ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF STYRENE-ACRYLIC COPOLYMERS AND THEIR USE IN PAINT

M.Sc. THESIS

Buğra ÖZDAMAR

Department of Polymer Science and Technology

Polymer Science and Technology Programme

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Thesis Advisor: Prof. Dr. İ. Ersin Serhatlı

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To my family,

FOREWORD

The research work presented in this thesis has been carried out at Istanbul Technical University, Chemistry Department of Science & Letters Faculty, POLMAG Laboratory (Polymeric Materials Research Group) under the valuable and expert guidance of Prof. Dr. İ. Ersin SERHATLI.

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December 2016 Buğra ÖZDAMAR
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ABBREVIATIONS

CIT/MIT : Chloroisothiazolinone / Methylisothiazolinone
EN : European Norm
ISO : International Organization for Standardization
ASTM : American Society for Testing and Materials
NaCI : Sodium chloride
APS : Amonyum persulfat
DPnB : Dipropylene glycol n-butyl ether
t-BHP : Tert-Butyl hydroperoxide
VOC : Volatile Organic Compounds
MMA : Methyl methacrylate
2-EHA : 2-Ethylhexyl acrylate
SO_4- : Sulfate
***T*g** : Glass transition temperature
UV : Ultraviolet
MFFT : Minimum Film Formation Temperature
NaOH : Sodium hydroxide
KOH : Potassium hydroxide
FT-IR : Fourier transform infrared spectroscopy
TFA : Thin Film Analyser
MAA : Metacrylic acid
AA : Acrylic acid
NMR : Nuclear magnetic resonance

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SYNTHESIS OF STYRENEACRYLIC COPOLYMER AND THEIR USE IN PAINT

SUMMARY

Silane coupling agents are silicon-based chemicals that contain two types of reactivity – inorganic and organic – in the same molecule. A silane coupling agent will act at an interface between an inorganic substrate (such as glass, metal or mineral) and an organic material (such as an organic polymer, coating or adhesive) to bond, or couple, the two dissimilar materials.

Silane coupling agents that contain three inorganic reactive groups on silicon (usually methoxy, ethoxy or acetoxy) will bond well to the metal hydroxyl groups on most inorganic substrates, especially if the substrate contains silicon, aluminum or a heavy metal in its structure. The alkoxy groups on silicon hydrolyze to silanols, either through the addition of water or from residual water on the inorganic surface. Then the silanols coordinate with metal hydroxyl groups on the inorganic surface to form an oxane bond and eliminate water.

Silane molecules also react with each other to give a multimolecular structure of bound silane coupling agent on the surface. More than one layer, or monolayer equivalents, of silane is usually applied to the surface. This results in a tight siloxane network close to the inorganic surface that becomes more diffuse away from the surface.

Silane coupling agents are effective adhesion promoters when used as integral additives or primers for paints, inks, coatings, adhesives and sealants. As integral additives, they must migrate to the interface between the adhered product and the substrate to be effective. As a primer, the silane coupling agent is applied to the inorganic substrate before the product to be adhered is applied. In this case, the silane is in the optimum position (in the interphase region), where it can be most effective as an adhesion promoter. By using the right silane coupling agent, a poorly adhering paint, ink, coating, adhesive or sealant can be converted to a material that often will maintain adhesion even if subjected to severe environmental conditions.

Organofunctional alkoxysilanes are used to couple organic polymers to inorganic materials. Typical of this application are reinforcements, such as fiberglass and mineral fillers, incorporated into plastics and rubbers. They are used with both thermoset and thermoplastic systems. Mineral fillers, such as silica, talc, mica, clay and others, are either pretreated with silane or treated in situ during the compounding process. By applying an organo-functional silane to the hydrophilic, non organo reactive filler, the surfaces are converted to reactive and organophilic. Fiberglass applications include auto bodies, boats, shower stalls, printed circuit boards, satellite dishes, plastic pipes and vessels, and many others.

In this study, different types of silanes, which have different structures, are added directly to the styrene-acrylic copolymers. These copolymers are formulated in high PVC paint formulation. These paints are tested in according to their scrub resistance, hardness and flexibility properties.

STİREN-AKRİLİK KOPOLİMERLERİN SENTEZİ VE BOYADA KULLANIMLARI

ÖZET

Silan kenetlenme ajanları, aynı molekülde inorganik ve organik olmak üzere iki tür tepkime içeren silikon esaslı kimyasallardır. Bir silan bağlama maddesi, iki benzer malzemeyi birbirine bağlamak ya da birleştirmek için inorganik bir substrat (cam, metal ya da mineral gibi) ile organik bir malzeme (organik bir polimer, kaplama ya da yapıştırıcı gibi) arasındaki bir arayüzde etki gösterir.

Silisyum üzerinde üç inorganik reaktif grup içeren silan kaplin ajanları (çoğunlukla metoksi, etoksi veya asetoksi), özellikle substrat yapısı içinde silikon, alüminyum veya ağır bir metal içeriyorsa, çoğu inorganik substrat üzerindeki metal hidroksil gruplarına iyi bağlanır. Silisyum üzerindeki alkoksi grupları ya inorganik yüzey üzerindeki su veya artık suyun ilavesiyle silanollara hidrolize olur. Ardından, silanoller bir oksan bağı oluşturmak ve suyu yok etmek için inorganik yüzeydeki metal hidroksil grupları ile koordine olurlar.

Silan molekülleri ayrıca yüzeyde bağlı bir silan bağlama maddesi çok moleküllü bir yapı vermek için birbirleriyle reaksiyona girer. Yüzeye genellikle birden fazla tabaka veya tek katmanlı muadili silan uygulanır. Bu inorganik yüzeye yakın sıkı bir siloksan ağına neden olur ve yüzeyden daha fazla dağılır hale gelir.

Silan çeşitli yollarla üretilebilir. Tipik olarak, hidrojen kloritin magnezyum silisid ile reaksiyonundan kaynaklanmaktadır. Ayrıca metalurjik dereceli silikondan iki aşamalı bir süreçle hazırlanır. İlk olarak, silikon yaklaşık 300 ° C'de hidrojen klorid ile muamele edilerek triklorosilan, $HSiCl_3$ ve hidrojen gazı üretilir.

Triklorosilan daha sonra silan ve silikat tetraklorür karışımına dönüştürülür. Bu yeniden dağıtma reaksiyonu bir katalizör gerektirir.

Bu işlem için en çok kullanılan katalizörler metal halidler, özellikle alüminyum klorürdür. Buna, aynı merkezi elemanı içeren çift bir yer değiştirme olan bir yeniden dağıtım reaksiyonu denir. Ayrıca, silikon için oksidasyon sayısında bir değişiklik olmamasına (Si'nin her üç türün nominal oksidasyon sayısı IV'dür) rağmen orantısızlaşma reaksiyonu olarak da düşünülebilir. Bununla birlikte, bir kovalent molekül, hatta bir polar kovalent molekül için oksidasyon sayısı kavramının faydası belirsizdir. Silikon atomu $SiCl_4$'te en yüksek formal oksidasyon ve kısmi pozitif yüke ve SiH_4'teki en düşük biçimsel oksidasyona sahip olduğu için rastlantısal hale getirilebilir çünkü Cl, H'den çok daha elektronegatiftir.

Silan, metanın silikon analoğudur. Hidrojenin silikona kıyasla daha büyük elektronegatifliği nedeniyle, bu Si-H bağ polaritesi metan C-H bağlarındaki zıtlıktır. Bu ters polaritenin bir sonucu, silanın geçiş metalleriyle kompleksler oluşturması yönündeki eğilimi arttırmasıdır. İkinci bir sonuç, silanın piroforik olmasıdır -

havadaki kendiliğinden yanmaya, dış ateşlemeye gerek duymadan yaşar. Bununla birlikte, mevcut (genellikle çelişkili) yanma verilerini açıklama zorlukları, silanın kendisinin dengeli olması ve üretim esnasında daha büyük silanların doğal oluşumunun yanısıra nem gibi maddelere ve yanmaya karşı yanma hassasiyetine bağlıdır. Konteynır yüzeylerinin katalitik etkileri piroforitesine neden olur. 420°C'nin üstünde, silan silikon ve hidrojen içine ayrışır; Bu nedenle silikonun kimyasal buhar birikiminde kullanılabilir.

Si-H bağlanma mukavemeti yaklaşık 384 kJ / mol olup, H_2'deki H-H bağından yaklaşık% 20 daha zayıftır. Sonuç olarak, Si-H bağları içeren bileşikler H_2'den çok daha reaktiftir. Si-H bağının gücü diğer sübstitüentlerden mütevazı bir şekilde etkilenir: $SiHF_3$, $SiHCl_3$ ve $SiHMe_3$'teki Si-H bağ kuvvetleri sırasıyla 419, 382 ve 398 kJ / mol'dir

Silan kenetlenme ajanları, boyalar, mürekkepler, kaplamalar, yapıştırıcılar ve sızdırmazlık malzemeleri için entegre katkı maddeleri veya astarlar olarak kullanıldıklarında etkin yapışma arttırıcı maddelerdir. Bütünleşik katkılar olarak, etkili olması için yapışmış ürün ve alt tabaka arasındaki ara yüze göç etmeleri gerekir. Bir primer olarak, silan bağlama maddesi, yapışacak ürün uygulanmadan önce inorganik substrata uygulanır. Bu durumda, silan, yapışma arttırıcı olarak en etkili olabileceği optimum konumda (ara faz bölgesinde). Doğru silan kaplin ajanını kullanarak, kötü bir şekilde yapışan bir boya, mürekkep, kaplama, yapışkan veya sızdırmazlık malzemesi, şiddetli çevresel koşullara maruz kalsa bile sıklıkla yapışmayı koruyacak bir malzemeye dönüştürülebilir.

Silan ve fonksiyonel silanlar için çeşitli endüstriyel ve tıbbi uygulamalar mevcuttur. Örneğin, silanlar cam elyafları ve karbon elyafları gibi elyafları belirli polimer matrislerine yapıştırmak için birleştirme maddesi olarak kullanılırlar ve kompozit malzemeyi stabilize eder. Başka bir deyişle, polimer matrisine daha iyi yapışma sağlamak için silan cam elyafı kaplar. Ayrıca titanyum implant üzerinde biyolojik olarak etkisiz tabakayı birleştirmek için de kullanılabilirler. Diğer uygulamalarda su iticileri, duvar koruma, grafiti kontrolü, yarı iletkenleri imal ederken silikon levhalar üzerine polikristalin silikon tabakaları ve sızdırmazlık malzemeleri uygulanmaktadır. Yarı iletken endüstrisi 1990'ların sonunda yılda yaklaşık 300 metrik ton silan kullandı. Daha yakın bir tarihte, düşük maliyetli güneş fotovoltanik parça üretimindeki bir artış, cam ve metal ve plastik gibi diğer yüzeylerde hidrojenli amorf silikon (a-Si: H) birikimi için silanın önemli bir tüketimine yol açtı. PECVD işlemi silisyumun boşa gitmesinin yaklaşık % 85'i ile malzeme kullanımında nispeten verimsizdir. Bu atık ve a-Si: H tabanlı güneş pillerinin ekolojik ayak izini azaltmak için birkaç geri dönüşüm çabası geliştirildi.

Silan, basınçlı hava akımı içinde yanmayı başlatmak için süpersonik yanma ramjetlerinde de kullanılır. Bir oksitleyici olarak karbon dioksit kullanarak yakabildiği için, Mars'ta çalışan motorların adayı bir yakıttır.

Si-H bağları içeren silan ve benzeri bileşikler organik ve organometalik kimyada indirgeyici ajanlar olarak kullanılır.

Silan metakrilatlar diş renginde kompozit dolgu maddesinin bir parçası olarak diş hekimliğinde kullanılırlar. Silan metakrilatlar, sert, silikat bazlı, seramik dolgu maddesi ve organik reçine esaslı oligomer matrisi arasında bir bağlama maddesi görevi görür.

Organofonksiyonel alkoksisilanlar, organik polimerleri inorganik malzemelere birleştirmek için kullanılır. Bu uygulamaya tipik olarak plastik ve kauçuklara dahil fiberglas ve mineral dolgu gibi takviye maddeleridir. Termoset ve termoplastik sistemler ile birlikte kullanılırlar. Silika, talk, mika, kil ve diğerleri gibi mineral dolgu maddeleri, silan ile ön işleme tabi tutulur veya karışım işlemi sırasında yerinde işlenir. Hidrofilik organik olmayan reaktif dolgu maddesine bir organo-fonksiyonel silan uygulandığında, yüzeyler reaktif ve organofilik hale dönüştürülür. Fiberglas uygulamaları, oto gövdeleri, tekneler, duş tezgahları, baskılı devre kartları, uydu antenleri, plastik boru ve kaplar ve diğerlerini kapsamaktadır.

Bu çalışmada, farklı yapılara sahip farklı silan türleri doğrudan stiren-akrilik kopolimerlere eklenmiştir. Bu kopolimerler yüksek PVC boya formülasyonunda formüle edilmiştir. Bu boyalar, ovalama direnci, sertlik ve esneklik özelliklerine göre test edilmektedir.

1. INTRODUCTION

Along with the continuous demand for improved performance, coating formulators are burdened with ever-tightening environmental protection regulations. The need to reduce volatile organic compounds (VOCs), heavy metals like chromium VI and trialkyl tin, and other hazardous materials creates opportunities for the suppliers of high-performance, compliant material technologies. Ongoing research at universities and commercial organizations has demonstrated the effectiveness of organosilane technology – alone or in combination with other materials – to improve the performance of a variety of coating systems. Owing to the unique capability of organosilane molecules to form covalent bonding between inorganic and organic compounds along with the inherent stability and flexibility of the siloxane (Si-O-Si) bond, those molecules can provide multiple benefits in a broad range of coating systems.

The value of silane coupling agents was first discovered in the 1940s in conjunction with the development of fiber glass reinforced polyester composites [1]. When initially fabricated, these composites were very strong, but their strength declined rapidly during aging. This weakening was caused by a loss of bond strength between the glass and resin. In seeking a solution, researchers found that organo-functional silanes – silicon chemicals that contain both organic and inorganic reactivity in the same molecule – functioned as coupling agents in the composites. A very small amount of an organo-functional alkoxysilane reacted at the glass-resin interface did not only significantly increase initial composite strength but also resulted in a dramatic retention of that strength over time.

Subsequently, other applications for silane coupling agents were discovered (e.g., mineral and filler treatment for composite reinforcement [2, 3]; adhesion of paints, inks and coatings [4-6]; reinforcement and crosslinking of plastics and rubber [7-9]; crosslinking and adhesion of sealants and adhesives [10-13]; and in the development of water repellents and surface protection [14]).

Different types of organo-functional silanes will be added into the synthesized styrene-acrylic copolymer during emulsion or as a post additive. Standard styrene-acrylic copolymers and organofunctional silanes added copolymers will be prepared in high PVC paint formulation for application to ceilings. Different types of organofunctional silanes will be compared with each other according to hardness, flexibility and scrub resistance performances.

2. THEOROTICAL PART

2.1 Emulsion Polymerization

Emulsion polymerization is a free-radical-initiated 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 a latex. The latex is described as a colloidal dispersion of a polymer particles in an aqueous medium. The monomer, water, surfactants, initiators and chain transfer agents are the main ingredients of emulsion polymers.[15]

Emulsion polymerization is known to be a resource-and energy-saving, eco-friendly process for the production of polymer lattices. This process is basically a free-radical polymerization of water-insoluble monomers in aqueous medium; the final latex is stabilized by surfactants or protective colloids. This polymerization process was first commercialized in the early 1930s, and since then it has been widely used to produce environmentally friendly latex products with a variety of colloidal and physicochemical properties.[16]

Emulsion polymerization is a heterogeneous polymerization method in which the polymer is combined from water insoluble monomers as particles suspended in water with the aid of suitable emulsifiers [17].

This heterogeneous free radical polymerization process includes emulsification of the relatively hydrophobic monomer in water by an oil-in-water emulsifier, followed by the initiation reaction either a water soluble initiator (e.g.sodium persulfate (NaPS)) or an oil-soluble initiator (e.g. azobisisobutyronitrile (AIBN)). Typical monomers used to synthesize emulsion polymers include ethylene, styrene, acrylonitrile, acrylate ester and methacrylate ester monomers etc., are suspended in water in which a surfactant has been added [18].

2.1.1 Main ingredients of emulsion polymerization

A regular emulsion polymerization formulation is consist of monomer, water, initiator and surfactant. Further auxiliaries, such as chain transfer agents, buffers, acids, bases, anti-aging agents, biocides, etc., can be used. Commercial emulsion polymerization recipes are usually much more complicated, with 20 or more ingredients [19].

2.1.1.1 Monomers

Emulsion polymerization needs free-radical polymerizable monomers which form the structure of the polymer. The most common monomers used in emulsion polymerization consist of styrene, butadiene, acrylonitrile, acrylate ester and methacrylate ester monomers, vinyl acetate, acrylic acid and methacrylic acid, and vinyl chloride. The principal arrangement of emulsion polymerization process is finished as for the way of monomers contemplated up to that time. This order depends on information for the distinctive solubilities of monomers in water and for the diverse starting rates of polymerization brought on by the monomer solubilities in water. As per this order, monomers are separated into three gatherings. The main gathering incorporates monomers which have great dissolvability in water, for example, acrylonitrile (solubility in water 8%). The second gathering incorporates monomers having 1-3% solubility in water (methyl methacrylate and different acrylates). The third gathering incorporates monomers essentially insoluble in water (butadiene, isoprene, styrene, vinylchloride, and so forth [20].

2.1.1.2 Emulsifiers

These materials performs many important functions in emulsion polymerizations [21-23] such as (i) reducing the interfacial tension between the monomer phase and the water phase so that the monomer is dispersed (or emulsified) in the water phase with agitation, (ii) generating micelles, (iii) stabilizing the monomer droplets in an emulsion form, (iv) serving to solubize the monomer within emulsifier micelles, (v) stabilizing the growing and final latex particles, (vi) acting to solubilize the polymer, (vii) serving as the site for the nucleation of particles, (viii) acting as chain transfer agents or retarders.

Emulsifier (also referred to as surfactant, soap and dispersing agent) are surface-active agents. These materials consist of a long-chain hydrophobic (oil-soluble) group (dodecyl, hexadecyl or alkly-benzene) and a hydrophilic (water-soluble) head group. They are usually classified according to the nature of this head group. This group may be anionic, cationic, zwitterionic or non-ionic [23].Anionic emulsifiers having negatively charged hydrophilic head group are the sodium, potassium and ammonium salts of higher fatty acids, and sulfonated derivatives of aliphatic, arylalilphatic, or naphtenic compounds. Sodium lauryl (dodecyl) sulfate, [$C_{12}H_{25}OSO_3^-Na^+$] and sodium dodecyl benzene sulfonate, [$(C_{18}H_7COOCH_2)_2SO_3^-Na^+$] are commonly used in emulsion polymerizations as anionic emulsifiers. Quaternary salts such as acetyl dimethyl benzyl ammonium chloride and hexadecyl trimethyl ammonium bromide may be given examples for cationic emulsifiers. Zwitterionic (amphoteric) emulsifiers can show cationic or anionic properties depending on pH of the medium. They are mainly alkylamino propionic acids. Non-ionic emulsifiers carry no charge unlike ionic emulsifiers. The most used type of these emulsifiers is that with a head group of ethylene oxide (EO) units. Polyoxyethylenated alkylphenols, polyoxyethylenated straight-chain alcohols and polyoxyethylenated polyoxypropylene glycols are the most commonly three classes of non-ionic emulsifiers used for emulsion polymerization formulations. Polyoxyethylenated alkylphenol type of emulsifiers includes two main members: nonlyphenol polyoxyethylene glycol, [$C_9H_{17}C_6H_4O\text{-}(CH_2CH_2\text{-}O)_nH$], and octylphenol polyoxyethylene glycol, [$C_8H_{15}C_6H_4O\text{-}(CH_2CH_2\text{-}O)_nH$].The number of (EO) units, (n), may be diversified from a few to about 100 (typically from 1 to 70 EO units), which characterize the distribution of polyEO chain lengths for each specific emulsifier.

In general, the anionic emulsifiers are extensively preferred in many emulsion polymerization systems. They serve as strong particle generations and stabilize the latex particles via electrostatic repulsion mechanism. But latexes stabilized with this type of emulsifiers are often unstable upon addition of electrolytes and in freeze-thaw cycles. Furthermore, these emulsifiers have limited stabilizing effectiveness at high solids (>40%) and present high water sensitively. To overcome these problems, non-ionic emulsifiers can be used to nucleate and stabilize the particles in the course of emulsion polymerization. In this case, it is the steric stabilization mechanism that protects the interactive particles from coagulation. In addition, the use of non-ionic types improves the stability of latex product against electrolytes, freeze-thaw cycles, water and high shear rates. As a result of them, in many emulsion polymerization recipes particularly in industry, mixtures of anionic and non-ionic emulsifiers have been widely used together in a synergistic manner to control the particle size and to impart enhanced colloidal stability [18,24,25].The cationic and zwitterionic emulsifiers are used infrequently in emulsion polymerization applications.

Besides all these type of emulsifiers, polymeric and reactive emulsifiers can be used in emulsion polymerizations. Polymeric emulsifiers are often non-ionic water-soluble polymers such as poly (vinyl alcohol), hydroxyethyl cellulose and poly (vinyl pyrrolidone), and called sometimes as a ‘protective colloid’. They are used to increase the particle stability in latexes against coagulation. Reactive emulsifiers (‘surfmers’), which have polymerizable reactive group, can copolymerize with the main monomer and be covalently anchored onto the surface of latex particles. When these compounds used in emulsion polymerizations, the emulsifier migration is reduced. Furthermore, surfmers improve the water resistance and surface adhesion as well as resistance against electrolytes and freeze-thaw cycles in comparison to conventional emulsifiers. Surfmers can be anionic with sulfate or sulfate head groups (sodium dodecyl allyl sulfosuccinate), cationic (alkyl maleate trimethylamino ethyl bromide), or non-ionic (functionalized poly (ethylene oxide)-poly(butylenes oxide)copolymer).The reactive groups can be in different types, for example, allylics acrylamids, (meth)acrylates, styrenics, or maleates [26,27].

2.1.1.3 Initiators

Emulsion polymerization occurs almost entirely following the radical mechanism. The function of the initiator is to generate the free radicals, which is in turn lead to the propagation of the polymer molecules. The free radicals can be commonly produced by two main ways: *(i)* thermal decomposition, *(ii)* detox reactions. In addition the free-radical initiators can be either water or oil-soluble.The most commonly used water-soluble initiators are persulfates (peroxodisulfates).For example, potassium-, sodium-, and ammonium-persulfate. Persulfate ion decomposes thermally in the aqueous phase to give two sulfate radical anions which can initiate the polymerization. Hydrogen peroxide and other peroxides are thermal decomposition type initiators and they are soluble in both the aqueous andmonomer-slowen polymer phases. Besides of these, oil-soluble compounds such as benzoyl peroxide and azobisisobutyronitrile (AIBN) can be employed as thermal initiators in emulsion polymerizations. The other initiation system consist of redox initiators (such as perfulfate-bisulfite system) which produce free radicals through an oxidation-reduction reaction at relatively low temperatures.

The main types of free radicals which are produced by thermally or redox system are:

a. Persulfates

$$S_2O_8^{-2} \rightarrow SO_4\bullet^{-1} + SO_4\bullet^{-1} \quad (2.1)$$

b. Hydrogen peroxide

$$HO\text{-}OH \rightarrow HO\bullet + HO\bullet \quad (2.2)$$

c. Organic peroxides

$$RO\text{-}OR^1 \rightarrow RO\bullet + R^1O\bullet \quad (2.3)$$

d. Azo compound

$$RN{=}\,NR^1 \rightarrow R\bullet + R^1\bullet + N_2 \quad (2.4)$$

e. Persulfate-bisulfite

$$S_2O_8^{-2} + HSO_3^{-1} \rightarrow SO_4\bullet\text{-}^1 + SO_3\bullet^{-1} + HSO_4^{-1} \quad (2.5)$$

Figure 2.1 : Free radical types of thermal and redox initiators

2.1.1.4 Other ingredients

The formulations of emulsion polymerization may include a wide variety of ingredients: *chain transfer agents* are added to a latex formulation to help regulate the molar mass and molar mass distribution of the latex polymer. The mercaptans are the most common type of chain transfer agents. The surface active transfer agents, *‘transfurs’*, are also used in emulsion polymerizations. *Buffers* are often added to a latex formulation to regulate the pH of the polymerization system.

Generally, for his purpose, sodium bicarbonite has been chosen. In addition, coalescing aids, plasticizers, thickening agents, antimicrobial agents, antioxidants, UV-absorbers, pigments, fillers, and other additives can take place in a recipe of emulsion polymerization.

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Generally, for his purpose, sodium bicarbonite has been chosen. In addition, coalescing aids, plasticizers, thickening agents, antimicrobial agents, antioxidants, UV-absorbers, pigments, fillers, and other additives can take place in a recipe of emulsion polymerization.

2.1.2 Kinetic and mechanism of emulsion polymerization

Emulsion polymerization is a type of free-radical addition polymerization. Such reactions are comprised of three principal steps, namely initiation, propagation and termination. In the first stage an initiator is used to produce free-radicals which react with monomer containing unsaturated carbon-carbon bonds (its general structure; $CH_2=CR^1R^2$, where R^1 and R^2 are two substituent groups) to initiate the polymerization. When the radical reacts with a monomer molecule a larger free-radical (active center) is formed which, in turn, reacts with another monomer molecule, thus propagating the polymer chain. Growing polymer chains are finally terminated (free electrons coupled) with another free radical, or with chain transfer agents, inhibitors, etc.

The three stages of the free-radical polymerization are shown in the following steps:

Initiation: The reaction of initiation can be described as a two-stage process. In the first stage the initiator is decomposed to free-radicals, in the second stage the primary radicals react with the monomer, converting it to a growing radical.

The first stage where free-radicals can be generated by two principal processes: 1)homolytic scission (i.e. homolysis) of a single bond which can be achieved by the action of heat or radiation, and 2)chemical reaction involving electron transfer mechanism (redox reactions).

The most common method used in emulsion polymerizations is thermal initiation in which the initiator (*I*) dissociates homolytically to generate a pair of free-radicals (R•) as shown below:

$$I \overset{k_d}{\rightarrow} 2R\bullet \tag{2.6}$$

where k_d is the rate constant for the initiator dissociation. The rate of this dissociation, R_d, is given by,

$$R_d = 2fk_d[I] \tag{2.7}$$

where $[I]$ is the concentration of the initiator and f is the initiator efficiency. The initiator efficiency is the fraction of primary free radicals (R•) which are successful in initiating polymerization, and is in the range 0.3-0.8 due to wastage reactions. The factor of *2* enters because two primary free radicals are formed from each molecule of initiator.

In the second stage, the free radicals generated from the initiator system attack the first monomer (M) molecule to initiate chain growth:

$$R\bullet + M \overset{k_i}{\rightarrow} RM\bullet \tag{2.8}$$

where k_i is the rate constant for the initiation. The rate of initiation, R_i, is equal to the rate of dissociation of an initiator. Because the primary radical adds to monomer is much faster than the first stage, and so the dissociation of the initiator is the rate-determining step in the initiation sequence. According to this, R_i is given by

$$R_i = 2fk_d[I] \tag{2.9}$$

Propagation: The propagation step is only one which produces polymer. This involves essentially the addition of a large number of monomer molecules (*n*) to the active centers (*RM*•) for the growth of polymer chain as shown below.

$$RM\bullet + nM \overset{k_p}{\rightarrow} P_{n+1}\bullet \tag{2.10}$$

where k_p is the rate constant for propagation.

The rate of polymerization, R_p, is known as the rate of monomer consumption. Monomer is consumed by the propagation reactions as well as by the initiation reaction. The corresponding rate of polymerization is then:

$$R_p = -\frac{d[M]}{dt} = k_i[R\bullet][M] + k_p[M\bullet][M] \tag{2.11}$$

where [R•] is the primary free-radicals concentration, [M] is the monomer concentration and [M•] is the total concentration of every size of chain radicals. The amount of monomer consumed in the initiation step can be neglected due to the number of monomer molecules reacting in the initiation step is far less than the number in the propagation step for a process producing high polymer, and a very close approximation of the polymerization rate can be given simply by the rate of propagation. Then, the polymerization rate can be written:

$$R_p = k_p[M\bullet][M] \tag{2.12}$$

Termination: In last step of the polymerization, the growing polymer chain is terminated. There are two main mechanisms, recombination and disproportionation, for termination reactions. In these mechanisms, the growing polymer chain react with another growing chain or another free radical of some kind.

Recombination;

$$P_n\bullet + P_m\bullet \overset{k_{tc}}{\rightarrow} P_{n+m} \tag{2.13}$$

in which two growing chains constitute the coupling with each other resulting in a single polymer molecule.

Disproportionation;

$$P_n\bullet + P_m\bullet \overset{k_{td}}{\rightarrow} P_n + P_m \tag{2.14}$$

in which one growing chain abstracts a hydrogen atom from another, leaving it with an unsaturated end-group. This mechanism occurs more rarely than recombination. It results in the formation of two polymer molecules, one saturated and one unsaturated. In the above equations, k_{tc} and k_{td} are the rate constants for termination by recombination and disproportionation, respectively. The overall rate constant for termination reaction is given as $k_t=k_{tc}+k_{td}$.

In addition to these main termination reactions, there are some other reactions which can terminate the growing chain radical. These reactions can be occurred by removal of an atom from some substances present in the reaction mixture to give a new radical which may or may not start another chain (chain transfer reactions), or by addition to some substance (such as retarder or inhibitor) into the reaction mixture to give a new radical having little or no ability to continue the propagation of the chain [28].

In the chain transfer reactions, some substances such as polymer, monomer, solvent, additives, impurities, or initiator can act as a chain transfer agent. An example of these reactions is given:

$$P_n \bullet + T - A \rightarrow P_n T + A\bullet \tag{2.15}$$

where *T-A* is a chain transfer agent. The chain radical abstracts *T*• (often a hydrogen or halogen atom) from *T-A* molecule to yield a terminate polymer molecule and a new free radical, *A*• which can initiate a new chain. The main effect of chain transfer is to reduce the molecular weight of the polymer. If the new radical *A*• is as reactive as the primary radicals, *R*•, there will be no effect on the rate of polymerization.

In polymerization kinetic, *steady state conditions* must obtain, i.e. where the rate of generation of free radicals (initiation) is equal to the rate at which they disappear (termination). This implies a constant overall concentration of propagating free radicals, [*M*•]. The equation for the steady state conditions is:

$$R_i = R_t = -\frac{d[R\bullet]}{dt} = 2k_t\,[M\bullet]^2 \tag{2.16}$$

In practice, most free-radical polymerizations operate under steady state conditions after an induction period which may be at most a few seconds. When Equation 2.16 is rearranged,

$$[M\bullet] = \left(\frac{R_i}{2k_t}\right)^{1/2} \tag{2.17}$$

and a general expression for the rate of polymerization can be obtained by combining Equation 2.12 and 2.17,

$$R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{1/2} \tag{2.18}$$

This equation show that the polymerization rate depends on the square root of the initiation rate. If we make an arrangement on this equation by using Equation 2.9, we can say that the polymerization rate depends on the square root of the initiator concentration:

$$R_p = k_p[M]\left(\frac{fk_d[I]}{k_t}\right)^{1/2} \tag{2.19}$$

In the emulsion polymerizations, the free-radical mechanism is very closely connected with the heterogeneous nature of the emulsion polymerization in which the micellar phase, the aqueous phase, the monomer droplet phase and the particle phase exist. After the emulsion of the monomer phase in the water phase and the presence of the emulsifier micelles established, the polymerization is initiated by the addition of initiator. According to the theories proposed by Harkings and Smith and Ewart [29, 30], conventional emulsion polymerization mechanism occurs into three intervals including the initial stage, the particle growth stage ant the completion stage.

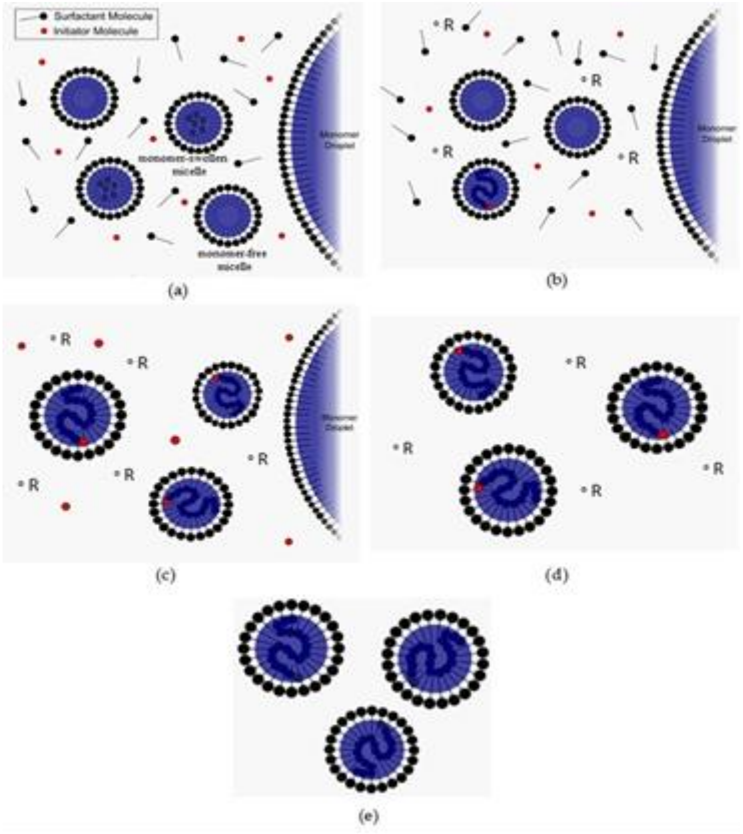


Figure 2.2 : Schematic representation for the mechanism of emulsion polymerization [31]

2.1.2.1 The initial stage (Interval I)

This stage is also called as '*particle formation'* or '*nucleation*'. With the addition of initiator to the reaction mixture, the free-radicals which initiate the polymerization are generated in the aqueous phase and diffuse into monomer-swollen micelles. These micelles act as a meeting place for the hydrophobic monomer and the water-soluble initiator. Since they exhibit an extremely large oil-water interfacial area for diffusing of free-radicals and have high monomer concentration. On the other hand, a small amount of particle initiation can occur within the continuous aqueous phase. Monomer molecules dissolved in this phase are first polymerized are waterborne free radicals. This would result in the increased hydrophobicity of oligomeric radicals.

When a critical chain length is achieved, these oligomeric radicals become so hydrophobic that they show a strong tendency to enter the monomer-swollen micelles and then continue to propagate by reacting with those monomer molecules.

But this nucleation becomes less significant as the amount of micellar emulsifier in the system increases. The amount of polymerization occurring in the monomer droplets is regarded as being a very minor proportion of the whole because of their small surface area for diffusing of the free-radicals.

As a result, monomer-swollen micelles are favored as the sites of the nucleation of polymer particles. Therefore, this nucleation mechanism, proposed by Harkins and Smith and Ewart and modified by Gardon, is called as “micellar” or “heterogeneous” nucleation [32].

After nucleation, monomer-swollen micelles are transformed into polymer particles swollen with monomer. With the continued adsorption of micellar emulsifiers onto growing particles, the micelles starts to disappear (Figure 2.2.b). The particle nucleation stage (Interval I) ends with this disappearance of the micelles at relatively early in the reaction (e.g. between 10% and 20% conversion). During Interval I, the rate of reaction increases with the increasing time of reaction and only one out of every 100-1000 micelles becomes a polymer particle. The number of particles nucleated per unit volume of water is proportional to the emulsifier concentration and initiator concentration to the 0.6 and 0.4 powers, respectively according to the Smith-Ewart theory. After the particle nucleation process is completed, this number remains relatively constant toward the end of polymerization.

2.1.2.2 The particle growth stage (Interval II)

After the particle nucleation process is completed, polymerization proceeds homogeneously in the polymer particles as the monomer concentration in the particles is maintained at a constant concentration by diffusion of monomer from the monomer droplets. The rate of polymerization in this stage is constant. In addition, during this stage, the number of monomer-swollen polymer particles and the monomer/polymer ratio remain constant. The monomer droplets decrease in size as the size of the polymeric particles increase. When monomer droplets completely disappear in the polymerization system (at 50-80% conversion), the particle growth stage (Interval II) ends (Figure 2.2.c). In this situation, the polymer particles contain all the unreacted monomer and essentially all of the emulsifier molecules are also attached to surface of polymer particles.

2.1.2.3 The completion stage (Interval III)

This is the final stage of reaction. In this stage, polymerization continues within the monomer-swollen polymer particles which were formed during Interval I, and persisted and grew during Interval II (Figure 2.2.d). In the ideal case, the number of reaction loci during this stage is essentially fixed at the number which had become formed at the end of Interval I. Whereas, the concentration of monomer in the reaction loci and the polymerization rate continues to decrease toward the end of polymerization. Finally, the polymerization is complete and the conversion of essentially 100% is usually achieved. The system now comprises a dispersion of small polymer particles stabilized with the molecules of the original emulsifiers (Figure 2.2.e).

2.1.3 Types of emulsion polymerization processes

Three types of processes that are used to produce emulsion polymerization: batch, semi-continuous, and continuous. Emulsion Polymerization Reactor Systems are shown in Figure 2.3.

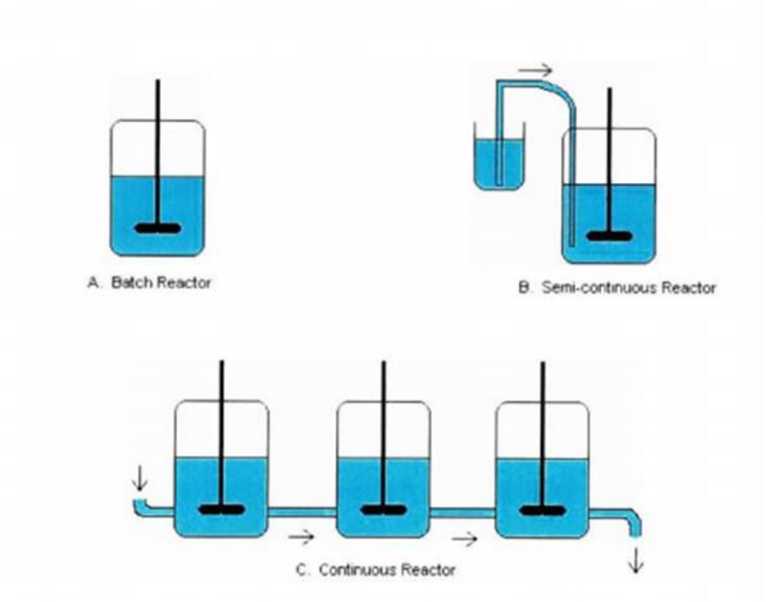


Figure 2.3 : Types of emulsion polymerization

2.1.3.1 Batch process

The batch type emulsion polymerization is generally used in the laboratory to study reaction mechanism, develop new latex products, and obtain kinetic data for process development and reactor scale-up.

All ingredients are placed in a reactor at the beginning of the reaction. The system is agitated, and heated to reaction temperature. Polymerization begins as soon as the initiator is added. Then, the reaction system is kept there by heating or cooling, as needed, and by agitating until the samples removed indicate the desired conversion of monomer to polymer. The only significant changes which can be made in such cases are to the reaction temperature, reactor design and the type and speed of agitation.

Most commercial latexes are not manufactured by this process because of their undesirable properties. This process has important disadvantages that limited control is exerts over either monomer/polymer ratio in the reaction loci, or over heat transfer in the reaction, or over copolymer composition [33].

2.1.3.2 Semi-batch process

In semi-continuous polymerization, the particles are nucleated in two ways: a small proportion of the monomer is charged initially and polymerized in batch to make a seed latex in situ or the continuous monomer addition and the polymerization are started at the same time. In the second case, nucleation proceeds concurrently with particle growth until it ceases and only particle growth occurs. In both cases, the number of particles nucleated may vary from batch to batch. This variation may be obviated by addition of a seed latex, which gives rigorous control of the number of particles and stoichiometric particle growth. The monomer is added either continuously or in increments, either neat or in emulsion. These different modes of addition give different results: the addition of neat monomer generally results in the growth of the particles nucleated early in the reaction; the addition of monomer in emulsion may give continual nucleation throughout the polymerization. The mode and rate of monomer addition control the rate of polymerization rigorously; moreover, they also control the copolymer compositional distribution and particle morphology, and furnish the means to minimize the formation of coagulum and achieve the requisite latex properties for the practical application. Semi-continuous polymerization is the preferred process for rigorous process control, and it is used to prepare many industrial latexes; however, our understanding of its fundamentals is still primitive.

2.1.3.3 Continuous process

In continuous emulsion polymerization, the polymerization is started as soon as the monomer emulsion is heated to the polymerization temperature, and particle nucleation occurs concurrently with particle growth. The number of particles nucleated (and hence the rate of polymerization and conversion of the exit stream) varies cyclically with mean residence time according to the local conditions in the reactor system. This variation can be obviated by the continuous addition of a seed latex or the use of a short tube reactor ahead of the continuous reactor, in which a seed latex is formed continuously in situ, to furnish the requisite number of particles to the system, so that the conversion of the exit stream becomes constant after a few mean residence times. Continuous polymerizations are run in series or cascades of stirred-tank reactors, a single stirred-tank reactor with an outside loop, tubular reactors, and other types. The process is economical and gives latexes of constant quality; however, without a detailed understanding of its fundamentals, it is difficult to alter the polymeric and colloidal properties of the latex. In the laboratory, it is often used for the study of fundamental reaction and transport phenomena [34].

2.1.4 Acrylic emulsion polymerization

Since their introduction decades ago, acrylic polymers have gained a strong foothold in the coatings and allied industries as a result of their improved flexibility and adhesion compared to polyvinyl acetate emulsions, phenolics, and styrene-butadiene latex combined with their moderate cost. In addition, their significantly improved outdoor durability, including resistance to ultraviolet degradation, has mandated their use in several applications. In many respects, the name “acrylic” has become synonymous with a high performance level in a polymer system.

Presently, acrylics are available in three physical forms: solid beads, solution polymers, and emulsions.

Monomers, are prepared by a reversible reaction between an acrylic acid and an alcohol as shown below:

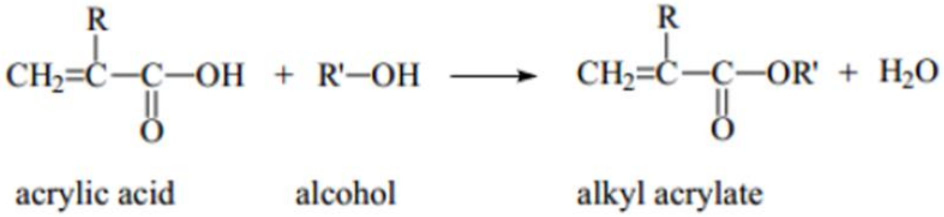

$$CH_2{=}C(R){-}C({=}O){-}OH + R'{-}OH \longrightarrow CH_2{=}C(R){-}C({=}O){-}OR' + H_2O$$

Figure 2.4 : Reversible reaction between an acrylic acid and alcohol.

The major monomers used are ethyl acrylate, methyl methacrylate and butyl acrylate, as well as non-acrylic monomers such as vinyl acetate and styrene which behave similarly. Homopolymers latexes of these monomers have wide range of application areas such as paint, coating, textile, leather, construction etc. These polymers are stable, have good pigment binding capacity, durability, chemical resistance, impact resistance. Wide range of copolymers can be produced, and by varying the ratio of their monomers a series of polymers with a wide range of glass transition temperatures can be produced with emulsion polymerization method [31, 35, 36].

Surfactant can be called emulsified, is a substance composed of mutually repellent polar and non-polar ends. The aim of the surfactants are reducing the surface tension of water and facilitate the wetting of surfaces and the emulsification of organic substances in water. The surfactant surrounds each monomer droplet with a layer of surfactant with the polar tails oriented towards the surrounding water thus forming a micelle [31].

Water, is used as the medium to disperse and wet the micelles. During the emulsion polymerization process the water acts as a solvent for the surfactants and initiators, as well as a heat transfer medium [31, 37]. Water based paints and solvent based paints are differentiated with regard to medium type, water or solvent.

The initiators (catalysts), usually used are water soluble peroxidic salts such as ammonium or sodium peroxydisulfate. The reaction can be initiated either by thermal or redox initiation. In thermal initiation the peroxydisulfate dissociates to give two SO_4^- radicals.

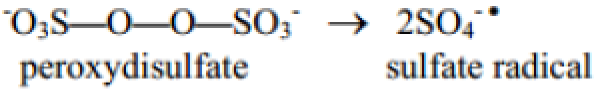
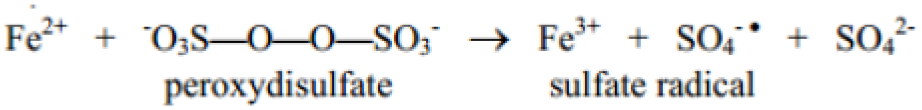

$$^-O_3S{-}O{-}O{-}SO_3^- \rightarrow 2SO_4^{-\bullet}$$

Figure 2.5 : Initiation of the peroxydisulfate.

In redox initiation a reducing agent (usually Fe2+ or Ag+) is used to provide one electron, causing the peroxydisulfate to dissociate into a sulfate radical and a sulfate ion.



$$Fe^{2+} + {}^{-}O_3S—O—O—SO_3^{-} \rightarrow Fe^{3+} + SO_4^{-\bullet} + SO_4^{2-}$$

Figure 2.6 : Dissociation of peroxydisulfate into a sulfate radical.

Straight acrylics are polymer dispersions composed exclusively of acrylate and/or methacrylate monomers. Styrene acrylic copolymers contain styrene as well. For both types of copolymer there are a host of monomers which differ greatly as regards glass transition temperature and the polarity of the homopolymers prepared from them [38]. Table 2.1 shows some monomer's water solubility and *Tg* values. Monomer composition is determined specify according to application conditions.

The special features of the polyacrylates and polymethacrylates that justify their relatively high price are the generally very good weatherability and UV stability, high transparency, good water resistance and yellowing resistance, great ease of variation in toughness, hardness and flexibility [39].

Table 2.1: Water solubilities and glass transition temperatures of the principal monomers for acrylic dispersions.

Monomer building blocks	Water solubility at 25ºC in g/100 cm^3	Glass transition temperature (Tg) of the homopolymer (ºC)
Acrylates		
Methyl acrylate (MA)	5.2	22
Ethyl acrylate (EA)	1.6	-8
n-Butyl acrylate (nBA)	0.15	-43
Methacrylates		
Methyl metacrylate (MMA)	1.5	105
n-Butyl metacrylate (nBMA)	0.08	32
Styrene	0.02	107
Acrylonitrile	8.3	105
Vinyl acetate	2.4	42

Special polymerization technique can be used in emulsion polymerization that comes from morphology of polymerization. Different kind of morphology is used in emulsion polymerization technology such as core-shell, raspberry, half-moon shaped particles. Core-shell technology is one of the most widely used methods in polymerization. By combining a soft, film forming occurs at low temperature, and a hard monomer, which film formation occurs at high temperature in one and the same particle, and by tailoring the particle morphology, it is even possible to achieve better polymer specialty. Such this core-shell system have a low MFFT and high elasticity, along with good freedom from tackiness, excellent blocking resistance and good coating hardness. Especially for the special coating application systems such as wood coating, metal coating, joinery, core-shell morphology is preferred [40, 41].

Acrylic resins are made essentially esters out of acrylic acids or methacrylic acid. They are for the most part utilized as a part of paint and coating. Additionally they can be utilized as a part of textile, adhesive, printing inks, paper coating and construction industries. Acrylic esters and methacrylic esters have quite different properties. Amount of these esters in polymer determine material properties, hardness, flexibility, chemical resistance, leveling during film formation [42].

Esters of acrylic acid or methacrylic acid are recognized by the reactivity of their double bonds. After initiation step these double bonds associate each other and polymerization happens. Esters of acrylic acid and metacrylic acid which go about as building blocks for polymers are called monomers. Advance building blocks are capable of polymers conjuction with acrylic and metacrylic esters are called comonomers [43, 44].

Acrylic resins can be characterized into two groups. To begin with first group called polyacrylates. These groups are set up by polymerizing acrylic or methacrylic esters by means of their double bonds. Polyacrylates are also separated two groups agreeing their polymerization procedure, solution polymerization and emulsion polymerization. With solution polymerization, polymerization process happens in organic solution and this polymer can be utilized directly in coating formulation. Also, such polymers can be changed into secondary aqueous dispersion a powder coating resins. Another procedure is emulsion polymerization, monomer blends are dispersed in water with the guide of suitable emulsifiers. Emulsion polymerization will be detailed into the following segments [43, 45].

The second group of acrylic resins for coatings involves acrylic or methacrylic ester resins that still contain double bonds. These binders are called reactive acrylic resins. Addition or condensation reactions are utilized to incorporate the acrylic or methacrylic ester into polymer or oligomer particles. The resultant binders are equipped for forming films by polymerization after application, and are for the most part by energy-rich radiation which yields three-dimensional crosslinked macromolecules [18].

Water-borne acrylic dispersions are commonly prepared via emulsion polymerization. Emulsion polymerization has more advantages in comparison to solution polymerization. First of all, much higher molecular weight polymers can be synthesis. High solid content (50% or higher) polymers can be produced with emulsion polymerization. Another advantage is that the resin has low viscosity, thus allowing fast air drying by evaporation of water [46, 47].

2.1.5 Emulsion copolymerization

In many cases latex products are composed of more than one monomer. In copolymerization two or more monomers are built-in into the polymer chains. The copolymer chains are produced by simultaneous polymerization of two or more monomers in emulsion. Emulsion copolymerization allows the production of materials with properties which cannot be obtained by latex products consisting of one monomer, that is, homopolymer latexes, or by blending homopolymers. The properties of the materials required are usually dictated by the market. Nowadays, most of the material properties are achieved by combination of more than two monomers in the copolymer product. Typical industrial emulsion polymerization formulations are mixtures of monomers giving hard polymers, and monomers leading to soft polymers. Styrene and methyl methacrylate are examples of monomers giving hard polymers, that is, polymers with a high glass transition temperature, *Tg*. Soft polymers, that is, polymers with a low *Tg*, are, for example, formed from n-butyl acrylate. The industrial emulsion polymerization formulations also contain small amounts of functional monomers such as acrylic and methacrylic acid to impart improved or special characteristics to the latex product. Note that the colloidal stability of the latex product can be seriously improved by acrylic and methacrylic acid. Moreover, a few applications may interest for the expansion of other claim to specialty monomers that make the kinetics of the copolymerization considerably more complex [19].

Vast amounts of polymers generated by emulsion polymerization are copolymers as the properties of the individual polymers can be synergistically increased by the generation of copolymers. However, as the different monomers have different reactivities in a particular system therefore there it is always complex to predict the final composition of the copolymer chains and if it would be same as the initial monomer ratios. Apart from that, as the reactivities are different from each other, the more reactive monomer may polymerize first, thus forming core of the particles rich in this polymer followed by a outer cover of particles more rich in less reactive monomers. This leads to a gradient of concentration of different monomers in these particles. There can similarly be also differences when the water solubilities of the monomers are quite different from each other. Figure 2.4 is an example of comparison of the homopolymers with copolymers. The pure polystyrene particles earlier shown in Figure 2.5 are compared with the copolymers of styrene with water soluble monomer N-isopropylacrylamide. The generated surface morphology is totally different in these particles. One should note here that the particles were achieved without using the surfactant, i.e. particle generation was achieved by homogenous nucleation mode. The more hydrophilic monomer starts polymerizing first followed by the polymerization of more hydrophobic monomer. The hydrophobic monomer polymerize inside these particles because of hydrophobicity thus pushing the hydrophilic chains of poly(N-isopropylacrylamide) on the surface of the particles. Monomer partioning is the term most commonly used to describe the emulsion copolymerization of two or more monomers. Owing to the different reactivity ratios of the monomers and the different ratio of monomers in the polymer particles (i.e., loci of polymerization), which is generally very different from the initial monomer ratios, the compositional drift in the copolymer composition takes place [17].

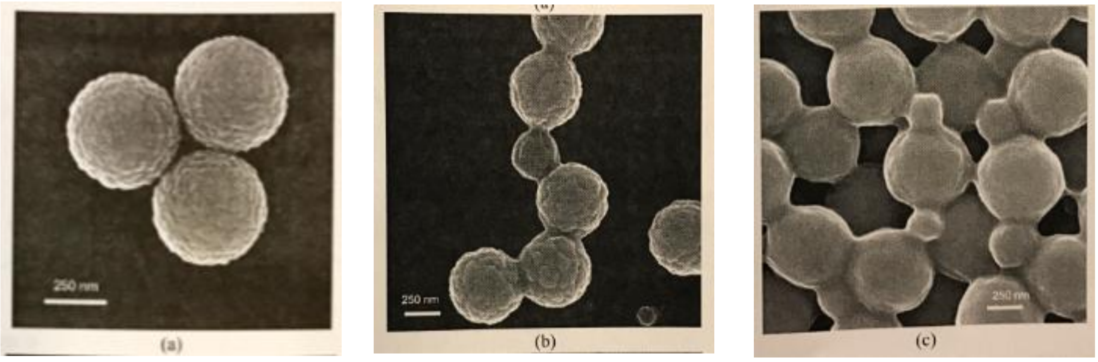


Figure 2.7 : SEM images of styrene-co-isopropyl acrylamide copolymer particles.

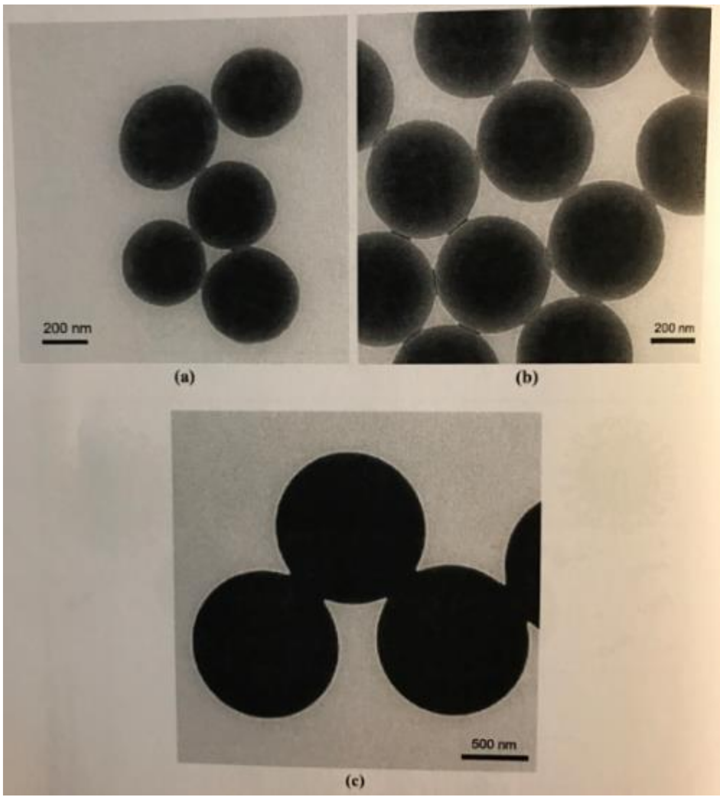


Figure 2.8 : Evolution of particle size as a function of conversion.

2.2 Silane coupling agents

The synergy between organic and silicon chemistries has been investigated for more than 50 years, and has led to the development of many organo-functional silanes that are essential today in many applications.

Monomeric silicon chemicals are known as silanes. A silane that contains at least one siliconcarbon bond (e.g., $Si-CH_3$) is an organosilane. The carbon-silicon bond is very stable and nonpolar, and in the presence of an alkyl group it gives rise to low surface energy and hydrophobic effects [48-50].

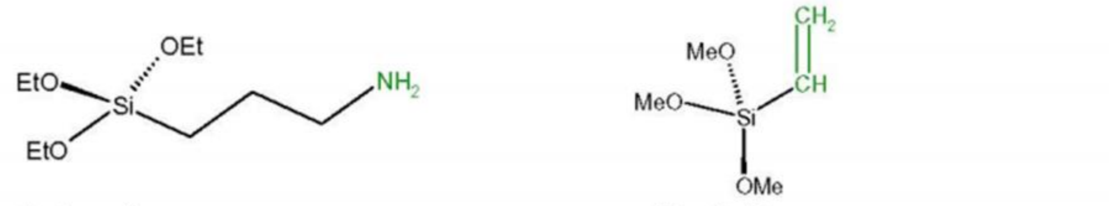
2.2.1 Chemistry of organofunctional alkoxysilanes

The general formula of an organosilane shows two classes of functionality.

$$R_nSiX_{(4-n)}$$

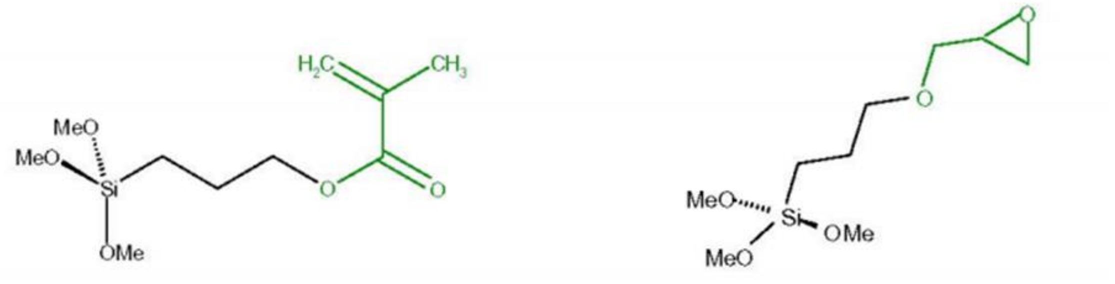
The X functional group is involved in the reaction with the inorganic substrate. The bond between X and the silicon atom in coupling agents is replaced by a bond between the inorganic substrate and the silicon atom. X is a hydrolyzable group, typically, alkoxy, acyloxy, amine, or chlorine. The most common alkoxy groups are methoxy and ethoxy, which give methanol and ethanol as byproducts during coupling reactions. Since chlorosilanes generate hydrogen chloride as a byproduct during coupling reactions, they are generally utilized less than alkoxysilanes.

R is a nonhydrolyzable organic radical that possesses a functionality which enables the coupling agent to bond with organic resins and polymers. Most of the widely used organosilanes have one organic substituent.



Amino-silane
γ-Aminopropyltriethoxysilane

Vinyl-silane
Vinyltrimethoxysilane



Methacryloxy-silane
γ-Methacryloxypropyltrimethoxysilane

Epoxy-silane
γ-Glycidoxypropyltrimethoxysilane

Figure 2.9 : Examples of organo-functional silanes

In most cases the silane is subjected to hydrolysis prior to the surface treatment. Following hydrolysis, a reactive silanol group is formed, which can condense with other silanol groups, for example, those on the surface of siliceous fillers, to form siloxane linkages. Stable condensation products are also formed with other oxides such as those of aluminum, zirconium, tin, titanium, and nickel. Less stable bonds are formed with oxides of boron, iron, and carbon. Alkali metal oxides and carbonates do not form stable bonds with Si – O –.

Water for hydrolysis may come from several sources. It may be added, it may be present on the substrate surface or it may come from the atmosphere. Water for hydrolysis may also be generated in situ by dissolving chlorosilanes in excess alcohol. Reaction with alcohol produces alkoxysilanes and HCl, which can react with additional alcohol to form an alkyl halide and water. Reaction of these silanes involves four steps. Initially, hydrolysis of the three labile X groups attached to silicon occurs. Condensation to oligomers follows. The oligomers then hydrogen bond with OH groups of the substrate. Finally during drying or curing, a covalent linkage is formed with the substrate with concomitant loss of water. At the interface, there is usually only one bond from each silicon of the organosilane to the substrate surface. The two remaining silanol groups are present either bonded to other coupling agent silicon atoms or in free form.

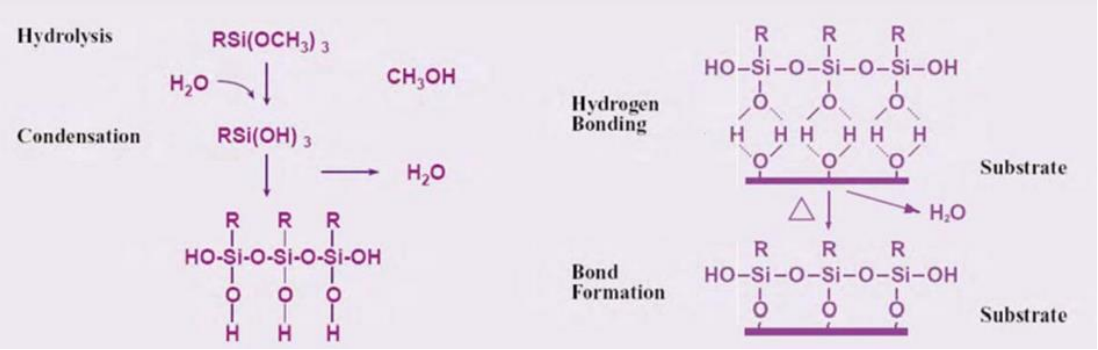


Figure 2.10 : Organo-functional silane hydrolysis, condensation and covalent bonding to an inorganic substrate.

The number of reactive sites on a surface area and the type of silane deposition sought, i.e. monolayer, multilayer or bulk, are all factors which can be used in calculating the amount of silane necessary to silylate a surface. In order to provide monolayer coverage, the concentration of reactive sites (silanols) should be determined. Most siliceous substrates have 4 – 12 silanols per $m\mu^2$. Thus, one mole of evenly distributed silane should cover an average of 7500 m^2. The oligimerization of silanes with multiple groups thwarts the capability of computing stoichiometries, but order of magnitude computations are successful. Silanes with one hydrolyzable group can be utilized to produce surfaces with monolayers of consistent stoichiometry. These materials are more expensive and produce surfaces with less hydrolytic stability. The number of silanols on a surface is varied by thermal history. In one example, a siliceous surface having 5,3 silanols per mμ^2 had only 2.6 after exposure to 400°C and less than one after exposure to 850°C. Higher concentrations of silanol groups may be produced by treating material with warm hydrochloric acid. Silanol anions may be produced by treating the surfaces with alkaline detergent or, more radically, by treatment with methanolic potassium hydroxide. Optimum deposition of silanes with more than one hydrolyzable group is often defined as the as the amount necessary to produce a surface of uniform energy. A value defined as the wetting surface (ws) describes the area in m2 one gram of silane deposited from solution will cover. In combination with data on the surface area of a siliceous substrate in m^2/g the amount of silane required for deposition may be calculated. Most composite, adhesive, and coating formulations do not follow any stoichiometry, but simply define optimal concentration by operation success. For most fillers, a treatment level of 0.02 – 1.00% by weight is used.

2.2.2 Selecting a silane coupling agent

Selection of the appropriate coupling agent is accomplished by empirical evaluation of silanes within predicted categories. Exact prediction of the best silane is extremely difficult. Increased bond strength by utilization of silanes is a result of a complex set of factors – wet out, surface energy, boundary layer absorbtion, polar adsorption, acid-base interaction, interpenetrating network formation and covalent reaction. Strategies for optimization must take into account the materials on both sides of the interface and their susceptibilities to the various coupling factors. Generally speaking the initial approach is to select a single coupling agent and assume a direct bond between the two materials. The most common application for silane coupling agents is to bond an inorganic substrate to a polymer.

2.2.2.1 Inorganic-Si-R-Organic

The number of hydrolyzable X groups on the silane is another important parameter in controlling bond characteristics. The traditional silane coupling agents contain three hydrolyzable groups and they have maximum hydrolytic stability. At the opposite end are the silanes with one hydrolyzable group. These yield the most hydrophobic interfaces but have the least long term hydrolytic stability. Silanes with two hydrolyzable groups form less rigid interfaces than silanes with three hydrolyzable groups. They are often used as coupling agents for elastomers and low modulus thermoplastics. Polymeric silanes with recurrent trialkoxy or dialkoxysilanes offer better film-forming and primer capabilities. For enhanced hydrolytic stability or economic benefit, non-functional silanes such as short chain alkyltrialkoxysilanes or phenyltrialkoxysilanes can be combined in ratios up to 3:1 with functional silanes. In more difficult bonding situations, mixed silanes or silane network polymers may be employed. These include inorganic to inorganic or organic to organic. In these cases, reaction of the silanes with themselves is critical.

2.2.2.2 Organic-O-Si-R-R-Si-O-Organic

An example of mixed silane application is the use of mixtures of epoxy and amine functional silanes to bond glass plates together. A more general use is bonding organic to organic. Primers, prepared by pre-hydrolyzing silanes to resins in order to form bulk layers on metal substrates, are examples of the application of silanes as network polymers. Thermal Stability Most silanes have moderate thermal stability, making them suitable for plastics that process below 350°C or have continuous temperature exposures below 150°C. Silanes with an aromatic nucleus have higher thermal stability. A relative ranking where Z is the functional groups is as follows [10]:

Table 2.2: Thermal stability of organo-functional silanes.

Class	Thermal limit
$ZCH_2CH_2SiX_3$	< 150ºC
$ZCH_2CH_2CH_2SiX_3$	390ºC
$ZCH_2AromaticCH_2CH_2SiX_3$	495ºC
Aromatic SiX_3	550ºC

2.2.2.3 Benefits of organo-functional silanes

Organo-functional silanes have shown greatest benefits in three areas: mineral filler treatment, cross-linking and as adhesion promoters.

Mineral Filler Treatment: Mineral fillers have become increasingly important modifiers for reinforcing organic polymers, thermoplastics or thermosets. Yet, the metal hydroxyl groups on the mineral filler surface are hydrophilic, and this translates to incompatibility with organic polymers. Organosilanes are ideal for treating the filler surface, making the filler more compatible and easier to disperse in the polymer. Any minerals with silicon or aluminum hydroxyl groups on their surfaces (e.g., silica, glass bead, quartz, sand, talc, mica, clay or wollastonite) can be treated with organo-functional silanes. These will ease dispersion of the fillers and improve wetting by, and adhesion to, the polymer. This results in lower filler/polymer mix viscosities and improved mechanical properties [51].

A typical example in equation 2.20 is the sulfido-silanes:

$$(OR)_3\,Si\text{-}(CH_2)_3\text{-}S_x\text{-}(CH_2)_3Si(OR)_3 \qquad \text{where } x = 2 \text{ to } 8 \quad (2.20)$$

Selecting the adequate sulfido-silane enables surface treatment of the silica used in green tires and bonding to organic rubber, which was proven extremely effective for optimizing the viscoelastic and mechanical properties of the silica-rubber composite for "more miles per gallon."

Cross-Linking. Polymers and polymeric composites are becoming increasingly attractive as engineering materials. They are highly competitive compared to metal or metal alloys due to their low cost and low density, ease of compounding using extrusion or injection molding processes, and inherent lack of corrosion-related problems.

One way to improve performance of such plastics is to cross-link them to some degree. One well-known example using organo-functional silanes is the cross-linking of polyethylene to give partially cross-linked polyethylene or PEX [52, 53].

This is achieved by grafting vinylfunctional alkoxy silanes on the PE chains using peroxide as an initiator. The vinyl groups allow for grafting on the PE backbone, and the alkoxy groups allow for subsequent crosslinking between the PE chains upon exposure to heat and moisture. The main applications are for piping of various kinds (e.g., under floor heating, drinking water) and wire and cable insulation.

Similarly, cross-linking is used to enhance mechanical properties in thermoplastic vulcanisates (TPVs), through dynamic vulcanization process and where the silanes play many roles: cross-linker, adhesion promoter and even intermediate to generate in situ filler.

Adhesion Promoter: Organo-functional silanes are known for surface modification. So as additives, they can enhance adhesion between dissimilar materials because of their low surface tension (which ensures good surface wetting), their reactivity to different surfaces and their ability to create interactions and make an adequate transition interphase between the adhesive layer and the substrate to bond [54, 55, 10].

2.3 Interior Paints

In the broadest sense, interior paints are all paints, which are used indoors - i.e. protected against the effects of weathering and UV radiation. In the narrower sense, the term interior paints is used to refer to matt paints as used to coat interior plaster, wood chip wallpapers, or the like. Gloss or wood paints, although they may be intended for use in the interior sector, are not included among the interior paints described below.

Interior paints represent by far the largest segment within the water-based paints market. The range of products offered in the market is virtually limitless and covers, from a technical standpoint, the size colors bound with water-soluble sizes (which are not considered in the text below), very highly filled, ultra-low-price emulsion paints, standard grades, and then high-quality varieties, such as the emission- and solvent-free interior paints. High technical qualities as far as interior paints are concerned means, primarily, ease and simplicity of use and economy through high coverage.

Because of their application in unexposed conditions, the binders used in interior paints, in contrast to those for exterior paints, do not need to be resistant to either UV or weathering. This means that suitable binders for interior- paints include all of the copolymer types offered in the market, i.e., styrene/acrylic dispersions, straight acrylics, vinyl acetate copolymers, and high-pressure polymers of vinyl acetate and ethylene. In contrast to exterior paints, interior paints need not afford any protection against moisture either. Consequently, the pigment volume concentration (PVC) of interior paints may be formulated at well above the critical PVC (CPVC). The resulting open-pored nature of the film is an advantage rather than a disadvantage, by virtue of what is known as dry hiding. What are the requirements imposed on an interior paint? For its production to be as economic as possible, the paint must produce the desired service properties with the smallest possible amount of binder. This means, in turn, that the principal requirements of the binder are — a high pigment binding capacity, and — an excellent price/performance ratio [46].

The major advantages of latex paints as compared to the older oil-based flat wall paints are:

Fast drying and less sagging. If desired, two coats can be applied to the walls of a room during a day, the furniture moved back, and the room used that night. The rapid increase in low-shear viscosity in the early stages of film formation reduces vulnerability to sagging, even when relatively thick films are applied.

Low odor. The odor of mineral spirits and byproducts from oxidation of drying oils in solvent-borne paints is unpleasant for days after walls are painted. Although the odors are less offensive, some odor from the slow evaporation of coalescing solvents from latex paints persists for up to a week. A reason for developing zero VOC paints is to eliminate this odor problem. Ease of cleanup. Spills, dripped spots, brushes, and rollers are easily cleaned with soapy water in the case of latex paints; solvent is required with oil paints. However, cleaning up must be done promptly because once latex has coalesced, cleaning it up is more difficult than with oil paints. *Low VOC emissions.* Latex paints were widely adopted before there was concern about VOC emissions. Progress is being made in reducing the already low VOC. There is also the advantage with water-borne paints of substantially reduced fire hazard. Not only is solvent-borne paint flammable, but also rags wet with oil-based paints in a confined space can undergo spontaneous combustion, that is, ignite as a result of heat generated by autoxidation.

Less yellowing and embrittlement. White and light color vinyl and vinyl/acrylic latex paints retain their color better than alkyd paints, which gradually turn yellow with age. Alkyds made with oils that contain very little linolenic acid, such as sunflower or safflower oils, yellow more slowly than alkyds based on soybean oil or tall oil fatty acids, but they still yellow with time. Alkyd films also eventually become brittle as autoxidative cross-linking continues far beyond the point of optimum film properties.

Flat wall paint is usually stocked as white paint, sometimes called a tint base, and tinting colors are added to make a color chosen by the customer from a large array of color cards. This requires that equal white tinting strength be maintained through quality control or the colors obtained will differ. Furthermore, any new formulation must have the same white tinting .strength as the formulation being replaced or else the color cards and formulations in dealer stores will have to be replaced. In each quality line, two, or sometimes three, white base paints are included. The base white paint is used alone as a white or tinted to make pastel colors. A deep tone base containing little TiO2 is used for tinting to deep colors that could not be made if the regular base paint were used. Frequently, a third base is in the line that is used for intermediate depths of shade.

Intermediate depths of shade could be matched using the base white paint, but he cost would be excessive because more tinting color would be needed to match the colors; hiding would be greater than needed.

Users are sometimes confused by the change in color of the latex paint as it dries; the color of a dry film is darker than the color of the wet paint. In the wet paint, the interfaces between the water (n=1.33), polymer particles (n=approximately 1.5), TiO_2 (n=2.73), and inert pigments (n=approximately 11.6) scatter light to a greater degree than when the paint is dry. The dry paint has fewer interfaces as a result of coalescence of the latex particles, and also there are smaller refractive index differences since the pigment particles are in a polymer matrix instead of water. Since light scattering decreases as water evaporates and the latex particles coalesce, the color gets darker; hiding also decreases as the paint dries.

When painting ceilings, one is particularly anxious to get hiding in one coat, since painting over one's head and moving the ladder is more of an effort than when painting walls. The problem is particularly challenging because ceiling paints are commonly plain white to reflect light diffusely. Since there are no color pigments in a white paint to absorb light, the hiding by white paints is poorer than any color paint made from it. The problem is compounded by the decrease in hiding when a latex paint film dries. The user thinks he or she has applied enough paint to hide marks on the ceiling, but comes back an hour or so later and finds that marks show through the dry paint. Special ceiling paints minimize this problem by formulating with PVC above CPVC. Dry paint films with PVC above CPVC have voids of air with n =1 that add additional light scattering by the new interfaces between air and polymer as well as air and pigment. Formulations can be adjusted so that wet hiding and dry hiding are approximately equal. The films do not have as high mechanical strength as films of paint with PVC < CPVC, and resistance to staining is poorer, but neither property is important for ceiling paints [56]

Water-borne ceiling paints

The ceiling paint has a softer binder and extender pigment, which means that the paint won’t stand up to rigorous scrubbing and cleaning in the same way that wall paints will.

Ceiling paint is manufactured to be flat so that the light doesn’t reflect on it, which serves to hide any small irregularities and imperfections that may exist on the surface. Using the flattest finish possible on a ceiling is important, as any kind of glossiness (even the slight sheen afforded by eggshell finishes) shows up on ceilings far more than on walls, can catch the light the wrong way, and can end up looking quite garish.

In addition, ceiling paint is thicker, allowing it to offer greater hiding ability overall. Ceiling paint is formulated with a greater amount of solids in it, which means that you can paint above your head (vertically) with less drips and splatter. This will also help eliminate unsightly areas on the ceiling where paint accumulates during the dripping process, which are difficult to fix once the paint has dried.

The increase in hiding above critical pigmented volume concentration (CPVC) can be useful. The hiding of white ceiling paints can be improved by formulating above CPVC. This permits hiding with one coat, which is particularly desirable in ceiling paints.

Composition: Ceiling paint is formulated to cover all the edges and to hide all the imperfections. It’s flat and the light doesn’t reflect on it so any small irregularities are not enhances but hidden. The paint is more viscous to eliminate drippiness. Ceiling paint has to cover well, stick well and hide well and this is usually achieved at the expense of other characteristics not needed for this portion of the room.

3. EXPERIMENTAL PART

Styrene-acrylic copolymers are synthesized by emulsion polymerization by using different functional monomers and post additions. These copolymers are used as a binder in water-based decorative ceiling paint formulations. All copolymer compositions are evaluated in terms of physical, chemical and mechanical performances.

3.1 Materials

Acrylic acid is a clear, colorless liquid with a characteristic pungent odor. It is miscible with water, alcohols and ethers. Acrylic acid as shown on Figure 3.1 will undergo the typical reactions of a carboxylic acid, as well as reactions of the double bond similar to those of the acrylate esters. It lends itself to polymer preparation as well as use as a chemical intermediate.

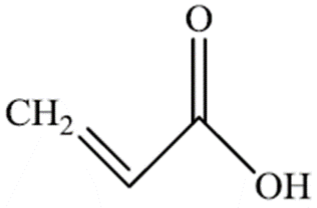


Figure 3.1 : Acrylic acid.

Styrene, also known as ethylbenzene, vinyl benzene, and phenylethene, is an organic compound with the chemical formula C6H5CH=CH2 is shown in the Figure 3.2. This derivative of benzene is a colorless oily liquid that evaporates easily and has a sweet smell, although high concentrations have a less pleasant odor. Styrene is the precursor to polystyrene and several copolymers. Styrene gives hydrophobicity to the polymer and scrub resistance properties to the paint.

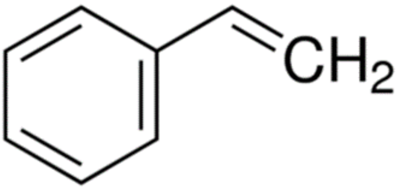


Figure 3.2 : Styrene.

Butyl acrylate is a clear colorless liquid with a characteristic fruity odor. It is readily miscible with most organic solvents. It is readily polymerized and displays a wide range of properties dependent upon the selection of the monomer and reaction conditions. Chemical composition is as Figure 3.3 as shown below.

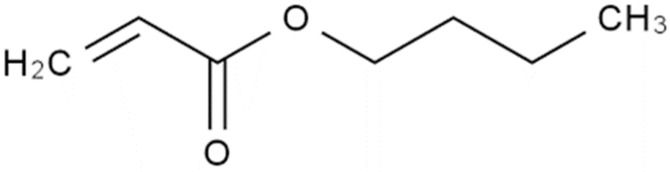


Figure 3.3 : Butyl acrylate.

Monomers are provided from Organik Kimya without giving any brand name.

Sodium persulfate is an initiator. Its role is that making free radicals to provide polymerization proceed. Sodium persulfate is provided from Organik Kimya without giving any brand name.

Sodium Formaldehyde Sulfoxylate, which received from Brueggemann Chemicals, is a formaldehyde-free reducing agent. It is capable of substantially reducing free monomers, reaction time and yellowing. Tert-Butyl hydroperoxide is an oxidative and used with Sodium Formaldehyde Sulfoxylate for redox reaction, buying from Sigma Aldrich. Chemical composition is as Figure 3.4 as shown below.

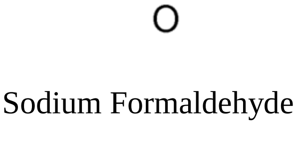


Figure 3.4 : Sodium Formaldehyde Sulfoxylate.

Sodium hydroxide (NaOH) is used for neutralization step.

Different types of organo-functional silanes are used. These silanes are listed below.

Vinyltrimethoxysilane is used in emulsion.

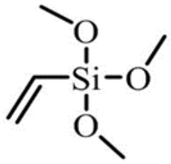


Figure 3.5 : Vinyltrimethoxysilane.

3-trimethoxysilylpropyl methacrylate is used in emulsion.

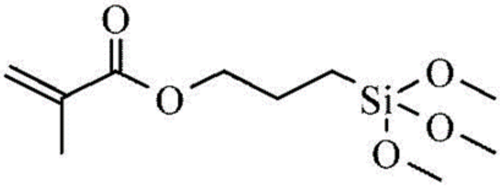


Figure 3.6 : 3-trimethoxysilylpropyl methacrylate.

VTET is synthesized and delivered by POLMAG Laboratory (Polymeric Materials Research Group) . This silane is added after polymerization as a post-additive.

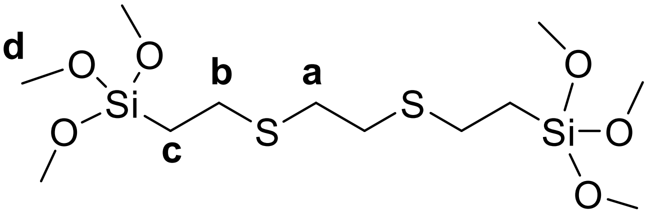


Figure 3.7 : 3,3,12,12-tetramethoxy-2,13-dioxa-6,9-dithia-3,12-disilatetradecane.

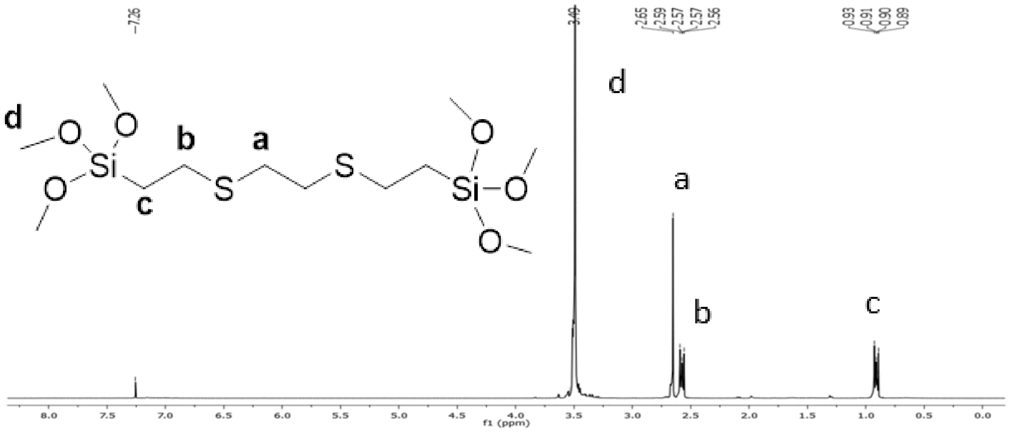


Figure 3.8 : H-NMR spectrum of VTET.

β-(3,4-epoxycyclohexyl) ethyltriethoxysilane is added as post-additive.

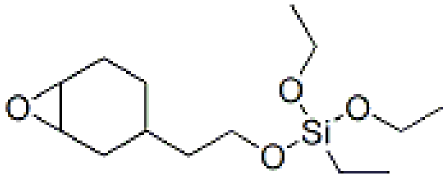


Figure 3.9 : β-(3,4-epoxycyclohexyl) ethyltriethoxysilane.

Octyltriethoxysilane is added as post-additive.

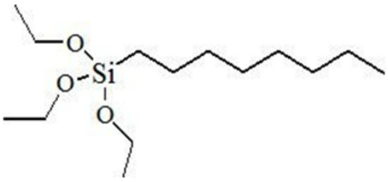


Figure 3.10 : Octyltriethoxysilane.

3-glycidyloxypropyl trimethoxysilane is used as post-additive.

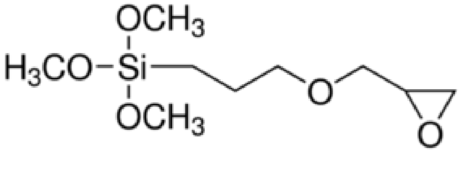


Figure 3.11 : 3-glycidyloxypropyl trimethoxysilane.

3.2 Copolymer Synthesis

Semi-continuous polymerization process is selected in this thesis. For preparation of pre-emulsion, 156 gram water is weighted in a beaker and under stirring 15 gram anionic surfactant (30% solution) , 25 gram nonionic surfactant (20% solution) are added on the beaker. While the water-surfactant mixture is agitating, 15 gram acrylic acid and 285 gram butyl acrylate are slowly added on the beaker. After adding butyl acrylate, the color of mixture is turned clear to white. 190 gram styrene is slowly added in the mixture and 5 minutes stirring is needed. 2 liter three-necked flask is cleaned and dried. 163 gram water is weighed in the flask and heated to 90°C. 3 gram anionic surfactant (30% solution) and 5 gram nonionic surfactant (20% solution) is added into flask. After addition of surfactants, the temperature of water-surfactant mixture in the flask is decreased to 85°C. Sodium persulfate is diluted with water 2:40 amounts and it is used as an initiator. 8.4 gram initiator solution is added into the flask. 40 gram of pre-emulsion is added into the flask and it is named as “seed”. After seed addition, the reaction temperature is decreased 80°C and the reaction starts. The rest of the initiator solution and pre-emulsion are parallel feed into the flask within 3 hours. The reaction goes on at 82°C under agitation. At the end of the feeding of pre-emulsion and initiator, the reaction continued to agitate at 82°C for 30 minutes to decrease free monomer amount and this step is called as “cooking”. After cooking, redox step is started. 1 gram t-BHP is diluted with 15 gram water and 1 gram Sodium Formaldehyde Sulfoxylate (SFS) is diluted with 15 gram water.t-BHP solution is added at 70°C and waited 10 minutes. After that, SFS solution is added at 70°C and waited 10 minutes under agitation. After 10 minutes, the heater is shut down. pH is checked and adjusted around 8-9 with sodium hydroxide solution(10% sol.). For the last step, biocide is added on the emulsion. CIT/MIT type of biocide is selected for this reaction and 1 gram CIT/MIT is diluted 2 gram water and added into the flask.

Table 3.1: Copolymer formulation.

Ingredients	Amount (%)
Water	45,1
Styrene	19,0
Butyl Acrylate	28,5
Acrylic Acid	1,5
Anionic surfactant (30% sol.)	1,8
Nonionic surfactant (20% sol.)	3,0
Sodium persulfate	0,2
t-BHP	0,1
Sodium Formaldehyde Sulfoxylate	0,1
Sodium hydroxide (10%)	0,6
Biocide	0,1

3.3 Formulation of Copolymer

In standard styrene-acrylic copolymer emulsion recipe, 6 different types of silane is added into recipe. Some of them are added during emulsion, some of them are added as post-addition. Table 3.2 shows the silanes used in copolymers.

Table 3.2: Types of additives used in emulsion polymerization.

Copolymer #	Type of additives
Copolymer 1	Standard styrene-acrylic copolymer emulsion
Copolymer 2	Styrene-acrylic copolymer emulsion + 1% vinyltrimethoxysilane
Copolymer 3	Styrene-acrylic copolymer emulsion + 1% 3-trimethoxysilylpropyl methacrylate
Copolymer 4	Styrene-acrylic copolymer emulsion + 1% VTET
Copolymer 5	Styrene-acrylic copolymer emulsion + 1% β-(3,4-epoxycyclohexyl) ethyltriethoxysilane
Copolymer 6	Styrene-acrylic copolymer emulsion + 1% Octyltriethoxysilane
Copolymer 7	Styrene-acrylic copolymer + 1% 3-glycidyloxypropyl trimethoxysilane

3.4 Water based interior ceiling paint

Water based interior ceiling paint formulation shown in Table 3.3 is selected and all the ingredients are compatible with seven copolymers. All copolymers are formulated with the same formulation to analyze the effect of different types of silanes used in emulsion polymerization.

In the paint formulation, cellulosic thickener is used for giving a body to the paint. 2-hydroxyethyl cellulose (HEC) is used in this formulation.

Dispersing agent (dispersant) is to disperse all the pigments and fillers by attaching to them and stabilizes them by electrostatic repulsion. Dispersant molecules adsorbed on the interface of a solid particle and liquid. Sodium salt of carboxylate polyelectrolyte based dispersing agent is used in the formulation and it is supplied by Tego.

For wetting agent, a non-ionic acetylenic diol surface active agent is chosen in this part, Tego's wetting agent is used.

Propylene glycol is the most popular open-time agent in the paint formulations, purchased from Sigma-Aldrich.

During dispersion, the air adsorbed on the particle surface is released, and air is also introduced by stirring. The purpose of the defoamer is to produce rapid and effective removal of the air [46].

Rutile type titanium dioxide is used in the paints, Kronos 2310 is preferred in this study is supplied from Kronos.

Calcites and talc are fillers and give the matting effect to the paint. Omyacarb 2µ and Omyacarb 5µ are used and supplied by Omya.

Table 3.3: Water-based interior ceiling paint formulation.

Ingredients	Amount (g)
Water	316,4
Cellulosic thickener	4,8
Ammonia (25% sol.)	2,4
Dispersing agent	4,5
Wetting agent	5,0
Open-time agent	4,0
Defoamer	2,4
Titanium dioxide	120,0
2µ calcite	140,0
5µ calcite	225,0
Talc	52,0
Open-time agent	8,0
Styrene-acrylic copolymer	114,3
Defoamer	1,2

First of all, water is measured on the 2 liter cup, the cup put under the high speed mixer which is called a dispermat and it is opened. Under stirring cellulosic thickener is added and mixed until homogenous. Cellulosic thickener break their bonds in alkaline media. Because of this reason, ammonia is added and dispermat speed is increased to 1300- 1500 rpm. Dispersing agent, wetting agent, open-time agent and defoamer are measured carefully and added on the cup at max. 800 rpm. The mixture is stirred 10 minutes. After that, titanium dioxide is added and dispermat speed is increased to 1300-1500 rpm and mixed 15 minutes to disperse it. After dispersion of titanium dioxide 2 µ and 5 µ calcites are added and mixed 20 minutes for dispersion. After 20 minutes stirring, the speed of dispermat is decreased as 750 rpm and then polymer (binder) is added. After adding polymer, open-time agent and defoamer are added and stirred 10 minutes. 10 minutes later dispermat is closed and paint is ready for testing.

3.5 Performance analysis of the paint

Water-based interior ceiling paint formulations are prepared and applied on different substrates for testing.

Wet scrub resistance

Coated surfaces need to be tested for resistance to abrasion/scrub caused by a brush, sponge, or other means. The wet scrub resistance test can examine washability and related properties that affect the stain resistance of coatings.

Wet scrub resistance test is done according to EN ISO 11998:2006 Paints and varnishes -- Determination of wet-scrub resistance and cleanability of coatings. According to the norm, paints are applied wet 200 µ on black PVC panels. After 28 days of curing, the panels are weighed and placed into the test machine. BYK Gardner Abrasion Scrub Tester machine is used for this test and shown in Figure 3.12.

Figure 3.12 : BYK Gardner Abrasion Scrub Tester machine.

This test uses “3M Scotch Brite 7448” pads and the washing liquid is manually applied before starting the test. The test is finished for evaluation after 200 scrub-cycles. The evaluation of the wash/scrub resistance is done by calculating the loss of mass and loss of micron thickness according to norm.

Hardness test

Evaluation of the hardness of paints and related coatings in accordance EN ISO 1522:2006. The procedure as per König is based on the measurement of the damping of a pendulum oscillating on the paint film. The application of this procedure is subject to the following conditions:

- Substrate must not deform or vibrate under load of pendulum
- Film thickness of at least 30µm (1.2 mils) to minimize substrate influences
- Paint films to be compared must not deviate more than 10% in their film thicknesses
- Surface of coating must be smooth and free of disturbances. Coarse pigment agglomerations, poor leveling properties, dust, etc. cause false measurements

The principle of the pendulum hardness test is based on the fact that the amplitude of oscillations of a pendulum resting on a sample decreases more rapidly the softer the films. The time in seconds (damping time) for the pendulum deflection to slow down to a specific value is taken as the hardness of the coating. The test methods are standardized as per König and Persoz.

Figure 3.13 : Pendulum hardness machine.

Elasticity of the paint

Paint should be flexible because of the surface properties to avoid cracks and shrinkage. Elastic modulus and maximum elongation values of paint are measured according to ASTM D 2370 norm with Zwick/Roell machine as shown Figure 3.14. Paint samples are poured in rubber molds. After 7 days curing, paint samples were cut with bone-shaped specimen mold as shown in Figure 3.14. The specimens were put in the Zwick machine and tested.

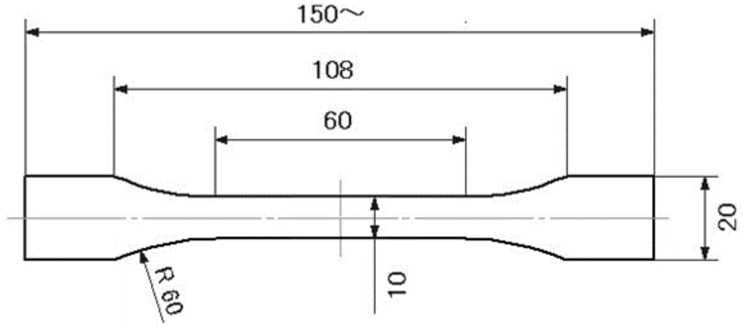


Figure 3.14 : Bone shaped mold.

Figure 3.15 : Zwick machine.

4. RESULTS AND DISCUSSION

Permeability of coatings to water and oxygen are affected by monomer’s hydrophobicity. A higher glass transition temperature (Tg) is preferable for reducing oxygen and water permeability. For this reason most hydrophobic monomers are selected for polymerization. Styrene and butyl acrylate (BA) are used in the laboratory trial.

Acrylic acid is used in the polymerization. Acid are decrease blistering effect and improve adhesion.

Water based paint is used in this study. General paint formulations are composed of four main components. These are binder, pigment, filler, solvent (water). Also additives must be added in the formulation. These additives are dispersing agents, defoamers, rheology modifiers etc.

High PVC paint formulation is designed for testing polymer-ketonic resin performance. PVC means that pigment volume concentration and formulation is shown below equation 4.1:

$$PVC\ \% = \frac{100\ x\ V_{pigment}}{V_{pigment} + V_{non-volatile\ binder}} \tag{4.1}$$

If we increase the binder amount, PVC will decrease.

Water is used as a mobile phase for water based paints, solvents are used in the solvent based paint as a mobile phase. Water based and solvent based differentiation is specified according to mobile phase. Tests are done with water based formulation.

Open-Time agent slows down the evaporation of water from paint. Paint applicators need a time for repainting brush to fix the paint or roller marks which occur during application. Propylene glycol is the most chosen open time agent in paint formulations.

Thickeners are adjust paint flow behavior. Cellulosic thickener is used in this paint formulation. Cellulose itself is not water-soluble. The structure shown in below Figure 4.1 will either swell or break up under alkaline conditions. HEC gives pseudoplastic behavior to the paint.

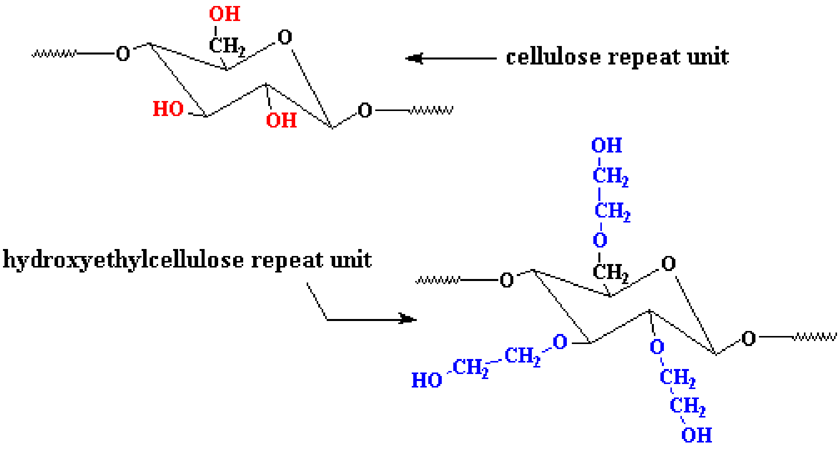


Figure 4.1 : Cellulosic bonds are broken under alkaline conditions.

Ammonia used as a neutralizing agent. Paint system generally alkaline, pH values are between 8 and 9. pH values important for pigment stabilization. Ammonia also used for cellulose thickener's alkaline media.

Dispersion Agent's main function is to disperse all pigments and fillers into the paint. Also, they avoid pigment agglomeration and provide paint stabilization. Sodium salt of a carboxylate polyelectrolyte based dispersing agent is used in the formulation.

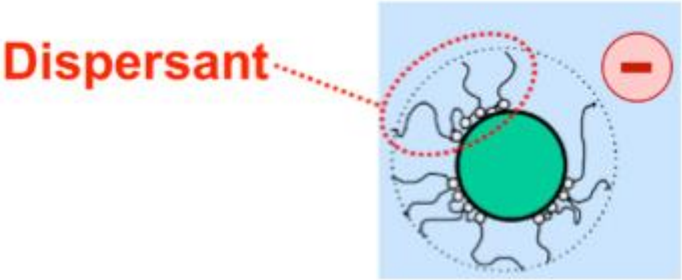


Figure 4.2 : Dispersing agent's working mechanism.

Wetting agent molecules adsorbed and oriented on a liquid-air interface. Wetting agents coordinate the interfacial energy between the substrate and the coating. Effects of wetting agents on coatings is shown in Figure 4.3.

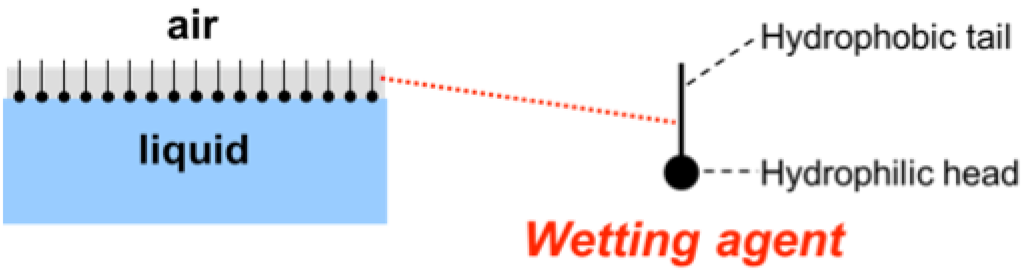


Figure 4.3 : Wetting agent's working mechanism.

Defoamer prevents to formation of excessive surface foam or microfoam during preparation, handling and transport. Defoamers can be divided two parts; mineral oil and silicone oil based. Mineral oil defoamer has less activity than silicon oil defoamers. Silicon oil defoamers can be added during titanium dioxide grinding because it is very active and can be caused some surface defects. Mineral oil defoamers are more compatible, less activity so they can be added during polymer mixing stage. Silicon oil defoamer is used in the grinding stage, mineral oil one is used with the polymer mixing. Defoamer working mechanism is shown in Figure 4.4.

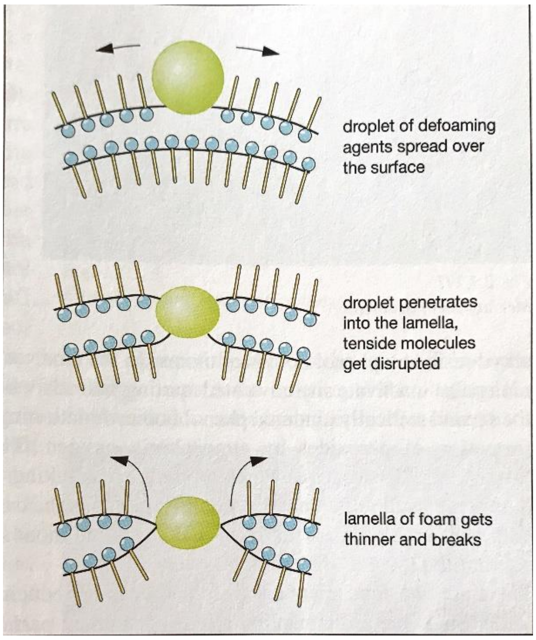


Figure 4.4 : Defoamer's working mechanism.

The pigment and the extenders should be added in order of increasing particle size. This facilities the removal of the adsorbed air (small particles adsorb more), in view of the fact that viscosity increases in the course of addition and so air removal becomes increasingly slow. Tasks and performance requirements are listed as below Table 4.1.

Table 4.1: Tasks and performance requirements of pigments and fillers.

Tasks of pigments	Requirements for pigments and extenders	Special tasks of extenders
• Selective absorption • Light scattering • Optical effects by oriented reflection or interference • UV-protection • Corrosion protection	• Dispersibility • Unsoluble • Lightfast and weather resistant • Heat resistance • Chemical resistant • Physiological compatible	• “filling” • Sandability • Improvement of mechanical-technological coating properties

Titanium Dioxide is a pigment. It occurs in two crystal forms: anatase and rutile. Anatase is less expensive than rutile type because of refractive index. Refractive index of anatase is 2.55 and rutile is 2.7. So rutile gives better hiding power and it has lower UV activity [57].

Calcite is crystalline calcium carbonate which contains no biogenic residues. Talc, a natural magnesium silicate, also has a lamellar structure. Talc is extremely soft and promotes the sandability of fillers and primers by reducing the cohesive strength [58].

4.1 Polymer Characterization

Styrene-acrylic copolymer polymer which is synthesis with emulsion polymerization method, analyzed in the laboratory. Table 4.2 is summarized polymer analysis results on below. Size distribution graph of polymer, *Tg* value of polymer and FTIR results of polymer are mentioned next parts. As shown on the table, high solid amount polymer is synthesized. Polymer pH value is 7-9 and this value is fit for paint preparation *Tg* values is 4°C and MFFT is <5°C.

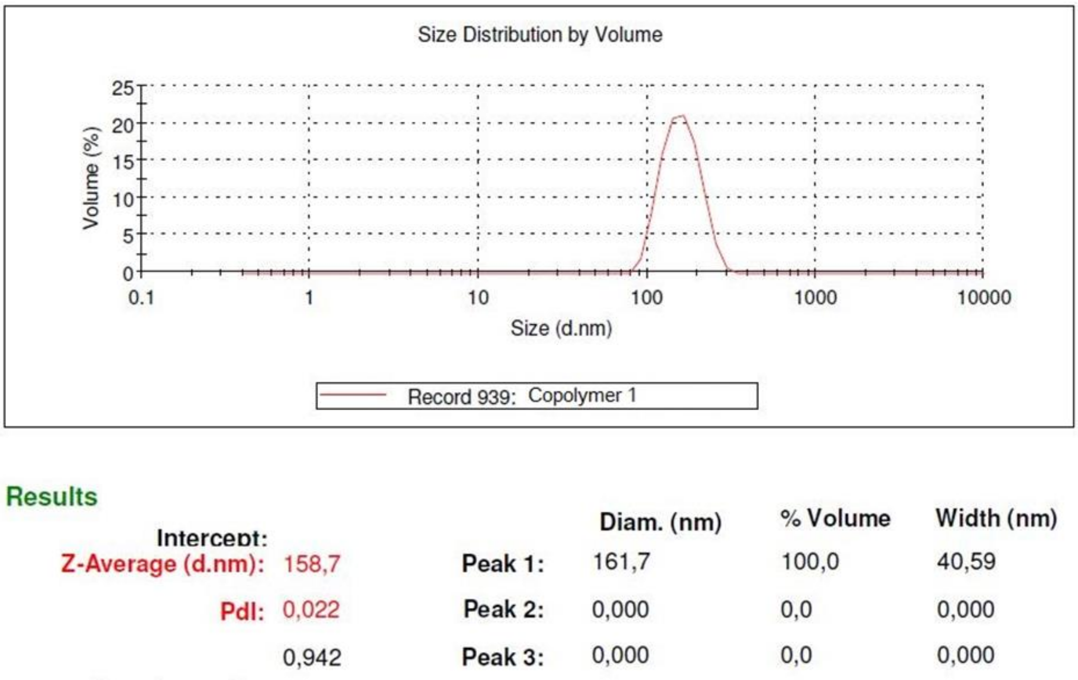
Table 4.2: Polymer analysis of standard formulation.

Properties	Results
Solid	50%
pH	8
FTIR	STY-BA
Tg	4ºC
MFFT	<5ºC
Particle size	161,7 nm

4.1.1 Particle size distribution results of polymers

Particle size distributions of copolymers are analyzed by Malvern Mastersizer (Figure 4.5) .Particle size distribution graphs are shown below figures.

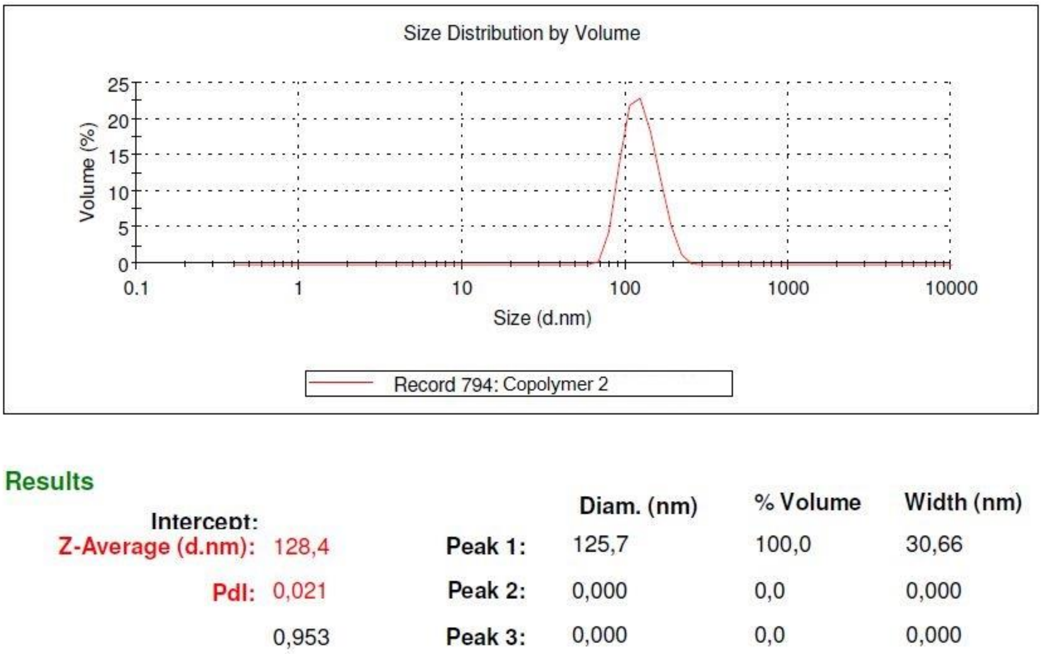
Figure 4.5 : Malvern Mastersizer machine.



Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	158,7	Peak 1:	161,7	100,0	40,59
PdI:	0,022	Peak 2:	0,000	0,0	0,000
	0,942	Peak 3:	0,000	0,0	0,000

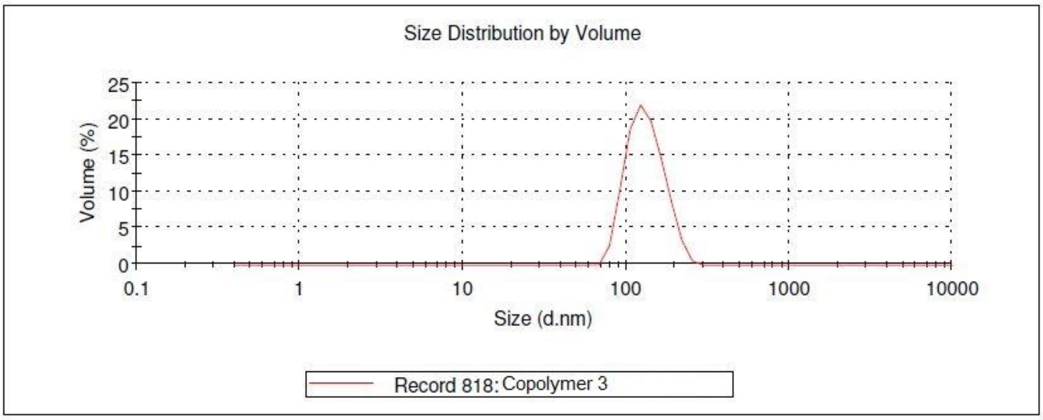
Figure 4.6 : Size distribution by volume graphic of copolymer 1.



Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	128,4	Peak 1:	125,7	100,0	30,66
PdI:	0,021	Peak 2:	0,000	0,0	0,000
	0,953	Peak 3:	0,000	0,0	0,000

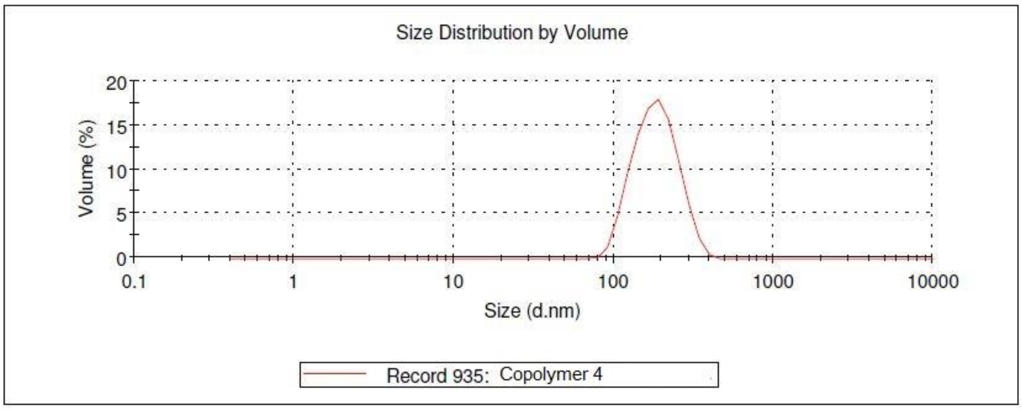
Figure 4.7 : Size distribution by volume graphic of copolymer 2.



Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	135,7	**Peak 1:**	134,5	100,0	34,45
PdI:	0,023	**Peak 2:**	0,000	0,0	0,000
	0,947	**Peak 3:**	0,000	0,0	0,000

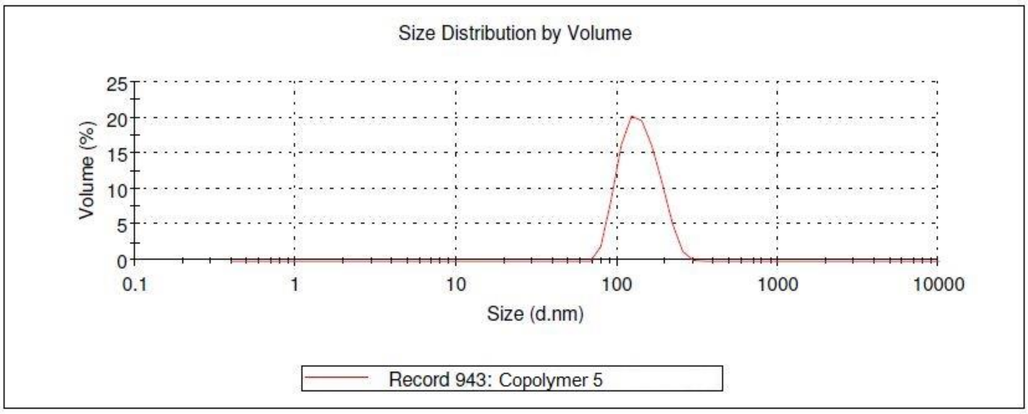
Figure 4.8 : Size distribution by volume graphic of copolymer 3.



Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	177,8	**Peak 1:**	189,6	100,0	58,00
PdI:	0,070	**Peak 2:**	0,000	0,0	0,000
	0,949	**Peak 3:**	0,000	0,0	0,000

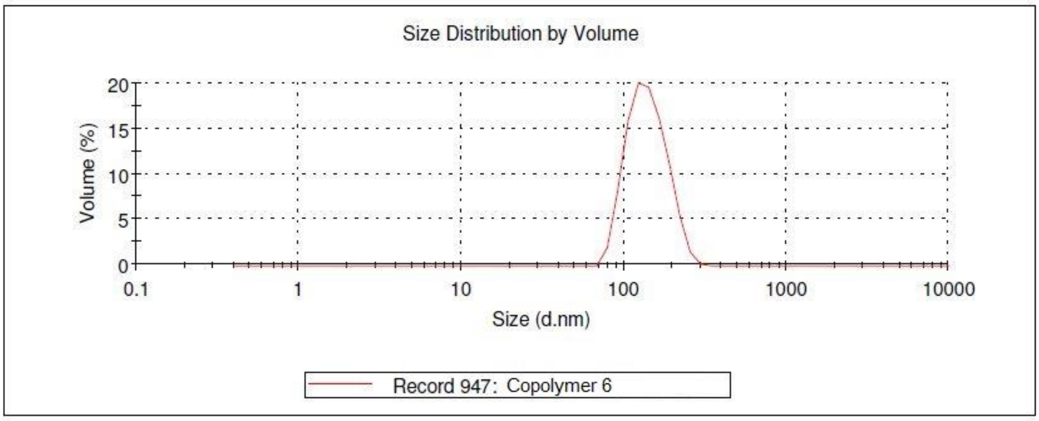
Figure 4.9 : Size distribution by volume graphic of copolymer 4.



Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	141,2	Peak 1:	141,0	100,0	37,91
PdI:	0,013	Peak 2:	0,000	0,0	0,000
	0,943	Peak 3:	0,000	0,0	0,000

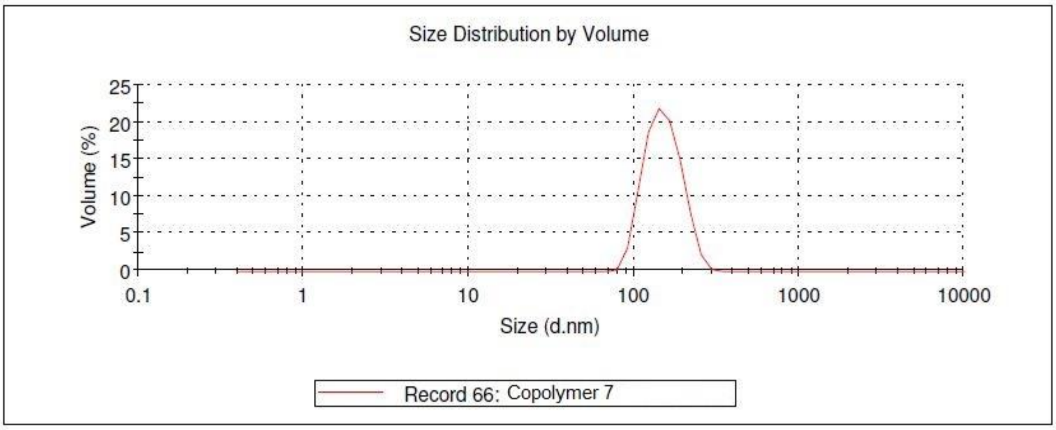
Figure 4.10 : Size distribution by volume graphic of copolymer 5.



Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	142,2	Peak 1:	142,2	100,0	38,50
PdI:	0,014	Peak 2:	0,000	0,0	0,000
	0,956	Peak 3:	0,000	0,0	0,000

Figure 4.11 : Size distribution by volume graphic of copolymer 6.



Results

			Diam. (nm)	% Volume	Width (nm)
Intercept:					
Z-Average (d.nm):	151,8	**Peak 1:**	153,4	100,0	37,99
PdI:	0,016	**Peak 2:**	0,000	0,0	0,000
	0,956	**Peak 3:**	0,000	0,0	0,000

Figure 4.12 : Size distribution by volume graphic of copolymer 7.

Average particle size of the copolymers are shown in Table 4.3.

Table 4.3: Particle size distribution results.

Copolymer #	Particle size (width),nm
Copolymer 1	161,7nm (40,59nm)
Copolymer 2	125,7nm(30,66nm)
Copolymer 3	134,5nm(34,45nm)
Copolymer 4	189,6nm(58,00nm)
Copolymer 5	141,0nm(37,91nm)
Copolymer 6	142,2nm(38,50nm)
Copolymer 7	153,4nm(37,99nm)

According to the graphs, when VTET is post-added into the polymer, it gives higher particle size value. Copolymer 5,6 and 7 have the lower particle size values than because they are added as post-addition to the polymer. Copolymer 2 and 3 have the lowest particle size values. According to these values, when silanes added during emulsion, polymer has lowest particle size values.

4.1.2 Diffential scattering calorimetry (DSC) analysis

DSC results are operated with one cycle. The cycle was heated -70ºC to 70ºC with 10ºC/min heating rate. Table 4.4 shows the Tg values of copolymers.

Table 4.4: DSC results of copolymers.

Copolymer #	Tg, ºC
Copolymer 1	3,8ºC
Copolymer 2	3,5ºC
Copolymer 3	4,0ºC
Copolymer 4	1,1ºC
Copolymer 5	5,5ºC
Copolymer 6	4,1ºC
Copolymer 7	2,9ºC

The T_g values of copolymers were in the range of 1-5,5 ºC. These values were not really different from the T_g value of standard copolymer. Copolymer 4 which has 1% VTET as post-additive gives the lowest Tg value.

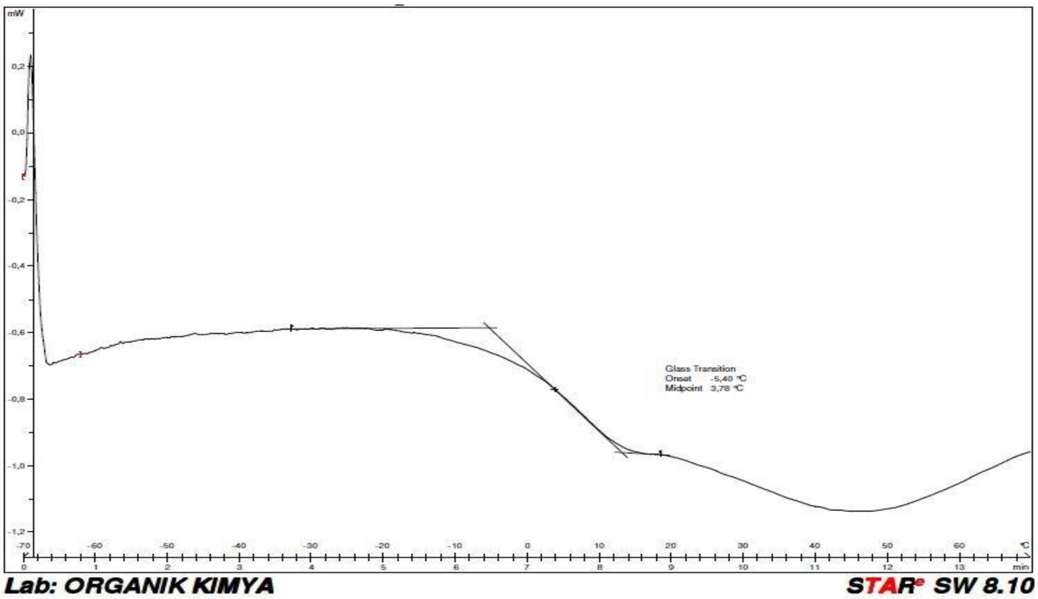


Figure 4.13 : DSC thermogram of copolymer 1

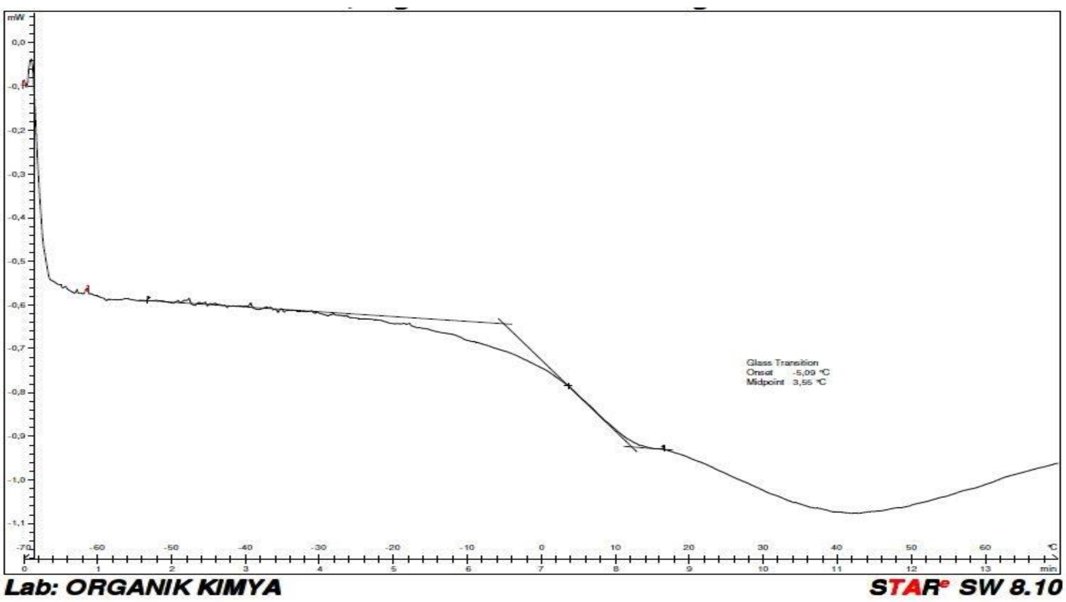


Figure 4.14 : DSC thermogram of copolymer 2.

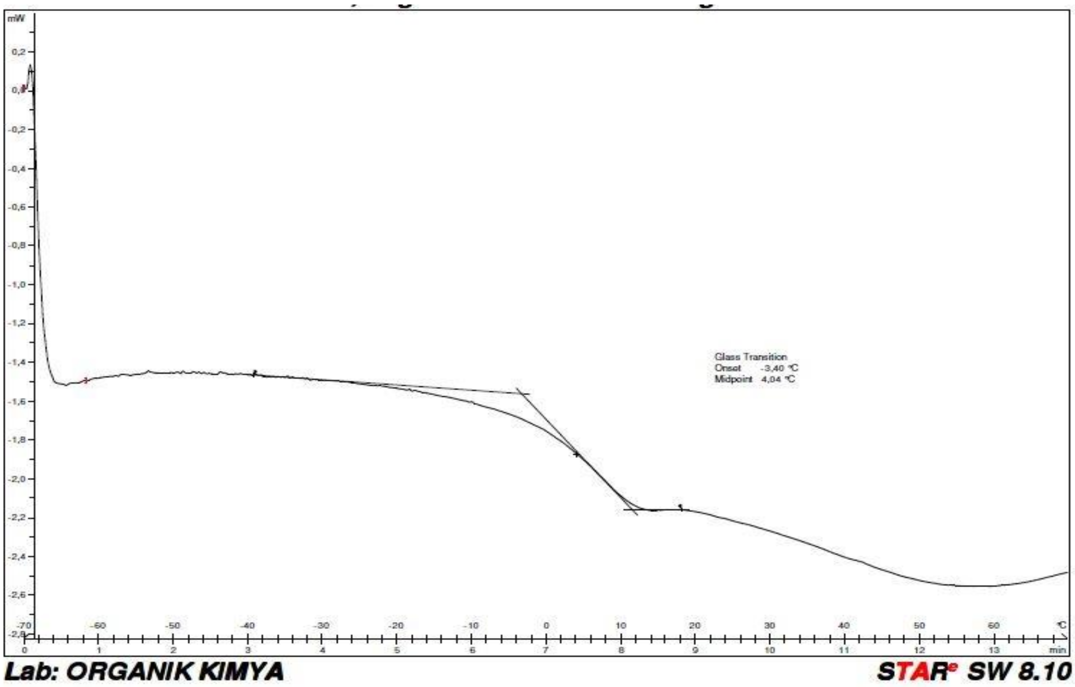


Figure 4.15 : DSC thermogram of copolymer 3.

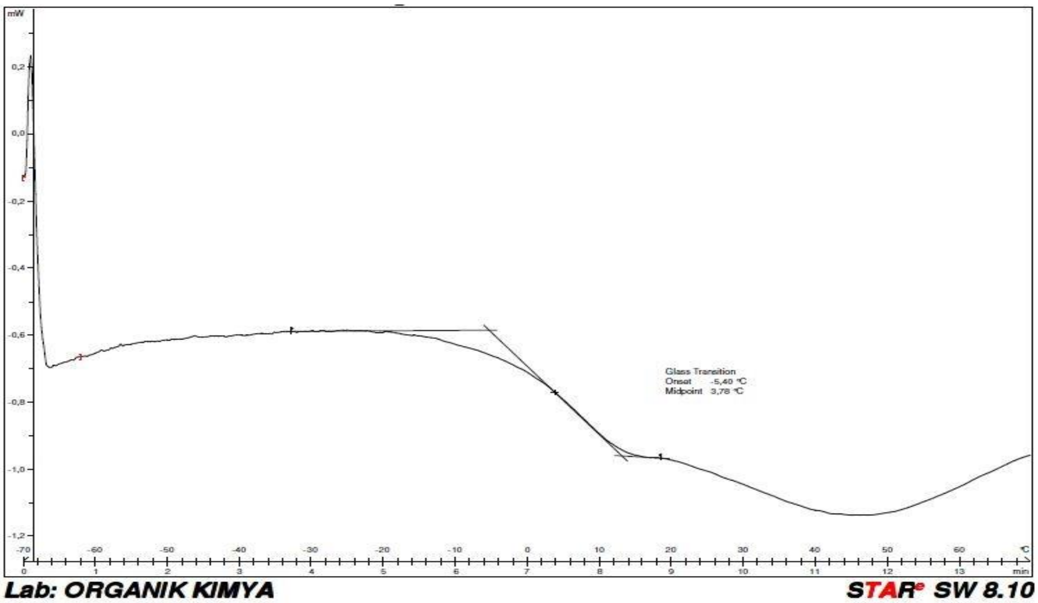


Figure 4.16 : DSC thermogram of copolymer 4.

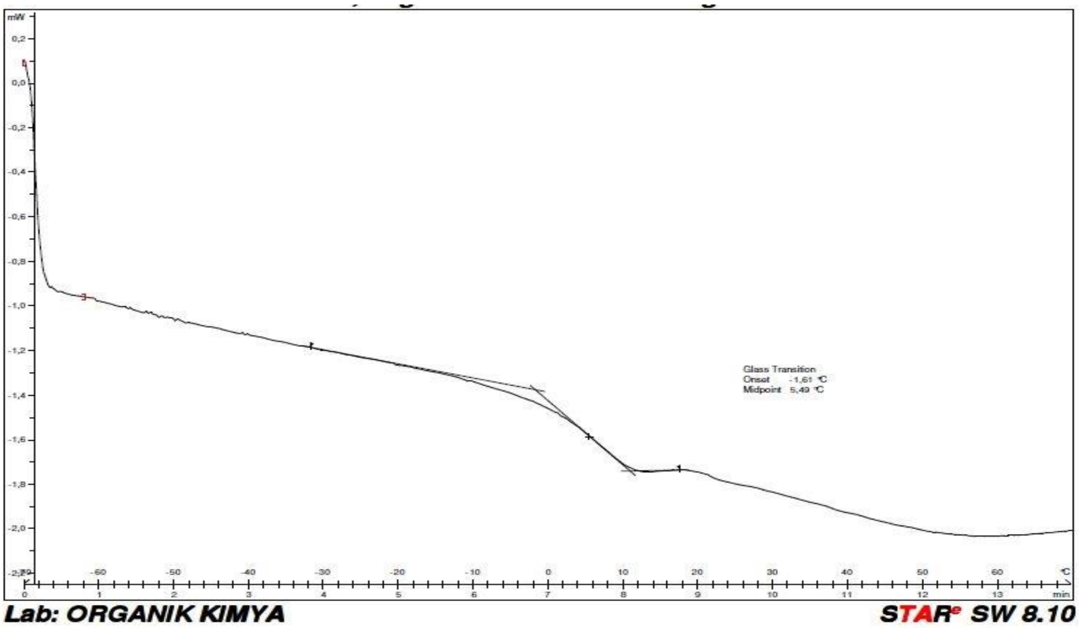


Figure 4.17 : DSC thermogram of copolymer 5.

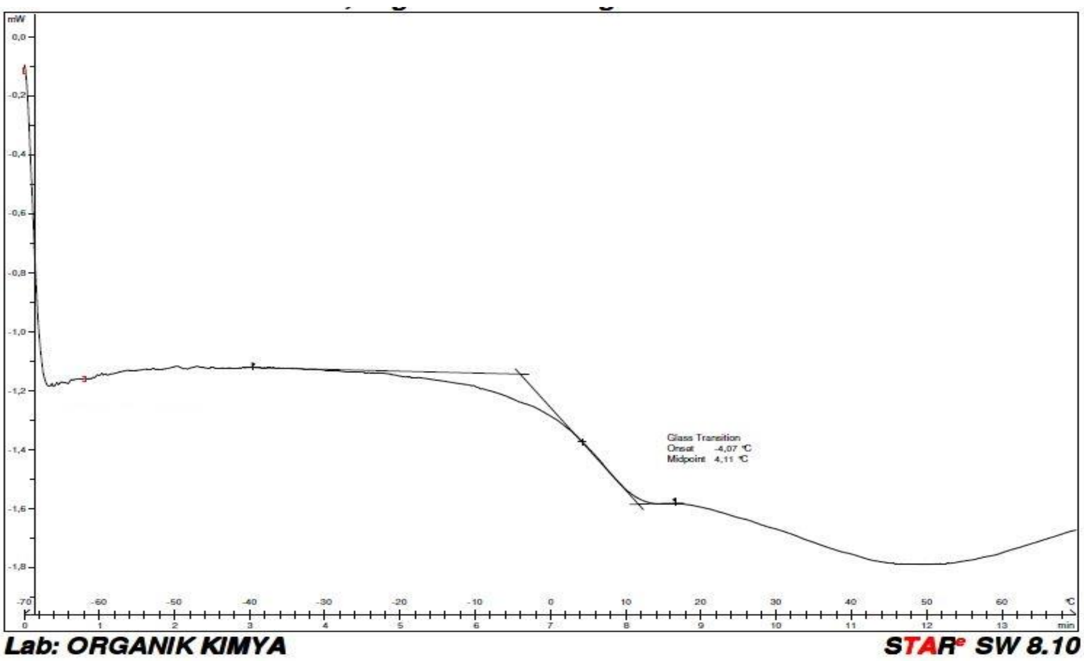


Figure 4.18 : DSC thermogram of copolymer 6.

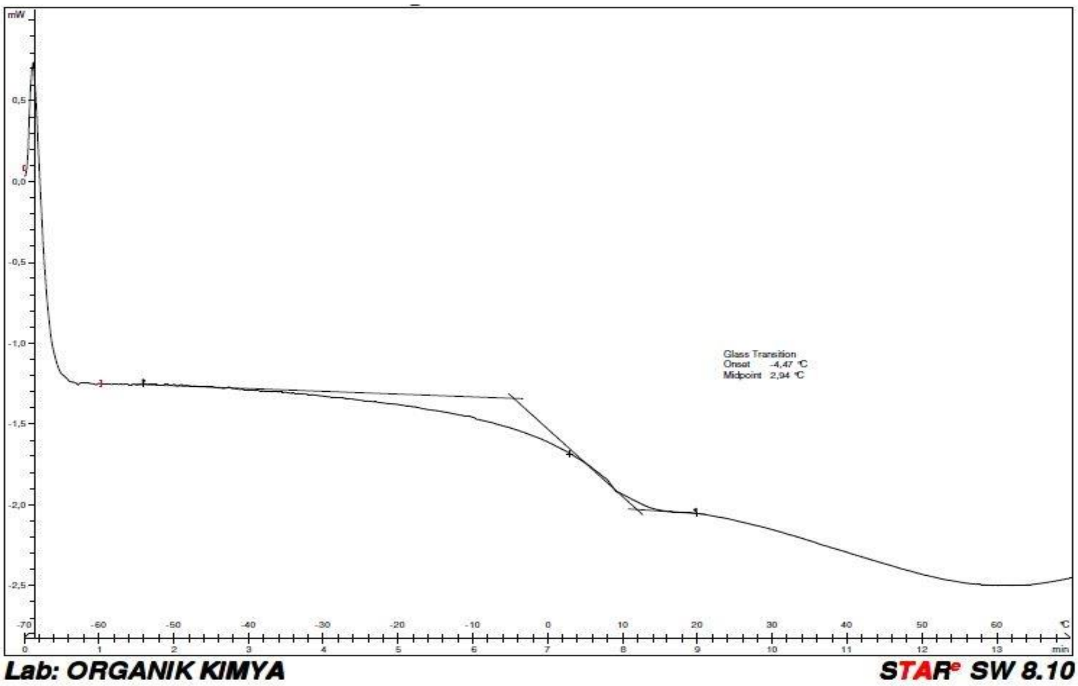


Figure 4.19 : DSC thermogram of copolymer 7.

4.1.3 FTIR analysis results

FTIR results were analyzed with Perkin Elmer FTIR Frontier.FTIR spectra in the region from 4000 to 550 cm^{-1} were recorded with a sample prepared by making filmof latex on the surface of a glass and drying it, and then removing the film from the glass. From FTIR spectra, the pekas at 3028, 1727 and 1602 cm^{-1} were associated with C-H of Ph, C=O and C=C of Ph strecth of poly (St-co-BA).

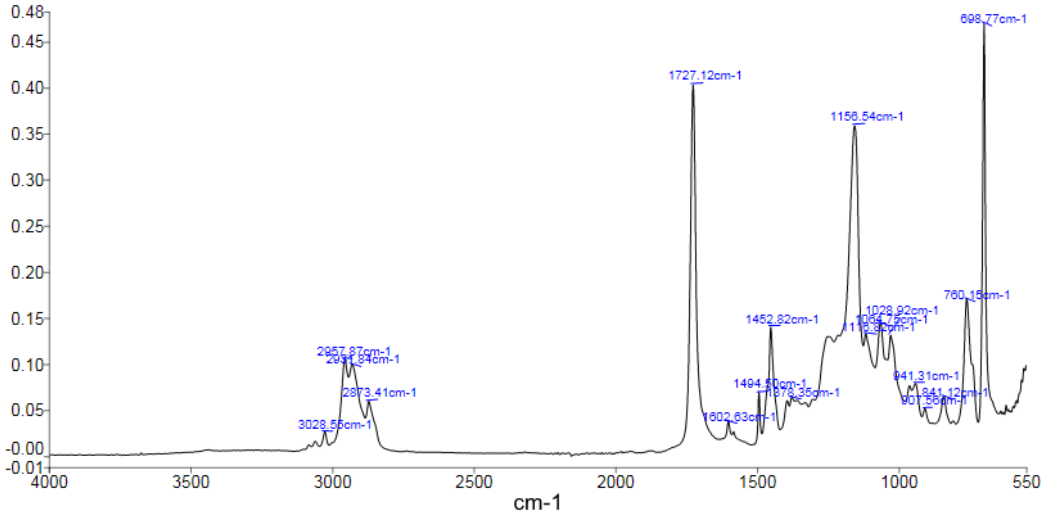


Figure 4.20 : FTIR spectra of poly(STY-co-BA).

Tensile-elongation analysis of polymers

Tensile-elongation test are done with Zwick/Roell machine and results are listed in Table 4.5.

Table 4.5: Tensile-elongation results of polymers.

Copolymer #	E-Modulus (MPa)	Maximum elongation at break (%)
Copolymer 1	0,585	1435,00
Copolymer 2	0,605	955,46
Copolymer 3	0,685	727,05
Copolymer 4	0,650	1568,44
Copolymer 5	0,600	2303,95
Copolymer 6	0,605	1400,26
Copolymer 7	0,678	1650,86

According to the results, when organo-functional silanes is added in emulsion, flexibility properties of copolymers are decreased. When organo-functional silanes are added as post-additive, they gives more flexibility to the copolymer.

4.2 Paint Analysis Results

Wet scrub resistance results are evaluated according to EN ISO 11998:2006 norm. All results summarized on Table 4.6 and copolymer numbers are correlated with paint numbers. For example; paint 1 is prepared with copolymer 1.

Table 4.6: Wet scrub results.

Paint #	Micron loss(μ)	g/m^2 loss
Paint 1	10,28	24,13
Paint 2	9,76	16,50
Paint 3	9,81	14,06
Paint 4	4,80	11,30
Paint 5	7,15	15,11
Paint 6	6,22	13,18
Paint 7	5,23	12,15

According to the results, copolymer 4 has the lowest micron and g/m^2 loss of paint. Copolymer 4 is in the Class 1 according to EN ISO 11998:2006 norm. Copolymer 2 and 3 have similar results with standard copolymer. This values shows that, when organo-functional silanes are added during emulsion, they don’t improve the wet-scrub resistance. Copolymer 4,5,6 and 7 has better wet-scrub resistance. This values shows that, when organo-functional silanes are added during emulsion, they improve the wet-scrub resistance.

Hardness test measured with Pendulum Hardness machine and results are evaluated according to EN ISO 1522:2006. The hardness results are summarized on Table 4.7. All results are in the same range. These values shows that, organo-functional silanes don’t affect the hardness of the standard copolymer.

Table 4.7: Hardness results.

Paint #	Hardness after 1 day curing (persoz)	Hardness after 7 days curing (persoz)
Paint 1	123	137
Paint 2	121	131
Paint 3	124	133
Paint 4	126	135
Paint 5	121	133
Paint 6	125	136
Paint 7	128	138

5. CONCLUSION

The aim of this study is to examine how organo-functional silanes affects the polymerization of styrene-co-acrylic emulsion and the end properties of an water-based ceiling paint system prepared with these copolymers.

Seven different types of organo-functional silanes were added during emulsion or post-added. These copolymers were analyzed in particle size distrubition, Tg values, FTIR and flexibilty of polymers.

These copolymers are formulated in water based high PVC ceiling paints. These paints are tested in wet scrub resistance, hardness and flexibility properties.

According to particle size values, when silanes added during emulsion, polymer has lowest particle size values. And also, when VTET is post-added into the polymer, it gives higher particle size value.

Tg values were not really different from the T_g value of standard copolymer. Copolymer 4 which has 1% VTET as post-additive gives the lowest Tg value.

According to the flexibilty results, when organo-functional silanes is added in emulsion, flexibility properties of copolymers are decreased. When organo-functional silanes are added as post-additive, they gives more flexibility to the copolymer.

According to wet-scrub resistance test results, when organo-functional silanes are added during emulsion, they don’t improve the wet-scrub resistance. This values shows that, when organo-functional silanes are added during emulsion, they improve the wet-scrub resistance.

Accoring to hardness results, organo-functional silanes don’t affect the hardness of the standard copolymer.

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