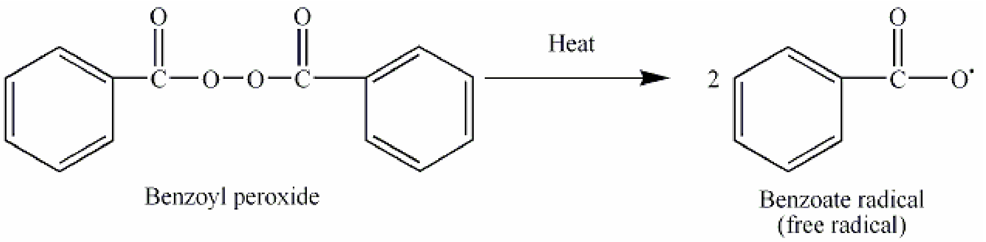
The free radicals produced by the decomposition of the initiator attacks the band of a manner to produce a monomer radical [9].

The most frequently used initiators are the salts of peroxydisulfate, i.e. persulfates. The thermal decomposition yields sulfate radical anions, which contribute to the charged character of the latex particle. Sodium, potassium and ammonium salts are generally interchangeable and used in the temperature range of 50-90°C [5].

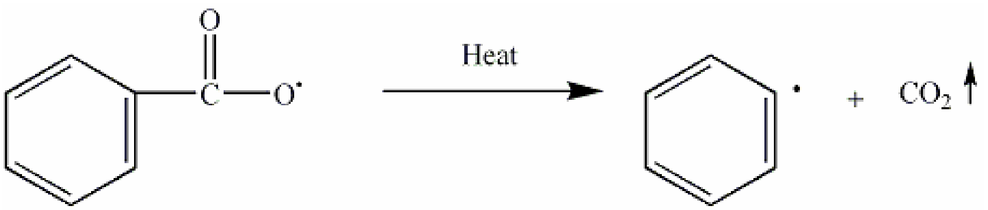
$$\underset{\text{Persulphate ion}}{S_2O_8^{2-}} \xrightarrow{\text{Heat}} \underset{\text{Radical ion}}{{}^{\cdot}2SO_4^{-}}$$

The initiators such as benzoyl peroxide, 2, 2-azobisisobutyronitrile (AIBN) are sometimes used [43].

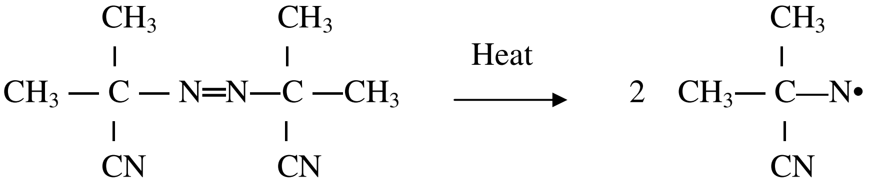
The thermal decomposition of peroxides and azo compounds can be represented as follows:



The benzoate radical may decompose further to give phenyl radicals.



The ratio of benzoate radicals to phenyl radicals depends upon the reaction conditions. Another example of thermal decomposition is that of AIBN:

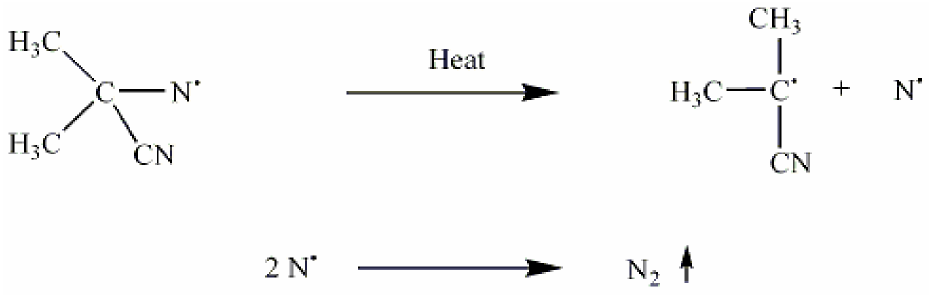


$$\mathrm{CH_3}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CN}}{\mathrm{C}}}-\mathrm{N{=}N}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CN}}{\mathrm{C}}}-\mathrm{CH_3} \xrightarrow{\text{Heat}} 2\ \mathrm{CH_3}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CN}}{\mathrm{C}}}-\mathrm{N}^{\bullet}$$

AIBN

Nitryl radical

Further decomposition of the nitryl radical can and frequently occurs forming nitrogen radicals which may combine to eliminate gaseous nitrogen.



1.4.1.3.2 Redox Initiators

Free radicals can be produced by chemical reactions. These are classed as redox initiators because a reducing agent catalyses the decomposition of a peroxide compound forming a redox couple. (Reduction- Oxidation couple)

Generation of free radicals by a redox mechanism can occur at relatively low temperatures (even below ambient) [9].

This can be particularly useful when high molar mass polymers are sought with low level of branching. Common redox systems are: persulfate-bisulfate[15,18] and persulfate-hyrosulfite [19].Sodium formaldehyde sulfoxylate has been used with a wide number of oxidizing agents like cumene hydroperoxide[20],tert-butyl hydroperoxide [21] and diisopropylbenzene hydroperoxide [22].The persulfate / iron(II) redox pair has been long known [23] and practically in all of the above redox systems iron (II) is used as a 'co-catalyst'.

1.4.1.3.3 Half Lives of Initiators

Polymerization can only proceed efficiently and economically, if sufficient free radicals are present in a given unit of time. Too many free radicals can have deleterious effect upon the properties of the resulting resin including excessive grafting, too low molecular weight or high degree of oxidation or polar chain ends. Thus, it is essential to know how the numbers of free radicals relate to the initiator, temperature and conditions used.

The stability of an initiator at any given temperature is measured in terms of its half life. Comprehensive details of half lives over a wide range of temperatures are available from the literature, particularly that of initiator suppliers. This detailed information is essential when formulating vinyl and acrylic polymers for surface coating applications. Half lives ($t_{1/2}$) for some common free radical initiators which have been taken from the literature are shown in Table 1.5 to illustrate the effect of temperature on the decomposition rate [9].

Table 1.5 Half Lives For Some Common Free Radical Initiators at Various Temperatures

Initiator	**Temperature**	**t ½ (half life)**	**Optimum Temperature Range**
di-cumyl peroxide	100 °C	20 hours	130 – 140 °C
	120 °C	5.5 hours	
	130 °C	2 hours	
	140 °C	35 hours	
	150 °C	12 hours	
	160 °C	4.5 hours	
di-tertiary butyl peroxide	130 °C	6 hours	140 – 150 °C
	140 °C	2 hours	
	150 °C	40 hours	
	160 °C	15 hours	
tertiary butyl perbenzoate	110 °C	15 hours	115 – 130 °C
	120 °C	1.75 hours	
	130 °C	35 hours	
	140 °C	12 hours	
	150 °C	4.5 hours	
tertiary butyl perpivalate	60 °C	6 hours	70 – 80 °C
	70 °C	1.25 hours	
	80 °C	20 hours	
	90 °C	9 hours	
di-benzoly peroxide	80 °C	4 hours	90 – 100 °C
	90 °C	1.25 hours	
	100 °C	25 hours	
	110 °C	8.5 hours	
Azobis-iso butryl nitrile	64 °C	10 hours	75 – 90 °C
	82 °C	60 hours	
	100 °C	6 hours	
	120 °C	1 hours	

1.4.1.4 Other Components Used in Emulsion Polymerization

1.4.1.4.1 Colloids

The term ‘protective colloid’ in an emulsion polymerization refers to high molecular weight water soluble materials such as polyvinyl alcohol, cellulose derivatives and alginate.

Most water soluble macromolecules act as protective colloids in emulsion polymerization. Macromolecule is a convenient term to denote a polymeric material whether prepared by polymerization of a vinyl monomer or by polycondensation.

1.4.1.4.2 Buffers

Buffers are often added to stabilize pH because:

(i) Some surfactants are pH sensitive with regard to micelle formation and latex stability.

(ii) Some initiators are pH sensitive.

(iii) Copolymerization may occur better at a specific pH; e.g. acrylic acid and methacrylic acid do not form copolymers easily above pH 5.

(iv) Some monomers maybe hydrolyzed; e.g. polyvinyl acetate is hydrolyzed at alkaline pH’s.

Typical buffers are borax, sodium hydrogen phosphate and sodium bicarbonate salts.

Most lattices are used as pH above 7.5. Where a buffer has been employed to keep the pH acidic during polymerization it is often necessary to adjust the final pH upon completion of polymerization. Ammonia is normally added to ensure an alkaline final product, but care must be exercised in its addition or destabilization, or lumps may form. The pH of the latex depends upon the chemical nature of the polymer [9].

1.4.1.4.3 External Plasticizers

Many of the commonly used external plasticizers can be used. As a general rule di-butyl phthalates are used with vinyl acetate and styrene is externally plasticized with phosphate esters or phthalates.

1.4.1.4.4 Coalescing Solvents

Glycols like ethylene and propylene are added to improve freeze thaw stability and rheological properties. In addition they also help in forming a continuous film, but not as much as lower evaporation rate glycols.

The solvents are considered to partition towards the hydrophilic network or polymer phase. Ethylene glycol is the former and ethylene glycol monobutyl ether acetate is the latter [9].

1.4.2 Steps of Emulsion Polymerization

The mechanism is very complicated and the approaches are more varied than other polymerizations. Classical approaches to emulsion polymerization mechanisms have been based on the theory by Harkins [6, 24, 25]. According to Harkins' theory, this process involves the following steps:

Surfactants emulsify the monomer in a water continuous phase and excess surfactant creates micelles in the water. Small amounts of monomer diffuse through the water to the micelle. Initiator (water-soluble and introduced into the water phase) reacts with monomer in the micelles. The micelles in total, comprise a much larger surface area in the system than the fewer, larger monomer droplets which is why the initiator typically reacts with the micelle and not the monomer droplet. Monomer in the micelle quickly polymerizes. More monomer from the droplets diffuses to the growing micelle/particle, where more initiators will eventually react. Monomer droplets and initiator are continuously and slowly added to maintain their levels in the system as the particles grow. When the monomer droplets have been completely consumed, the initiator is typically added in for a little while longer to consume any residual monomer. The final product is an emulsion of polymer particles in water.

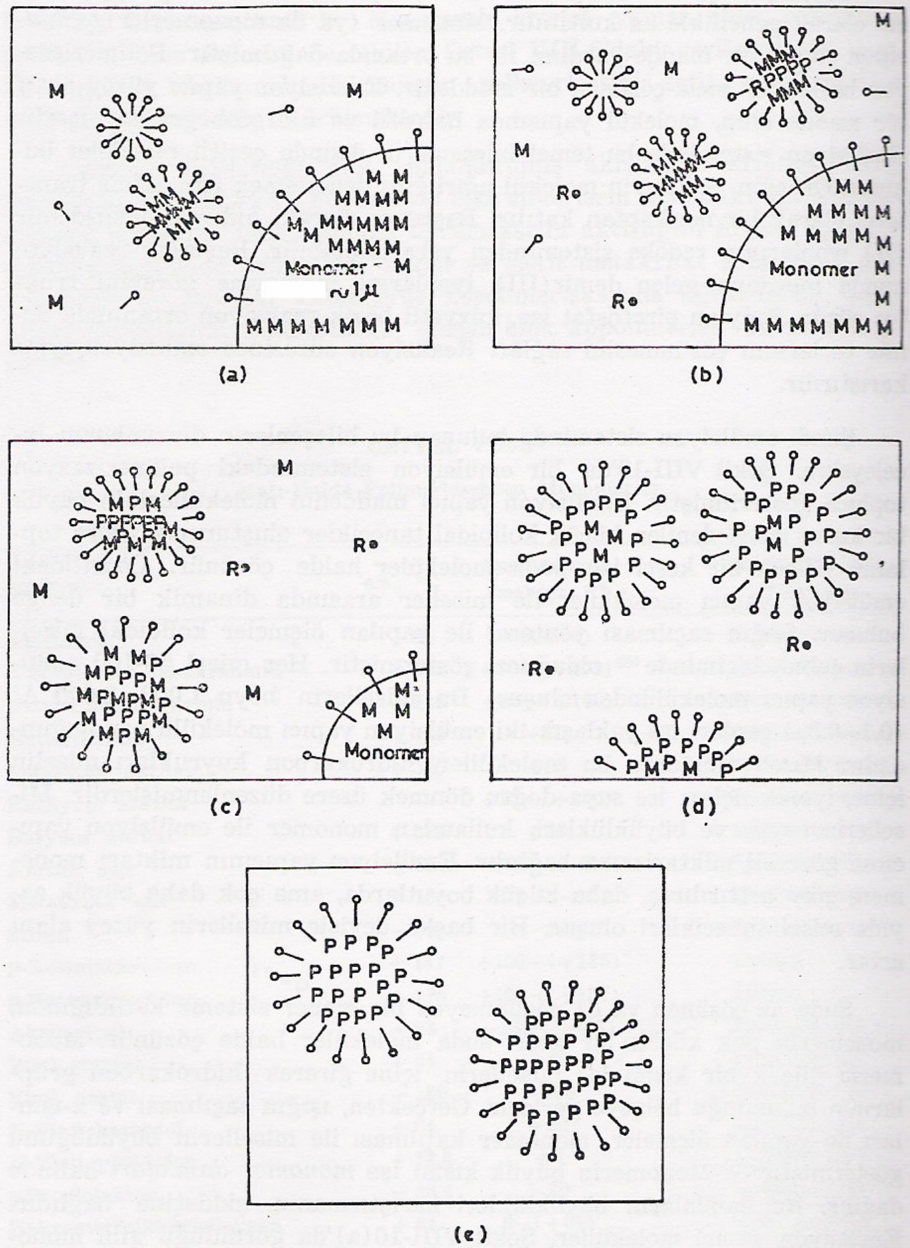


Figure 1.2 The Steps of Emulsion Polymerization a) before starting b) starting of polymerization c) polymerization, all micelles are used up d) finishing monomer droplets e) finishing polymerization (o— emulsifier, M monomer, P polymer, R• free radical)

1.4.3 Emulsion Polymerization Process

Three types of processes are commonly used in emulsion polymerization: batch, semi-continuous (or semi-batch), and continuous.

In a batch polymerization, all ingredients are added at the beginning of the polymerization. Polymerization begins as soon as the initiator is added and the temperature is increased, with the simultaneous formation and growth of latex particles. Thus, little further control can be exerted over the course of the polymerization other than the rate of removal of the heat generated by the polymerization. In order to exercise some control over the reproducibility of the particle number, pre-made seed latex is often used at the start of the polymerization.

In the semi-continuous process, one or more of the ingredients is added continuously or in increments. The monomers may be added neat, or as emulsions. The various modes of addition of the ingredients usually lead to different profiles of particle nucleation and growth throughout the polymerization process. The advantage of this process is the ability to exercise rigorous control over the various aspects of an emulsion polymerization, which includes the rate of polymerization and thus the rate of generation and removal of the heat of polymerization, the particle number, colloidal stability and coagulum formation, and copolymer composition and particle morphology.

In the continuous process, the polymerization ingredients are fed continuously into a stirred tank, or more than one stirred tank reactor connected in series, while the latex product is simultaneously removed at the same rate. Continuous processes can offer the advantages of high production rate, steady heat removal, and uniform quality of latexes [5].

1.5 Silane Coupling Agents (SCA)

A silicone compound that contains both organic and inorganic reactivities in the same molecule, R-Si-X_3, where R is an organofuctional group, can function as a coupling agent [26]. A coupling agent, or adhesion promoter, can change the interface between an organic polymer and in an inorganic substrate [26-28]. They are used in a variety of applications, including reinforced plastics, coatings, paints, inks, sealants, adhesives, and elastomers. Their use result in improved bonding and upgraded mechanical properties.

A silane coupling agent may function as [29]:

i) a finish or surface modifier- a film several monolayers thick that function only to chemically modify a surface without contributing any mechanical film properties of its own.

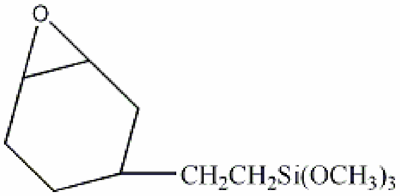
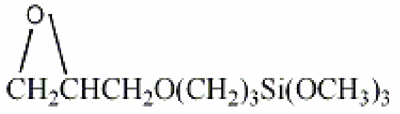
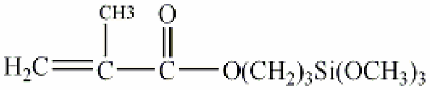
ii) a primer or size- forms a film 0.1 to 10 μm thick and must have adequate film properties (rigidity, tensile strength, etc.).

iii) an additive-silane may be added directly to the resin to modify the interfacial layer.

iv) An adhesive-silanes are rarely used as adhesive, they are usually used to improve the adhesive properties of organic resin.

A list of the different types of the silane coupling agents (SCA) is given in Table 1.6. The SCAs have the structure of $R - Si - X_3$. R is a nonhydrolyzable organic radical that possesses functionality and enables the coupling agent to bond with organic resin and polymers. X is hydrolyzable organofuctional group, typically, alkoxy, amine or chlorine. The most common alkoxy groups are methoxy, ethoxy or acetoxy, which reacts with water to form silanol (Si-OH) and ultimately forms an oxane (Si-0-M) bond with the inorganic substrate [27,30].

Table 1.6 Types of Silane Coupling Agents

Types of Silane Coupling Agents	Chemical Formula
(Amino Silane) gamma-Aminopropyltriethoxysilane	$H_2NCH_2CH_2CH_2\text{Sİ}(OC_2H_5)_3$
(Amino Silane) N-beta-(Aminoethyl)-gamma-Aminopropyltrimethoxysilane	$H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$
(Epoxy Silane) beta-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane	
(Epoxy Silane) gamma-glycidoxypropyltrimethoxysilane	 $\overset{O}{CH_2CH}CH_2O(CH_2)_3Si(OCH_3)_3$
(Mercapto Silane) gamma-mercaptopropyltrimethoxysilane	$HSCH_2CH_2CH_2Si(OCH_3)_3$
(Vinyl Silane) Vinyl-tris-(beta-methoxyethoxy)silane	$CH_2{=}CHSi(OC_2H_40CH_3)_3$
(Methacrylo Silane) gamma-methacryloxypropyltrimethoxysilane	 $H_2C{=}\overset{CH3}{\overset{\mid}{C}}-\overset{O}{\overset{\|}{C}}-O(CH_2)_3Si(OCH_3)_3$

1.6 Silicone-Acrylic Resin in Water-borne Coatings

Water-borne coatings generally are composed of resins containing hydrophilic functional groups (e.g. neutralized carboxylic acid groups, polyethylene oxide groups, etc.) [31].

Since weatherable coatings require special film properties, it has been difficult to meet the needs with common synthetic resins. Since the 1980s, coatings containing fluorine resin which are copolymerized by fluoroethylene and alkyl vinyl ether have been used as weatherable coatings. However, coatings containing fluorine resin have some disadvantages, such as being expensive, environmentally pollutive, poor in hardness, and workability. Recently, coatings containing silicone-acrylic resins have gained recognition as weatherable coatings. Since the coating containing silicone-acrylic resins are a composite of organic and inorganic polymeric materials, it is easy to control the film hardness and to apply them to various substrates [32].

1.7 Previous Studies

In 1990, Rau and Babu studied the synthesis of copolymer of vinyltriacetoxysilane and bromomethacrylate and investigated its thermal behavior. They reported that the copolymer shows higher T_gs than the corresponding polybromoacrylates suggesting increased intermolecular interactions in the copolymers with increase in silane content due to polar acetoxy groups [33].

In 1993, Yasuyuki et.al studied the phase separation of a silicone-acrylic rubber prepared by grafting silicone emulsion and acryl emulsion [34].

Witucki prepared a silicone-arcylic emulsion by cold blending an alkoxy silane and acryl emulsion through the following two-step processes. The first step was hydrolysis of an alkoxy functional group, and the second step was the formation of silicone polymer. He reported that the existence of 10% silicone increases gloss retention and decreases chalk phenomenon and color difference [35].

Kagaku Kogyo Co., Dupont Co. and PPG Co. did some works similar to these studies. The weather resistant coatings, in which curing catalysts are used, consist of hydroxyl group-containing acrylic polymer / hydroxyl or alkoxy group-containing siloxane [36].

However, there have been few papers reporting on the synthesis of the silicone - acrylic resin in water-borne coatings that is synthesized by emulsion polymerization.

1.8 Aim of This Work

The major objective of the present research is to obtain silicone-acrylic resin by using hydrophilic functional group with emulsion polymerization. Since the variety of parameters in emulsion polymerization, to synthesize the silicone-acrylic resin for water-borne coatings is difficult. Lots of initiators, initiator ratios and monomer ratios were investigated to synthesize the silicone-acrylic resin. The samples were characterized by FTIR and DSC spectroscopies. This research includes the physical and mechanical properties of the silicone-acrylic resin. The acrylic resin without silane coupling agent by using the same monomers and polymerization technique was also synthesized to compare the physical properties between them.

CHAPTER 2

EXPERIMENTAL

The synthesis and characterization of silicone-acrylic resin consists of three main parts:

1. The synthesis and characterization of silane coupling agent containing silicone-acrylic resin.
2. The synthesis and characterization of acrylic resin without silane coupling agent.
3. The tests on physical and thermal properties of these resins.

The following chemical and characterization method are used for this purpose.

2.1 Raw Materials

The materials used to prepare samples are given in Table 2.1.

Table 2.1 Raw Materials

Monomers	Initiators	Neutralizing and pH Adjusting Agents	Surfactants	Solvents	Chain Transfer Agents.
Butyl Acrylate (Merck)	Ammonium Sulfate (Merck)	Morpholine (Merck)	Disponil 25S (Cognis)	Toluene (Merck)	n-octylmercaptane (AkzoNobel Kemipol)
Butyl Methacrylate (Merck)	Benzoyl peroxide (Poliya Polyester)	Triethanolamine (Merck)	Disponil OP25 (Cognis)	Xylene (Merck)	t-dodecyl mercaptane (Aldrich)
Methyl Methacrylate (Merck)	t-Butyl peroxide (Merck)	Triethylamine (Merck)			
Acrylic Acid (Merck)	2,2'-azobis[2-(2-imidazolin-2yl)propane] dihydrogenchloride (CHT Tekstil Kimya)	Ammonium hydroxide (Merck)			
3-Methacryloxypropyltrimethoxysilane (Aldrich)	2,2'azoisobisbutyronitrile (Merck)				
	t-Butyl hyroperoxide (CHT Tekstil Kimya)				

2.2 Synthesis of Water-borne Silicone-Acrylic Resin

2.2.1 Preliminary Experiments

First attempt was to use solution polymerization to get the silicone-acrylic resin. The procedure of Park et.al [32] was directly applied to get the silicone-acrylic resin with the addition of acrylic acid. Temperature, time and the amount of acrylic acid were investigated by performing ten different experiments. In all of these experiments gel formation could not be avoided. The next synthesis was carried by emulsion polymerization instead of solution polymerization. In this series, according to the film-forming properties of the polymer, five different experiments were performed by changing the amount of monomer ratios. Unfortunately, these syntheses were not successful as the films formed were brittle.

The experiments were repeated in the presence of co-solvents such as toluene and xylene to investigate if there were any changes in the properties of the product and the results were still unsuccessful which proved no change.

Next group of experiments involved changes in the type of initiators, their concentrations and temperatures, in some cases some monomer amounts as well; yet no successful product was obtained (about 35 experiments). The initiators used were : ammonium sulfate, t- butyl peroxide, methyl ethyl ketone peroxide, 2,2'-azobisisobutyronitrile, 2,2'-azobis[2-(2-imidazolin-2yl)propane]di hydrogenchloride and t-butyl hydroperoxide. Also some activators like cobalt and dimethylaniline were used to activate the initiators. When investigating the initiators and their concentrations, temperature was also changed between 20°C and 85°C to obtain the desired resin. As a result, 2,2'-azobis[2-(2-imidazolin-2yl)propane]dihydrogenchloride as thermal initiator and t-butyl hydroperoxide / sodiummetabisulfite as redox couple initiator were selected as the best effective initiators for the production of silicone-acrylic resin. Tromsdorff effect was the main reason for the gel formation with increasing temperature. High temperature accelerated the reaction of monomers thus enhancing crosslinking. In general Tromsdorff effect can be avoided by chain transfer agents.

Different surfactants with varying concentrations were also tried in these experiments and Disponil 25S and Disponil OP25 were used to get good dispersion.

Several experiments were performed to adjust by different neutralizing agents using ammoniumhydroxide, triethanolamine, morpholine and triethylamine. Triethylamine gave the best result. The acrylic acid was neutralized by two different methods: neutralization before polymerization and after polymerization. The film property of the neutralized product after the polymerization was clearer than before polymerization.

As a result of all experiments (≈70) it was possible to adjust the optimum monomer ratios, initiators, their concentrations, temperature and time. The silicone-acrylic resin was synthesized according to these conditions given in the next part.

2.2.2 Synthesis of the Silicone-Acrylic Resin in This Work

Silicone-acrylic resin was synthesized by emulsion polymerization using batch process. Emulsion polymerization processes consist of two parts: (i) preemulsion, and (ii) reactor charge.

Preemulsion was prepared with two different solutions. For solution 1, water (50.0g.), Disponil 25S (10.0g.) and OP 25 (1.25gr.) were mixed in a 100 mL beaker. For solution 2, butylmethacrylate (84.52g.), butylacrylate (70.0g.), methylmethacrylate (75.0g.), acrylic acid (5.0g.) and 3-methacryloxpropyltrimethoxysilane (1.5g.) and 2,2'-azobis[2-(2-imidazolin-2yl)propane]dihydrogenchloride (0.472g.) were put in a separate 250 mL beaker and mixed for 5 minutes after the addition of each substance. Then, the two separate solutions were mixed and stirred for 15 minutes. After obtaining a homogeneous pre-emulsion, the second part-reactor charge, was started. The experimental set-up is shown in Figure 2.1.

The reaction was performed in a 500 ml five-neck glass flask. Apparatus consisted of mechanical stirrer, condenser, thermometer, a feed inlet and another inlet of nitrogen gas. The reactor was heated in an oil bath.

Water (245.0g.) and all of the preemulsion were decanted into the reactor. The t-butylhydropreoxide (0.0944g.) and sodiummetabisulfite (2.0g.) were fed to the reactor at three times (1/3 in each) in 1 hour at room temperature. After the completion of the addition process, the temperature was slowly increased to 50°C in about 30 minutes and held at 50°C for about 2.5 hours to complete polymerization. The completion of reaction was controlled with the method for nonvolatile content of varnishes [37].

After obtaining the polymer, triethylamine was added to neutralize the carboxylic groups and the mixture was stirred for another 30 minutes while maintaining the temperature at 50°C.

The same procedure was followed by using the same amounts of the chemicals for the synthesis of acrylic resin without silane coupling agent.

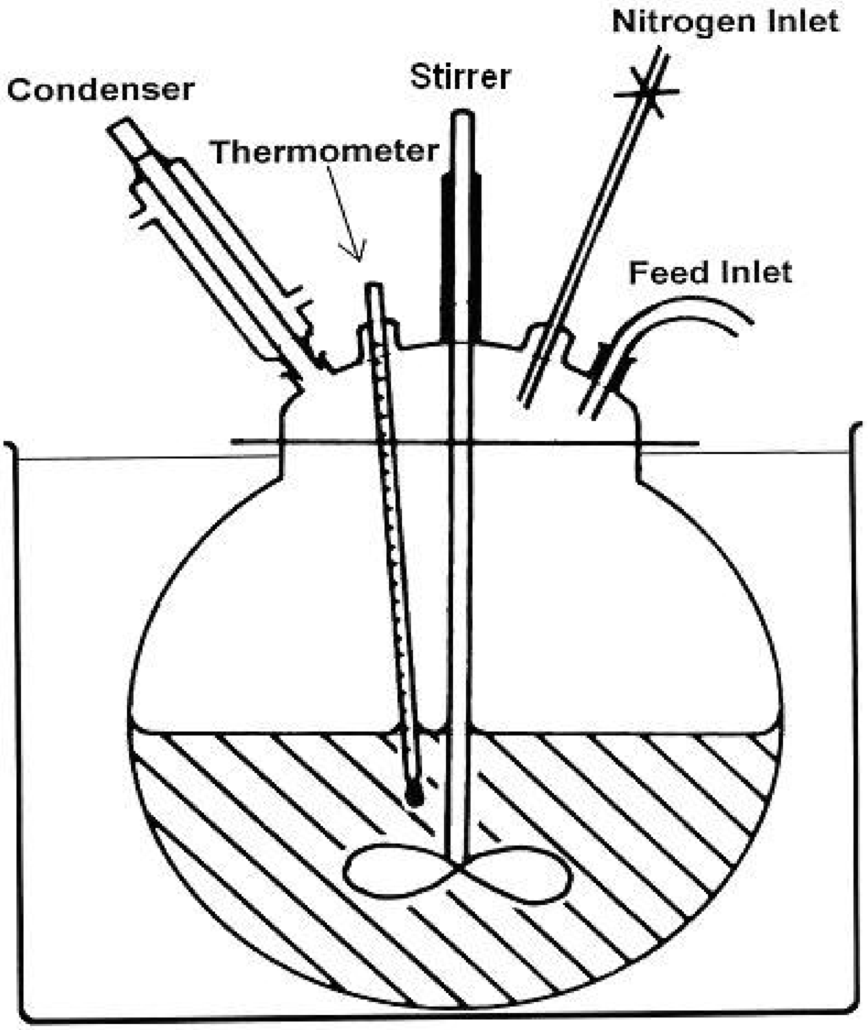
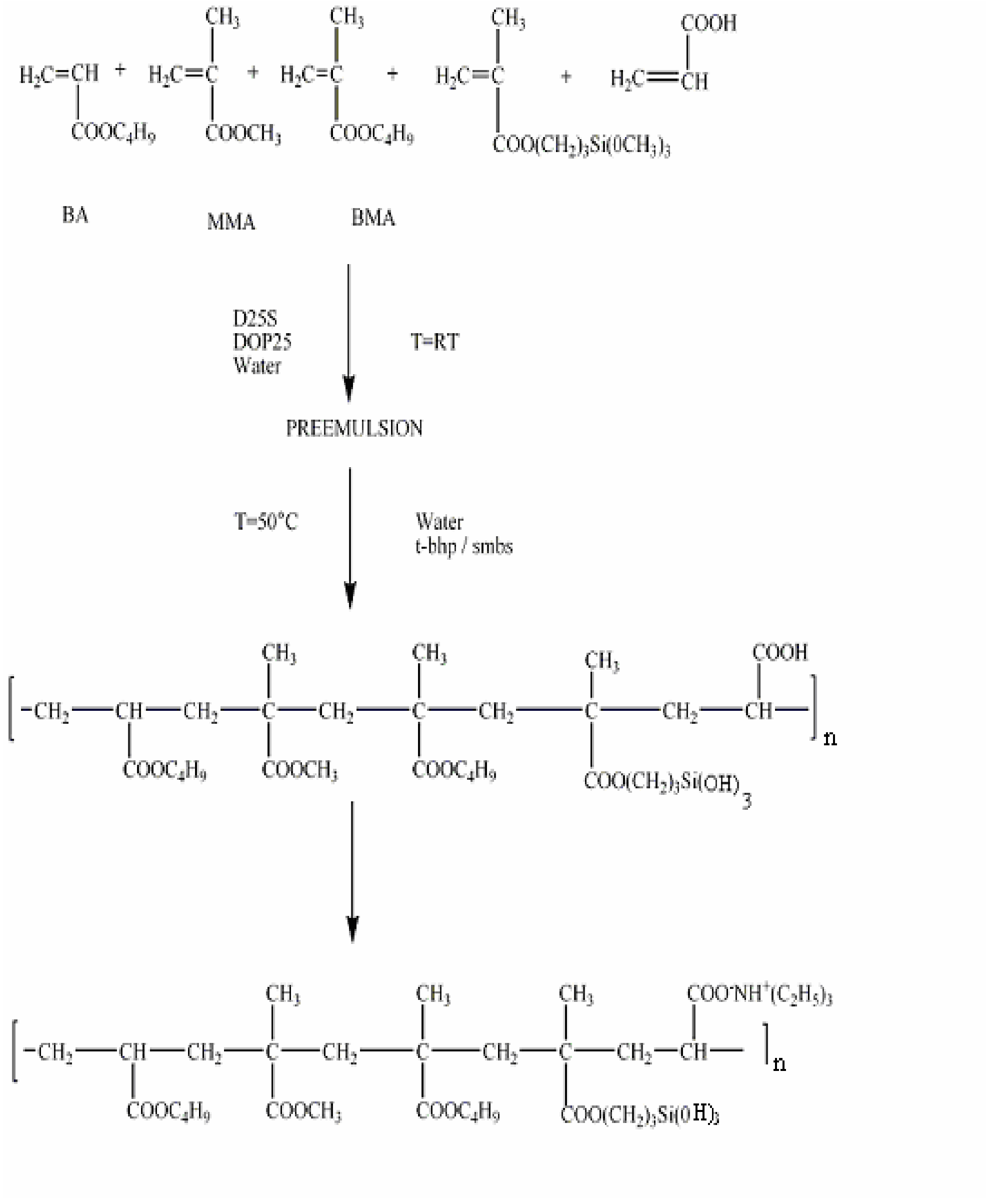


Figure 2.1 Experimental Setup

The representation of the reaction scheme for the production of waterborne silicone-acrylic resin is given below:



2.4. Characterization Methods

2.4.1 Fourier Transform Infrared Spectrophotometer (FTIR)

A Perkin Elmer Spectrum One ATR spectrophotometer was used to characterize the acrylic and silicone-acrylic resin.

2.5 Thermal Test

2.5.1 Differential Scanning Calorimeter (DSC)

A Perkin Elmer (DSC-4) Differential Scanning Calorimeter was used to determine the glass transition temperature (T_g) under nitrogen. The rate of heating was 10ºC/min from 0 to 350ºC.

2.6 Physical and Mechanical Tests

2.6.1 Preparation of Test Panels

After applying 90µm wet film thickness on glass and metal test panels using film casting knife, the test panels were left for air-drying for 1 weak.

2.6.2 Film Thickness Measurement

An Elcometer Thickness Gauge was used to measure the thickness of the resins on metal plates [38].

2.6.3 Pendulum Hardness Test

A Braive-Instruments Persoz Pendulum (Model: 3034) was used. The hardness of the coating is measured from the number of oscillations of pendulum swinging on the test panel. As the hardness of the resin increases, the number of oscillations increases because of the less friction [39].

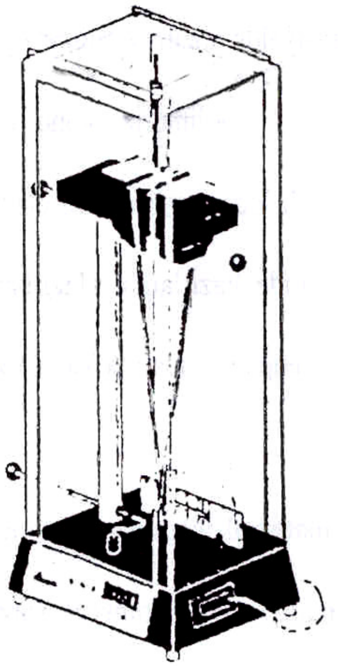


Figure 2.2 Hardness Pendulum Testing Instrument

2.6.4 Impact Resistance Test

A Gardner Impact Tester (Model: 5510) was used for impact test. A standard weight(1+0.9kg) is dropped on a film coated metal plate from different heights and the value of potential energy at which failure occurred by cracking referred to impact value [40].

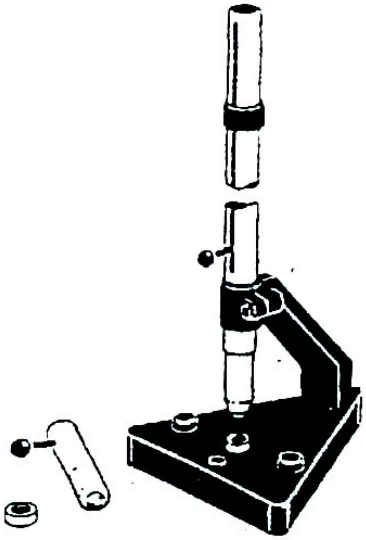


Figure 2.3 Impact Resistance Testing Instrument

2.6.5 Mandrel Bending Test

A Conical Mandrel Bending Tester (Braive-Instruments, Model: 1510) was used. The prepared test panel was fastened and bent over to observe the resistance of coating to cracking along the increasing radius of the conical mandrel. The ability of resin to resist cracking when elongated shows the flexibility of coatings [41].

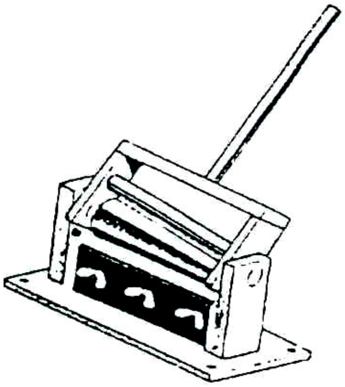


Figure 2.4 Mandrel Bending Instrument

2.6.6 Abrasion Resistance Test

This test method determines the resistance of coating film to abrasion produced by abrasive falling from a specified height through a guide tube onto a coated metal panel. Silica sand which was used as an abrasive agent was poured onto the coated panel until some starching was detected. Abrasion value was determined from the change of thickness of the film [42].

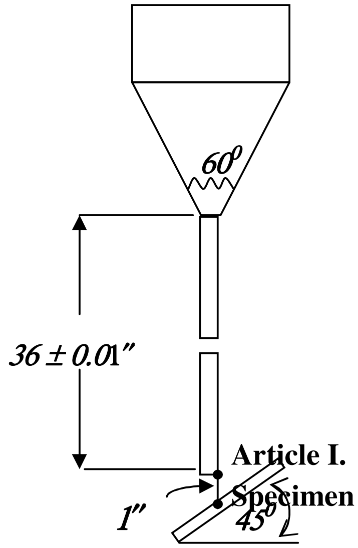


Figure 2.5 Abrasion Resistance Measurement Instrument

2.6.7 Gloss Measurement Test

A Braive-Instruments Glossmeter was used. Metal and glass plates were used to measure the intensity of light reflected from coated plates in three different directions [43].

2.6.8 Adhesion Test

A crosshatch cutter was used to cut the film to produce a lattice pattern. After making a cross cut, the coating film was brushed with a soft tissue to remove any detached flakes of coating. Then, the pattern was checked according to ASTM D 3359B. The maximum number of adhesion is 5, and the minimum is 0 [44].

2.6.9 Storage Stability at 60ºC

The silicone-acrylic resin is stored in the oven at 60ºC for 10 days. If there is no sedimentation, the storage stability at 60ºC can be said “good” [32].

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Characterization

3.1.1 FTIR Spectroscopy

The waterborne silicone-acrylic resin synthesized in this work is a novel one and in general, silanes are not stable in aqueous systems due to the hydrolysis of alkoxy groups and subsequent self-crosslinking into siloxane networks [31, 45]. As a result, the FTIR spectra of with and without silane coupling agent resins were taken for both completely dried samples and for samples taken directly from the reactor. Figures 3.1 and 3.2 represent the FTIR spectra for the resins taken directly from the reactor (wet) with silane coupling agent (R-1) and without silane coupling agent(R-2) respectively. The broad and intense peak at 3368 cm^{-1} in Figure 3.1 was assumed to be due to Si-OH stretching, together with N-H stretching. The two figures are almost identical and the characteristic absorption peaks are summarized in Table 3.1.

Figure 3.1 FTIR Spectrum of Silicone-Acrylic Resin with Silane Coupling Agent (Wet)

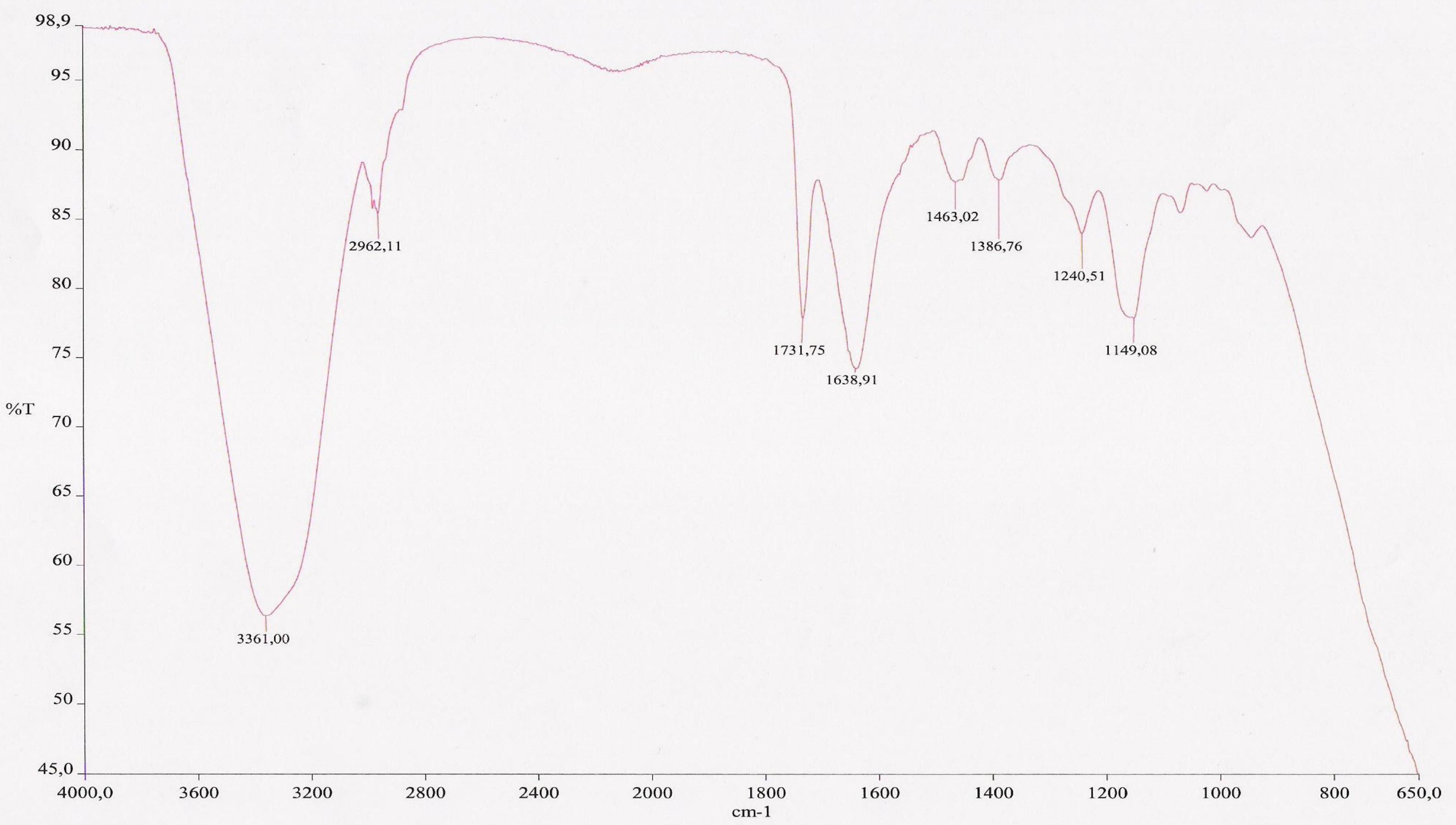


Figure 3.2 FTIR Spectrum of Acrylic Resin without Silane Coupling Agent (Wet)

Table 3.1 The Absorbance Peak Positions for Resins (Wet)

Absorbance peak position(cm^{-1})		Sample 1	Sample 2
R-1	R-2	R-1	R-2
3367.96	3361.00	OH stretching N-H stretching	O-H stretching N-H stretching
2961.04	2962.11	C-H stretching	C-H stretching
1731.05	1731.75	-C=O stretching	-C=O stretching
1639.28	1638.91	-C=C- stretching	-C=C- stretching
1450.25	1463.02	C-H bending	C-H bending
1387.44	1386.76	C-H bending	C-H bending
1240.19	1240.51	-C-O stretching	-C-O stretching
1147.81	1149.08	O=C-O- stretching	O=C-O- stretching

Figure 3.3 and 3.4 were taken for the samples with having silane coupling agent(R-1) and not having silane coupling agent(R-2) after being completely dried respectively. Again, not much difference is observed as we look at the peak positions and vibrational modes represented in Table 3.2.

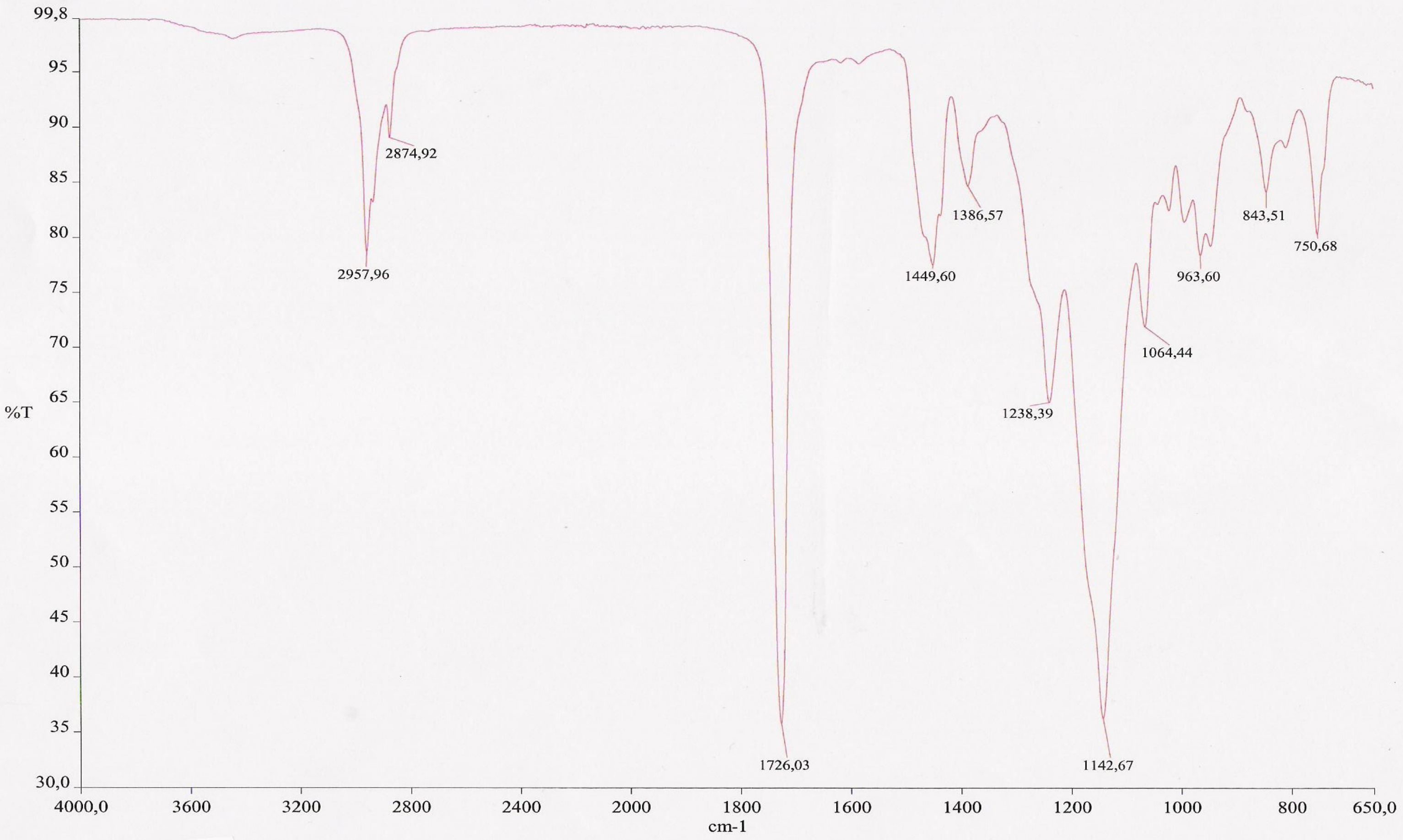


Figure 3.3 FTIR Spectrum of Silicone-Acrylic Resin with Silane Coupling Agent (Dry)

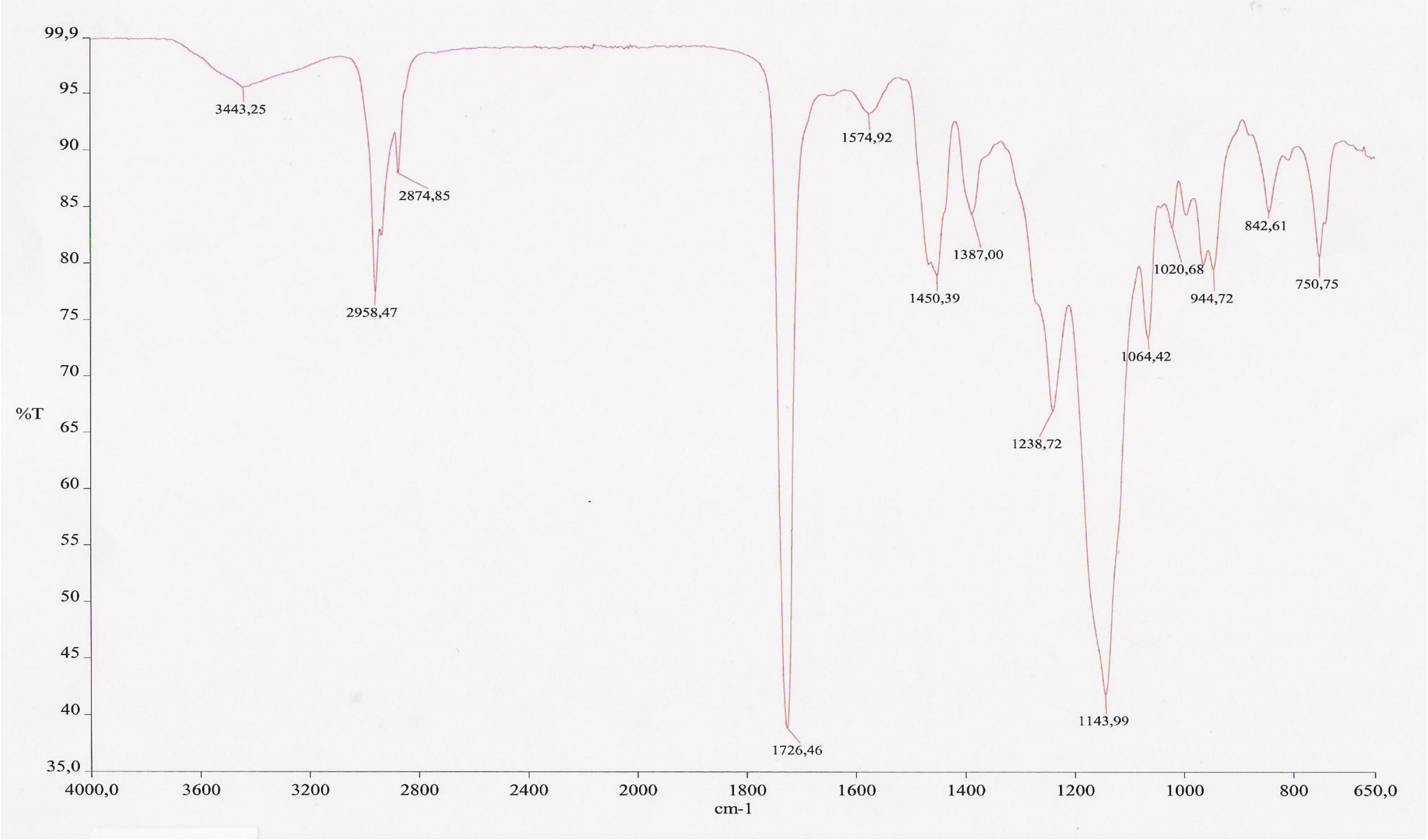


Figure 3.4 FTIR Spectrum of Acrylic Resin without Silane Coupling Agent (Dry)

Table 3.2 The Absorbance Peak Positions For Resins (Dry)

Absorbance peak position(cm^{-1})		Sample 1	Sample 2
R-1	R-2	R-1	R-2
around 3400	3443.25	N-H stretching	N-H stretching
2957.96	2958.47	C-H stretching	C-H stretching
2874.92	2874.85	C-H stretching	C-H stretching
1726.03	1726.46	-C=O stretching	-C=O stretching
around 1570	1574.92	-N-H bending from $O=C-O^{-}$ NH^{+}-	-N-H bending from $O=C-O^{-}$ NH^{+}-
1449.60	1450.39	C-H bending	C-H bending
1386.57	1387.00	C-H bending	C-H bending
1238.39	1238.72	-C-O- stretching	-C-O- stretching
1142.67	1143.99	O=C-O- stretching	O=C-O- stretching
1064.44	1064.42	-C-O- stretching	-C-O- stretching
963.60	944.72	-C-C- stretching	-C-C- stretching
843.51	842.61	-C-C- stretching	-C-C- stretching
750.68	750.75	C-H bending	C-H bending

Figures 3.3 and 3.4 showed the FTIR spectra for completely dry R-1 and R-2. The spectra are again very similar and the characteristic absorption peaks are summarized in Table 3.2. Yet, there are some points which need some emphasis on them. N-H stretching band is broader and more profound and N-H bending due to $O=C-O^{-}NH^{+}$ is more apparent in resin R-2. This maybe due to the experimental error in adjusting the pHs.

When the FTIR spectra of wet (R-1 and R-2) are compared with the dry (R-1 and R-2) , O-H stretching peaks are not present in the dry samples; therefore the broad and intense peak at 3361 cm^{-1} disappear in Figures 3.3 and 3.4. Another important point is the disappearance of the absorption peak at 1639 cm^{-1} due to C=C in Figures 3.3 and 3.4. During drying, resins are expected to harden and this is achieved by crosslinking. It was experimentally determined that, dry R-1 and R-2 are insoluble in common solvents. Last apparent difference between Figures 3.1, 3.2 and 3.3, 3.4 is the broad absorption peaks at 2000-2400 cm^{-1} in the wet samples, which probably is due to CO_2 of the air. This is due to different sample preparations for dry and wet resins.

3.2 Thermal Test

3.2.1 DSC Spectroscopy

The thermal transition temperatures of silicone-acrylic resin and acrylic resin without silane coupling agent were detected by DSC thermograms illustrated in Figures 3.5 and 3.6, respectively. No other thermal transition temperatures were observed and this is expected since the resin becomes a thermoset with drying. The silicone-acrylic resin melted at 374ºC and the acrylic resin without silane coupling agent at 373ºC.

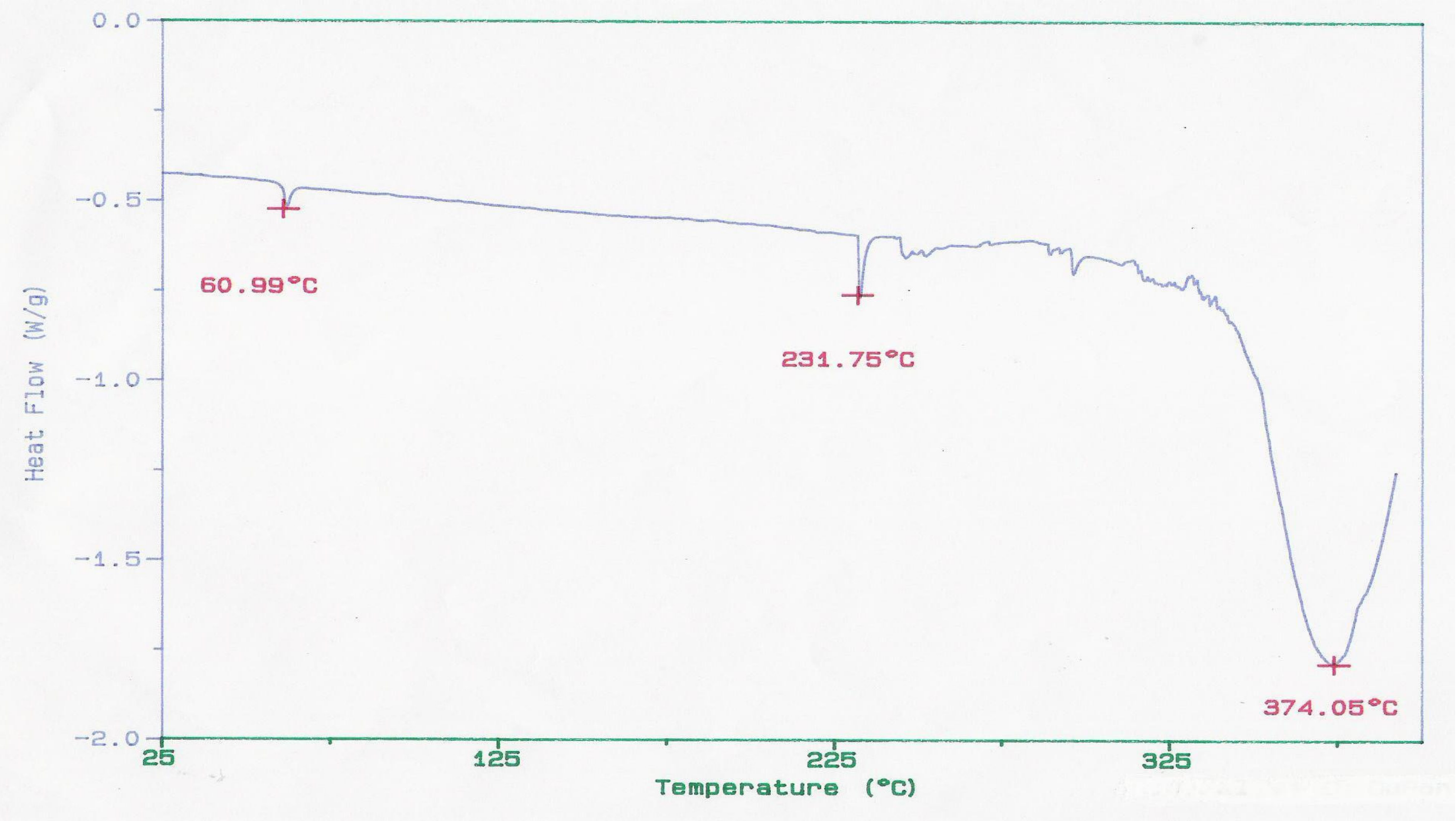


Figure 3.5 DSC of Silicone-Acrylic Resin with Silane Coupling Agent

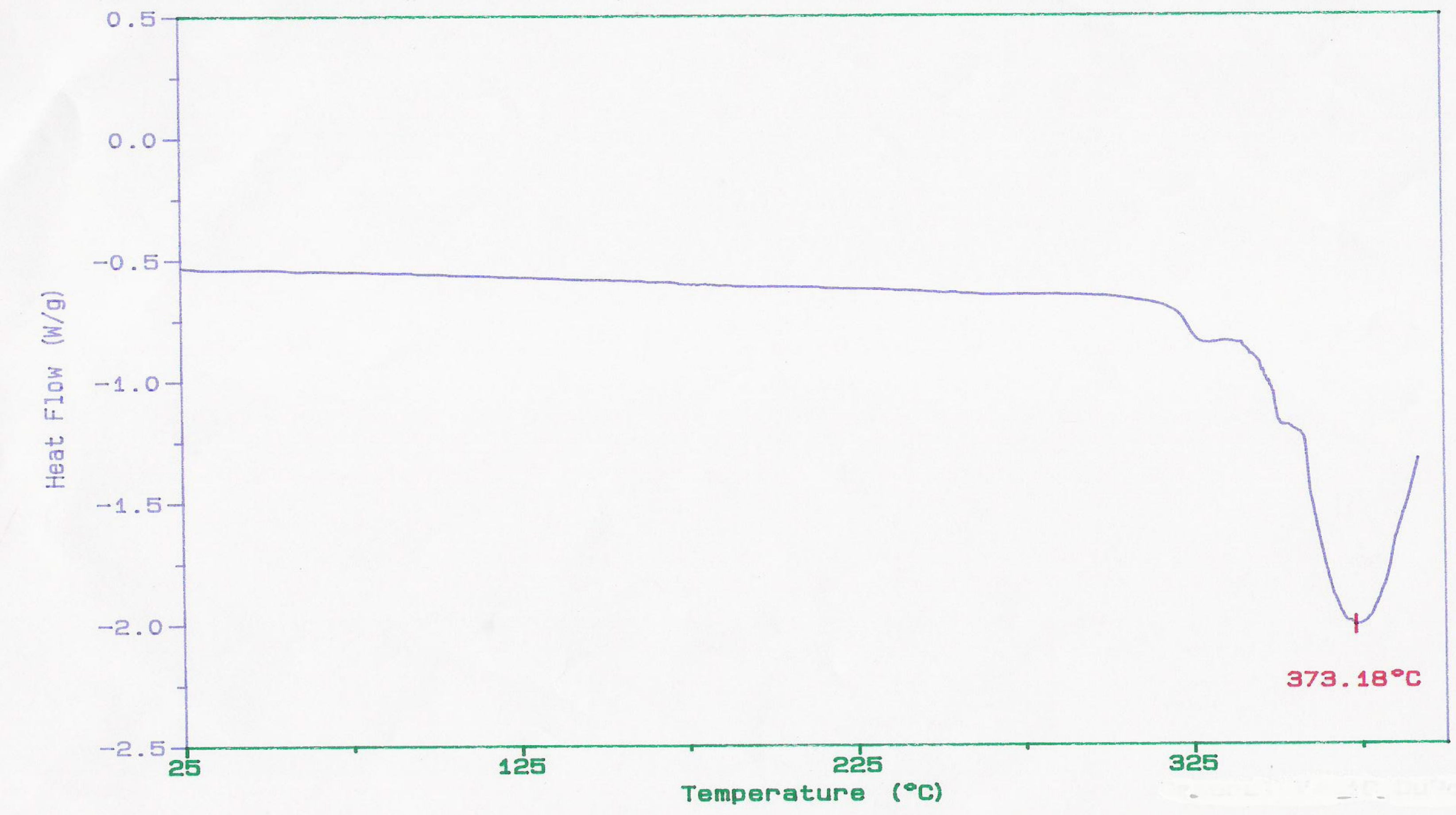


Figure 3.6 DSC of Acrylic Resin without Silane Coupling Agent

3.3 Physical and Mechanical Tests

3.3.1 Pendulum Hardness Test

The hardness value of silicone-acrylic resin (R-1) and acrylic resin without silane coupling agent (R-2) are shown in Table 3.1.

Table 3.3 Persoz Hardness Values of the Resins on Glass Plates

Sample	Persoz Hardness Values
R – 1	85.8 Persoz
R – 2	41.1 Persoz

The results of the pendulum hardness test indicated that there is an increase in Persoz Hardness value when the resin contains silane coupling agent.

3.3.2 Mandrel Bending Test

All samples passed the mandrel bending test without any crack on the resin surface. This implies that silicone-acrylic resin and acrylic resin without silane coupling agent have sufficient flexibility.

3.3.3 Impact Resistance Test

No crack formation was observed on the surface of both types of resins up to 5.9 J energy. Beyond this value crack formation started.

3.3.4 Abrasion Resistance Test

The Abrasion resistance is also a measure of the coating's toughness, hardness and impact resistance. The test results are given in terms of the amount of sand required to remove a certain thickness from coating. The abrasion resistance value of silicone-acrylic resin (R-1) and acrylic resin without silane coupling agent (R-2) are shown in Table 3.2.

Table 3.4 Abrasion Resistance Values of the Resins

Sample	Abrasion Resistance Values
R – 1	2.12 ± 0.2 L/μm
R – 2	1.93 ± 0.2 L/μm

3.3.5 Gloss Test

The gloss values of silicone-acrylic resin (R-1) and acrylic resin without silane coupling agent (R-2) are listed in Table 3.3 for metal and glass plates at angles of 20°, 60° and 85°.

Table 3.5 Gloss Values of the Resins on Glass and Metal Plates

Sample / R-1	**20°**	**60°**	**85°**
Glass	145.5	134.5	108.8
Metal	76.9	99.8	78.8
Sample / R-2	**20°**	**60°**	**85°**
Glass	126.6	130.3	100.5
Metal	63.6	98.8	88.2

A gloss meter measures the specular reflection. The light intensity is registered over a small range of the reflection angle. The intensity is dependent on the material and the angle of illumination. The amount of reflected light increases with the increase of the illumination angle. The remaining illuminated light penetrates the material and is absorbed or diffusely scattered. The gloss value of the resins on glass plate was found to be higher than the ones on metal plate as seen from the Table 3.3. The glass plate having higher refractive index than metal has higher ability to reflect light. The glass surface reflects the diffracted light yielding higher gloss. If the gloss value observed at 60° is higher than 70°, it is said to be in 'high gloss' range. Therefore, it can be easily said that the resins have high gloss property.

3.3.6 Adhesion Test

The adhesion test value of silicone-acrylic resin (R-1) and acrylic resin without silane coupling agent (R-2) are shown in Table 3.4. These results show that silane coupling agent containing silicone-acrylic resin gives better adhesion than acrylic resin without silane coupling agent. This is because silane coupling agents have good adhesion properties.

Table 3.6 Adhesion Values of the Resins on Glass and Metal Plates

Sample / R-1	**Adhesion values**
Glass	5B
Metal	5B
Sample / R-2	
Glass	1B
Metal	3B

3.3.7 Storage Stability

Resins have good storage stability at room temperature and also at 60°C.

CHAPTER 4

CONCLUSION

1. For the preparation of the water-borne silicone-acrylic resin, the best initiators were 2,2'-azobis[2-(2-imidazolin-2yl)propane] dihydrogen chloride and t-butyl hydroperoxide / sodiummetabisulfite.

2. The optimum amount of initiators was found to be 0.24 % of the total monomer content.

3. The reaction temperature of the preparation of silicone-acrylic resin should be maximum 50°C to prevent gelation and agglomeration.

4. The amount of surfactants should be 4.77 % of the total monomer content of the resin to obtain a good dispersion.

5. The batch polymerization process should be preferred to get the desired polymer.

6. Mechanical test results showed that the synthesized product using silane coupling agent in the formulation provided better hardness.

7. The resultant polymer which contains silane coupling agent showed excellent gloss properties in all angles.

8. No cracks on the film were observed after bending test.

9. The storage stability of resins at 60° C is passed.

10. The produced polymer which contains silane coupling agent showed excellent adhesion properties on glass and metal plates.

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