ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF FUNCTIONAL KETONIC RESINS

M.Sc. THESIS

Derya ÇELİK

Department of Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

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YÜKSEK LİSANS TEZİ

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Derya ÇELİK, a M.Sc. student of ITU Graduate School of Science Engineering and Technology 515101005, successfully defended the thesis entitled "**SYNTHESIS OF FUNCTIONAL KETONIC RESINS**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Derya ÇELİK
Chemist

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ABBREVIATIONS

CFR	**:** Cyclohexanone Formaldehyde Resin
CMCFR	**:** Chalcone Modified Cyclohexanone Formaldehyde Resin
ACFR	**:** Acrylated Cyclohexanone Formaldehyde Resin
ACMCFR	**:** Acrylated Chalcone Modified Cyclohexanone Formaldehyde Resin
FT-IR	**:** Fourier Transform Infrared Spectroscopy
NMR	**:** Nuclear Magnetic Spectroscopy
UV	**:** Ultraviolet
TGA	**:** Thermogravimetric Analyzer
HDDA	**:** Hexanedioldiacrylate
DPGDA	**:** Dipropyleneglycoldiacrylate

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SYNTHESIS OF FUNCTIONAL KETONIC RESINS

SUMMARY

Polymeric materials can be classified as thermoplastic and thermoset resins according to their thermal behaviours. As a result of being reshaped with heating, thermoplastics are mostly used materials in plastic industry.

Thermosets can't be reshaped with heating because these materials can be cured with heating. Thermosets are used especially in coating industry because of being hard and rigid after curing.

Cyclohexanone formaldehyde resins are used to increase gloss and light transmittance of systems that incorporated into. Also, it can be soluble most of the organic solvents. These properties make these resins to compatible to other resin systems.

Because of rapid cure, low shrinkage, being applicable in adhesive systems, high thermal stability and show resistance against chemicals, epoxy resin is widely used polymeric material in industy.

Incorporation of epoxy resins into thermoplastic resin systems are widely investigated subject to improve flexibility and applicability of epoxy resin systems. As a result of this, thermal and mechanical behaviours of epoxy thermoplastic blends have wide attention during last years.

Radiation curable coating applications is an important technology and this technique combines a number of advantages such as low energy consumption, less environmental pollution and very rapid curing even at ambient temperatures. The UV curing technique represents a major advance in the development of the coating, adhesive and ink industries. UV curable system is contains unsaturated oligomers, reactive diluents and photoinitiators.

Photocrosslinking reactions are another important research subject. Photoactive substances have chromophore group, increasing the photosensitivity of the products. Because of high solubility, film forming properties, high photosensitivity, resistance against solvents and thermal resistance, chalcones can be used in photocrosslinking reactions.

Photocrosslinkable polymers found many application areas. UV curing method is applied to crosslink rapidly these photosensitive polymers in order to obtain thick cross sections. Among the various photocrosslinkable groups, α,β-unsaturated carbonyl unit gained attention because of its photoreactivity at UV absorption wavelength. α, β-unsaturated carbonyl compounds, chalcones have conjugated double bonds and a completely delocalized π-electron system on both benzene rings. Polymers with chalcone units undergo crosslinking through [2π + 2π] cycloaddition of the carbon–carbon double bond upon UV irradiation.

In this thesis, cyclohexanone formaldehyde resin was modified with having photosensitive chalcone and radically polymerizable vinyl groups in the structure. Characterization of oligomers were performed by FT-IR and ^{1}H-NMR spectroscopic techniques. Formulations containing functional cyclohexanone formaldehyde resin, epoxy acrylate, reactive diluents and photoinitiator were applied and polymerized under UV irradiation. Mechanical and thermal properties of UV cured films and coated samples were evaluated.

FONKSİYONEL KETONİK REÇİNELERİN SENTEZİ

ÖZET

Polimerik malzemeler ısıl davranışlarına göre termoplastikler ve termosetler olarak sınıflandırılırlar. Termoplastikler düz zincir yapısındadır ve sert olmayan maddelerdir. Bağ yapıları nedeniyle ısıtıldıklarında şekillenelebilirler. Camsı geçiş sıcaklığının üzerine çıkıldığında zincirler belirli bir hareketlilik kazanır. Isıtılan malzeme soğutulduğunda yeniden kullanılabilir. Termal dayanımları düşüktür. Isıl davranışlarındaki bu özelliklerinden dolayı termoplastikler, plastik endüstrisinde çok fazla kullanılan malzemelerdendir. Ayrıca, ısıtılıp yeniden kullanılma özelliği, bu malzemeleri geri dönüştürülebilen malzemeler haline getirmektedir. Termoplastikler amorf ya da yarı kristal yapıda olabilirler. Amorf yapıda moleküller rastgele sıralanırken, yarı kristal yapıda kısmi olarak düzgün sıralanma vardır.

Termosetler ise çapraz bağ yapısında sert maddelerdir. Kuvvetli bağ yapıları nedeniyle ısıtıldıklarında eritilemezler ve ısı etkisi ile şekillenemezler. Yüksek ısılara çıkıldığında yapılarında bozulmalar meydana gelir. Bu nedenle termosetler sert ve dayanıklı malzemelerdir. Isıya, korozyona ve kimyasallara dayanımları çok yüksektir. Kaplama endüstrisinde çok fazla kullanılırlar. Ayrıca, ısıtıldıklarında yeniden şekillenememeleri bu malzemeleri geri dönüştürülemeyen malzemeler yapmaktadır. Termosetler kürlenme adı verilen işleme tabi tutularak sert, çapraz bağlı yapı elde edilir. Kürlenmede malzeme öncelikle sıvı haldedir, kürlenmenin ilerleyen aşamalarında sıvı malzeme katı ve sert yapıya dönüşmektedir.

Siklohekzanon formaldehit reçinesi düz zincir yapısında bulunan termoplastik tipi reçinedir. Reçine, siklohekzanon ile formaldehitin bazik ortamda meydana gelen kondenzasyon reaksiyonu sonucu elde edilir. Boya ve kaplama endüstrilerinde katkı maddesi olarak kullanımı çok fazladır. Yapısına katıldığı sistemlerin parlaklığını, ışık geçirgenliğini arttırması, organik çözücülerin çoğunda çözünmesi gibi özelliklerinden dolayı, farklı reçine sistemleriyle karıştırılarak kullanılmaktadır. Ayrıca, siklohekzanon formaldehit reçinesinin modifikasyonu, üzerinde çalışılan konulardandır. Modifikasyon, reçinenin başka polimerik sistemler ile karıştırılarak kullanılmasına olanak sağlar.

Epoksi reçineler, çapraz bağ yapısında bulunan termoset tipi sert reçinelerdir. Epoksi reçineler bisfenol A ile epiklorohidrinin bazik ortamda meydana gelen reaksiyonu sonucu elde edilir. Epoksi reçinelerin akrilik asit ile reaksiyonu vinil fonksiyonelitesine sahip epoksi akrilatların elde edilmesini sağlar. Epoksi akrilatlar, akrilat ve hidroksil fonksiyonelitesine sahiptirler. Bu fonksiyonel gruplar, yapının çapraz bağlanmaya gitmesini sağlar ve kürlenme meydana gelir.

Epoksi reçineler hızlı kürlenmesi, düşük büzülme yüzdesi, yapıştırıcı olarak kullanılabilmesi, ısıl dayanımının yüksek olması, kimyasallara ve korozyona karşı direnç göstermesi gibi sebepler nedeniyle, UV kürlenme teknolojisinde en fazla kullanılan polimerlerdendir. Epoksi reçinelerin kürlenmesinde kürlenme ajanları adı verilen maddelerden yararlanılır.

Epoksi reçinelerin esnekliklerinin arttırılması için düz zincir yapısındaki termoplastik reçinelerle modifikasyonları, üzerinde çok fazla çalışılan konulardandır. Bu nedenle epoksi reçinelerin termoplastik reçinelerle oluşturduğu karışımların ısıl ve mekanik özellikleri literatürde incelenen konulardandır.

Fotopolimerizasyon reaksiyonları UV ışını etkisiyle başlatılan polimerizasyon reaksiyonlarıdır. En büyük avantajı reaksiyonun oda sıcaklığında meydana gelmesi ve ısıtmaya gerek duyulmamasıdır. Bu yöntemle yüksek molekül ağırlıklı polimerler elde edilebilir. UV kürlenme teknolojisi fotopolimerizasyonun en fazla kullanıldığı alanlardandır.

Günümüzde UV kürlenme teknolojisi çevre duyarlılığı, enerji tüketiminin az olması, işlemlerin oda sıcaklığında meydana gelmesi, çok hızlı olması ve çözücüye gerek duyulmaması gibi özelliklerinden dolayı endüstride, kaplamalarda, baskı malzemesi yapımında, yapıştırıcı uygulamalarında çok fazla kullanım alanına sahiptir.

UV kürlenmesi ile elde edilen ürünlerin yüksek direnç gibi fiziksel özellikler göstermesi bu ürünlerin fotoduyarlı polimerler, kaplama reçineleri ve yapıştırıcı üretiminde oldukça fazla kullanılmasını sağlamaktadır. Fotopolimerizasyonla elde edilen reçineler yüksek çapraz bağlı polimer ağ yapısı nedeniyle yüksek adhezyon özelliği, kimyasal direnç ve aşınma direnci göstermektedir. Fotopolimerizasyon reaksiyonları oksijen tarafından engellenmemekte, bu da fotopolimerizasyonu diğer serbest radikal polimerizasyonuna göre avantajlı duruma getirmekte ve kürlenme sistemini inert gazla korumaya gerek göstermemektedir. Ayrıca, çözücüye ihtiyaç duyulmaması bu yöntemin uygulamasında kolaylık sağlar.

UV kürlenmesinde kullanılan formülasyonlar fonksiyonel reçineler, reaktif incelticiler ve fotobaşlatıcıları içermektedir. Uygun formülasyonun belirlenmesi için hangi maddeden ne kadar konulması gerektiği ve uygun fotobaşlatıcının belirlenmesi için denemeler yapılır.

Fonksiyonel reçineler, sistemde kürlenmeye gidecek asıl maddeyi oluştururlar. Fonksiyonel reçineler genellikle yapısında akrilat ve metakrilat sistemleri içeren oligomerik yapılardır. Fotopolimerizasyonda kullanılan akrilat ve metakrilat bazlı reçineler epoksi akrilatlar, üretan akrilatlar, poliester akrilatlar, silikon akrilatlar ve polieter akrilatlar olarak sınıflandırılabilir.

Reaktif incelticinin görevi ise ortamın viskozitesini düşürmek ve formülasyonun elemanı olarak sisteme katılmaktır. Reaktif incelticiler de aynı şekilde vinil fonksiyonelitesine sahip, yapısında akrilat ve metakrilat sistemleri içeren maddelerdir. Ayrıca, çözücü yerine de kullanılarak çözücü ihtiyacını ortadan kaldırmaktadır.

Fotobaşlatıcı ise fotopolimerizasyon reaksiyonunu başlatarak reaksiyonun ilerlemesini sağlamaktadır. Fotobaşlatıcılar Tip I ve Tip II olarak sınıflandırılan maddelerdir. Fotobaşlatıcılar UV ışınını absorblayarak, fotopolimerizasyonun başlamasını sağlarlar.

Üzerinde çalışılan bir diğer konu fotoçaprazbağlanma reaksiyonlarıdır. Fotoaktif kromofor grup etrafında bulunan çifte bağlar, maddelerin fotoduyarlılıklarını arttırmaktadır. Kalgon grupları olarak adlandırılan çifte bağ içeren maddeler, yüksek çözünürlük, film oluşturma, yüksek fotoduyarlılık, kürlendikten sonra çözücülere karşı dayanıklılık ve termal kararlılık özelliklerine sahiptirler.

Kalgonlar, yapılarında benzen halkaları ve –C=C– çifte bağları bulunduran organik maddelerdir. Aldehit ve keton arasında bazik ortamda meydana gelen aldol kondenzasyonu reaksiyonu sonucu elde edilirler. Aldol kondenzasyonu –C=C– çifte bağı oluşumunu sağlar.

Yapıda bulunan –C=C– çifte bağları UV ışığı etkisiyle açılarak halkalı yapının elde edilmesini sağlar. Bu halkalı yapı, sistemin sertliğini ve dayanıklılığını arttırır.

Kalgonların UV ışınına karşı olan duyarlılıkları, düşük büzülme yüzdeleri, solvent dayanımları ve termal kararlılıklarının yüksek olması, özellikle sıvı kristaller ve fotoduyarlı polimerik sistemlerde kullanılmasını sağlamaktadır.

Araştırma planı kapsamında öncelikle 4,4'-dihidroksikalgon maddesi sentezlenmiştir. Bu maddenin sentezlenmesi için 4-hidroksiasetofenon ve 4-hidrokibenzaldehit pyran maddesiyle koruma reaksiyonuna sokulmuştur. Korunan malzemeler bazik ortamda reaksiyona sokularak korunmuş kalgon elde edilmiştir. Pyran grupları kaldırılarak 4,4'-dihidroksikalgon elde edilmiştir.

Sentezlenen 4,4'-dihidroksikalgon ile kalgon modifiye siklohekzanon formaldehit sentezlenmiştir. Ayrıca, karşılaştırma yapılması amacıyla düz siklohekzanon formaldehit reçinesi de sentezlenmiştir.

Elde edilen kalgon modifiye ve kalgon modifiye olmayan reçinelerin, polimerizasyon sistemine katılabilmesi için vinil fonksiyonelitesine sahip olması gerekmektedir. Kalgon modifiye ve kalgon modifiye olmayan malzemelere vinil fonksiyonelitesi kazandırılması için akrilleme reaksiyonu yapılmıştır. Akrilleme reaksiyonu acryloyl chloride ile yapılmıştır.

Akrilleme reaksiyonunda reçine yapısında bulunan hidroksil grupları ile acryloyl chloride reaksiyona girerek, hidroksil grubu yerini vinil gruplarına bırakmaktadır. Bu da reçineye uygun fonksiyonelitenin kazandırılıp, polimerizasyon sistemine uygun olmasını sağlamıştır.

Ürünlerin karakterizasyon calışmaları FT-IR, ^{1}H-NMR spektroskopik yöntemleri ile yapılmıştır. FT-IR ve ^{1}H-NMR yöntemleri, sentezlenen maddelerin fonksiyonel gruplarının tanımlanmasına yardımcı olarak, sentezlerin doğru olup olmadığını ya da reaksiyonların tamamlanıp tamamlanmadığının anlaşılmasını sağlamıştır.

Akrillenen ürünler, ticari epoksi akrilat, reaktif incelticiler ve fotobaşlatıcı bulunan formülasyon sistemlerine katılarak UV ışını etkisiyle kürlenmiştir. Kürlenme işlemi formülasyonların UV ışını etkisiyle serbest film haline getirilmesi ve uygun malzemenin kaplanmasıyla yapılmıştır.

Kürlenen ve kaplanan ürünlerin termal, mekanik ve yüzey özellikleri incelenmiştir. Serbest film üzerinde çekme kopma, termal dayanım, jel yüzdesi, solvent dayanımı testleri yapılmıştır. Kaplanan malzeme ile temas açısı, parlaklık, pendulum sertliği, kalem sertliği deneyleri yapılmış ve sonuçları yorumlanmıştır.

Akrillenmiş siklohekzanon formaldehit ve akrillenmiş kalgon modifiye siklohekzanon formaldehit reçineleri sentezlenmiş ve uygun yöntemlerle karakterizasyon çalışmaları yapılmıştır. Sentezlenen reçinelerin epoksi filmlerinin ve kaplamalarının termal, mekanik ve yüzey özelliklerine olan etkileri incelenmiştir.

1. INTRODUCTION

Photopolymerization science and technology has attracted a significant amount of attention due to its various industrial applications, such as inks, coatings, photoresists and pressure sensitive adhesives. Among the various methods of photocuring, UV curing systems are widely used due to their advantages, such as their rapid production rate in a small place of work, lower process costs, high chemical stability, high dimensional stability and solvent free curing at ambient temperatures. In many industries, epoxy acrylate oligomers, which introduce vinyl ester groups with carbon–carbon double bonds at the end of the epoxy resin, are generally used, because they have excellent adhesive and non yellowing properties, flexibility, hardness and chemical resistance. [1]

The VOC (volatile organic compounds) of this type of coating is very low (almost zero) and it consumes relatively low energy for curing. Therefore, this coating system is considered as one of the cleanest and most environmental friendly coating systems. Radiation curing of coatings, inks, adhesives and sealants is known as a rapid process. In this process monomers and oligomers can instantaneously polymerized and crosslinked. This process usually results in an effectively complete conversion of the liquid formulations into a solid, i.e., radiation cured coatings are essentially 100% solid in nature. Having both good properties of epoxy and acrylic resins, epoxy acrylates are among the most frequently used resins in UV curing systems.

Because of the high viscosity of radiation curable oligomers or prepolymers, reactive diluents are incorporated in the formulations to make thin film applications possible. They are also required for the production of prepolymers, to facilitate processing and bulk handling of raw materials. Reactive diluents or modifiers are typically acrylates or methacrylates, usually more than one, which are capable of reducing the viscosity of the prepolymers and being incorporated into the structure of cured films. [2]

Ketone aldehyde resins especially cyclohexanone formaldehyde resins are important multi functional polymer additives and they have excellent compatibility with the resins used in coatings, which is able to not only make the dye to be well wetted and dispersed, but also can enhance effectively the adherence, gloss and hardness of coatings. However, CF resins also have some disadvantages such as the poor thermal stability and yellow stain resistance, and the deep color, which limits its application in coatings to a certain degree. [3]

It is known that methyl ketones and cyclic ketones add to formaldehyde under preferably basic conditions to form the corresponding methylol compounds. Depending on the pH and temperature, such methylol compounds dehydrate to form corresponding vinyl ketones. Under basic conditions, vinyl ketones in turn add to active hydrogens of the ketones, resulting in ketone formaldehyde resins as the end product. [4]

In this work, it seemed appropriate to combine the advantages of resole type cyclohexanone formaldehyde resins and photoactive chalcone moiety in the same structure. UV curable chalcone modified cyclohexanone formaldehyde resins were synthesized and characterized to utilize for further applications in UV curable systems.

2. THEORETICAL PART

2.1 Thermoplastic Resins

Thermoplastic materials are, in general, ductile and tougher than thermoset materials and are used for a wide variety of nonstructural applications without fillers and reinforcements. Thermoplastics can be melted by heating and solidified by cooling, which render them capable of repeated reshaping and reforming. Thermoplastic molecules do not cross link and therefore they are flexible and reformable.

In amorphous thermoplastics, molecules are randomly arranged; whereas in the crystalline region of semicrystalline plastics, molecules are arranged in an orderly fashion. It is not possible to have 100% crystallinity in plastics because of the complex nature of the molecules.

Their lower stiffness and strength values require the use of fillers and reinforcements for structural applications. Thermoplastics generally exhibit poor creep resistance, especially at elevated temperatures, as compared to thermosets. They are more susceptible to solvents than thermosets. Thermoplastic resins can be welded together, making repair and joining of parts more simple than for thermosets. [5]

Thermoplastic materials can be repeatedly reformed by the application of heat, similar to metallic materials. They are long chain linear molecules that are easily formed by the application of heat and pressure at temperatures above a critical temperature referred to as the glass temperature. Because of this ability to be reformed by heat, these materials can be recycled. However, thermal aging that results from repeated exposure to the high temperatures required for melting causes eventual degradation of the polymer and limits the number of reheat cycles. Polymers are formed as the result of a polymerization reaction of a monomer that is a single molecule or substance consisting of single molecules.

Copolymers are long chain molecules formed by the addition reaction of two or more monomers. In essence, they are chains where one mer has been substituted with

another mer. When the chain of a polymer is made up of a single repeating section, it is referred to as a homopolymer in contrast to a copolymer. Thermoplastic polymers can be either homopolymers or copolymers.

Alloy polymers are blends of different polymers. In general, thermoplastic materials tend to be tougher and less brittle than thermoset polymers, so they can be used without the need for incorporating fillers. However, all thermoplasts do not fall into this category. Some tend to craze or crack easily, so each case must be considered on its individual merits. By virtue of their basic structure, thermoplastics have been less dimensionally and thermally stable than thermosetting polymers. Therefore, thermosets have offered a performance advantage; although, the lower processing costs for thermoplastics have given the latter a cost advantage. Because of three major developments, thermosets and thermoplastics are now considered on the basis of their performance. First, stability of thermoplastics has been greatly improved by the use of fiber reinforcement. Second, has been the development of the so called engineering or high stability, higher performance polymers that can be reinforced with fiber filler to increase their stability even further. Third, to offset the gains in thermoplastics, lower cost processing of thermoset polymers, has been developed specifically the screw injection molding technology. [6]

The semicrystalline and amorphous types of plastic referred to above are more generally known as thermoplastics. This is because they are capable of going through an almost indefinite cycle of being softened by heat and becoming solid again when the heat is removed. The most distinguishing feature of this type of plastic is that the polymer chains remain linear and separate after molding.

Some of the commercially used thermoplastics are indicated below.

1. ABS: Easily molded, tough, hard, plastic with a relatively high modulus. Good dimensional stability with low water absorption. Good wear resistance and some grades can be electroplated.
2. Acetal:Available as a homopolymer or copolymer. Strong engineering plastic with a good modulus, low water absorption, and excellent dimensional stability. High resistance to wear and chemicals and excellent property retention in hot water. Low tendency to stress crack.

3. Acrylic: Hard, glossy plastic with high optical clarity and excellent resistance to outdoor weathering.

4. Cellulosics: Family of tough, hard plastics comprising cellulose acetate, butyrate, propionate, and ethyl cellulose. Dimensional stability is generally fair. Moisture and chemical resistance is variable depending on the grades.

5. Fluoroplastics: Large family of low strength, high cost plastics that have a number of distinguishing features.

6. Ionomers: Tough, tear resistant plastics with excellent outdoor weathering resistance. Can be transparent and have good chemical resistance.

7. Polyamide: Engineering plastic with high toughness and wear resistance. Coefficient of friction is low and chemical resistance is excellent. Water absorption is high, so dimensional stability tends to be low.

8. Polyamide-imide: A high cost amorphous plastic that offers high strength, high temperature performance.

9. Polyarylates: Family of tough, heat resistant plastics with excellent outdoor weathering resistance. Very low inherent flammability and high resistance to creep and warpage.

10. Polyaryletherketones: Strong, heat resistant crystalline plastics capable of continuous service at 250°C.

11. Polycarbonate: An amorphous plastic with outstanding toughness. Excellent outdoor weathering resistance and good creep resistance. Susceptible to chemical attack and stress cracking.

12. Polyester: Polybutylene terephthalate (PBT) and polyethylene terephthalate (PET). Characterized by toughness with excellent dimensional stability. Good chemical resistance (except to strong acids and bases) and low water absorption. Generally notch sensitive and not suitable for outdoor use. PET is capable of high optical clarity if prevented from crystallizing.

13. Polyetherimide: A strong, tough amorphous plastic suitable for use at high temperatures. Easily processed, with good dimensional stability and broad chemical resistance.

14. Polyethylene: Basically a commodity plastic but capable of performing in load bearing applications if properly designed. Easily processed, tough, inexpensive plastic with excellent chemical resistance. Medium and high density grades are stronger and harder.

15. Polyimide: A tough plastic with good wear resistance and low coefficient of thermal expansion. Outstanding high temperature properties but expensive and not easy to process.

16. Polyphenylene ether: The homopolymer is frequently referred to as polyphenylene oxide (PPO). Rigid, amorphous plastics offering a broad working temperature range. Very low water absorption and so excellent dimensional stability. Very amenable to blending with other plastics to produce alloys.

17. Polyphenylene sulfide: Good strength characteristics from low to high temperatures. Inert to most chemicals and inherently flame retardant.

18. Polypropylene: Part of the same generic group as polyethylene. Low density, tough plastic (above room temperature) and very easy to mold. Outstanding fatigue resistance and stress crack resistance.

19. Polysulfone: A clear, rigid, tough plastic capable of continuous use at 160°C. Excellent chemical resistance but notch sensitive and expensive. Polyether sulfone is one of the most commercially successful members of the polysulfone family.

20. Polyurethane: Versatile material available in a wide range of forms. Very tough, with high abrasion and chemical resistance. Popular foaming material (rigid or flexible foams). Susceptible to ultraviolet attack. Also available as a thermoset.

21. Polyvinyl chloride: Wide range of formulations from hard rigid to soft flexible material. Hard and tough with excellent electrical insulation properties. Good outdoor weatherability and resistance to moisture and chemicals. [7]

2.2 Thermoset Resins

Thermoset materials once cured cannot be remelted or reformed. During curing, they form three dimensional molecular chains, called cross linking. Due to cross linkings, the molecules are not flexible and cannot be remelted and reshaped. Higher number of cross linkings, more rigid and thermally stable material will be. Thermosets are brittle in nature and are generally used with some form of filler and reinforcement. Thermosets offer greater thermal and dimensional stability, better rigidity, and higher electrical, chemical, and solvent resistance. [8]

Thermoset polymers assume a permanent shape or set once cured. Once set, they cannot be reshaped. They are formed by a large amount of cross linking of linear prepolymers (a small amount of cross linking will produce elastomers) or by direct

formation of networks by the reaction of two monomers. The latter is the more prominent of the two methods. It is a stepwise or condensation method that has been defined as “the reaction of two monomers to produce a third plus a by-product, usually water or alcohol.” Because in some cases a by-product is not produced, this definition is no longer exactly correct. The reaction is now referred to as a stepwise polymerization. When the reaction results in a by-product, it is condensation reaction.

Compared to the thermoplastics, they are more brittle, stronger, harder, and generally more temperature resistant. In addition, they offer the advantages of better dimensional stability, creep resistance, chemical resistance, and good electrical properties. Their disadvantages lie in the fact that most are more difficult to process and more expensive. [9]

A thermosetting plastic is produced by a chemical reaction which has two stages. The first stage results in the formation of long chain like molecules similar to those present in thermoplastics, but still capable of further reaction. The second stage of the reaction (cross linking of chains) takes place during moulding, usually under the application of heat and pressure. The resultant moulding will be rigid when cooled but a close network structure has been set up within the material. During the second stage the long molecular chains have been interlinked by strong bonds so that the material cannot be softened again by the application of heat. Since the cross linking of molecules is by strong chemical bonds, thermosetting materials are characteristically quite rigid materials and their mechanical properties are not heat sensitive. [10]

2.2.1 Curing of Thermosets

The term cure refers to the hardening, setting or crosslinking process in thermosetting resins. During crosslinking, a thermosetting resin undergoes several changes, usually (but not always) starting as a liquid, becoming progressively more viscous, undergoing a solidification process known as gelation, then becoming a soft, rubbery or cheese like substance, and eventually becoming a hard, relatively brittle solid.

Once the gelation stage is passed, some of the material is insoluble and infusible, making chemical analysis of the extent of reaction extremely difficult, so the

determination of the extent of cure frequently relies on the measurement of changes in physical, electrical and mechanical properties. The disadvantage of this approach is that complete reaction of the chemical groups involved cannot be assumed simply on the grounds that there is no further change in these properties. It may be necessary to increase the temperature in order to make the functional groups accessible. [11]

A high degree of cross linking gives rise to three dimensional or space network polymers in which all polymer chains are linked to form on giant molecule. Thus, instead of being composed of discrete molecules, a piece of highly cross linked polymer constitutes, essentially, just one molecule. At high degree of cross linking, polymers acquire rigidity, dimensional stability, and resistance to heat and chemicals. Because of their network structure such polymers cannot be dissolved in solvents and cannot be softened by heat; strong heating only cause decomposition. Polymers or resins which are transformed into a cross linked product, and thus take on a set on heating, are said to be of thermosetting type. Quite commonly, these materials are prepared, by intent, in only partially polymerized states (prepolymers), so that they may be deformed in the heated mold and then hardened by curing (cross linking). [12]

In contrast to this it is possible to have thermosetting plastics, which can be softened only once to take up the shape of the mold. Once these materials have solidified they cannot be softened by the application of heat or by any other method. When heat and pressure are applied to a thermosetting plastic during the initial molding process, the structure undergoes a chemical reaction that locks it into a three dimensional network. This is called crosslinking; it is initiated by heat, chemical agents, irradiation, or a combination of these. As a result of this cross linking, thermosets have an obvious advantage in that they will not soften in high temperature environments. Thermosets also have improved resistance to chemical attack, stress cracking, and creep. However, they are not so easy to mold as the thermoplastics, and generally they cannot offer the same level of toughness.

Some of the commercially used thermosets are indicated below.

1. Alkyd: Easy, fast molding material with no volatile by-products. Excellent electrical insulation with good heat resistance and low moisture absorption.
2. Allyl: Excellent all round electrical properties even under long term heat and moisture. Also good resistance to chemicals even at high temperatures.
3. Bismaleimide (BMI): Excellent high temperature performance but, like most thermosetting materials, it lacks toughness.
4. Cyanates: Tough materials with excellent adhesive peel strength. Good dimensional stability.
5. Epoxies: Excellent combination of mechanical strength, electrical resistance, and adhesion to most materials. Low mold shrinkage, and some formulations cure without heat or pressure. Most grades are relatively brittle.
6. Melamine formaldehyde: The hardest of all plastics, this material is excaellent for food contact applications and is fire resistant. Requires higher pressure than phenolics to mold but its color properties are superior to those of the polyesters.
7. Phenolics: General purpose, cost effective resins. One of the first synthetic plastics. Color limited to black or brown. Easily molded into complex shapes with good dimensional stability. Good creep resistance and very hard surface.
8. Polyesters: Unlimited colors and also available transparent. Easy to mold but shrinkage is high. Very popular resin for use with glass fibers; product is often referred to as fiberglass. Also form basis for the popular (easily molded) bulk molding compound (BMC) and sheet molding compound (SMC).
9. Polyimides: These materials chemical resistance and creep resistance are both excellent. Also available as a thermoplastic.
10. Polyurethane: Wide range of formulations. The greater the degree of cross linking, the greater the hardness. Excellent toughness, good traction properties, and resistance to wear make it ideal for skate wheels and shoe heels. Also available as a thermoplastic.
11. Silicones: Can be available as elastomeric or rigid materials. They are very inert and can be used over a broad temperature range.
12. Urea formaldehyde: Can be available in a range of colors. Good surface hardness and electrical properties but relatively poor heat resistance. [7]

2.3 Cyclohexanone Formaldehyde Resins

Cyclohexanone can be reacted with aldeyhdes, especially formaldehyde, to give defined methylol compounds or resinous products. In this case it is the molar ratio and the reaction conditions which determine the properties of the end products. A high formaldehyde excess promotes the formation of methylol compounds, whereas basic catalysis leads to resin formation. Higher aldehydes can likewise be used to produce resins, but have not found any industrial significance. On the other hand, methylcyclohexanone or mixtures with aliphatic ketones and, more recently, trimethylcyclohexanone have been employed. The modification of the resins with phenols, epoxides, polyesters and sulphonamides is known. Small beads are obtained by addition of dispersants. The continious preparation process has been described. Hydrogenation and treatment with reducing agents are ways in which the light stability can be increased.

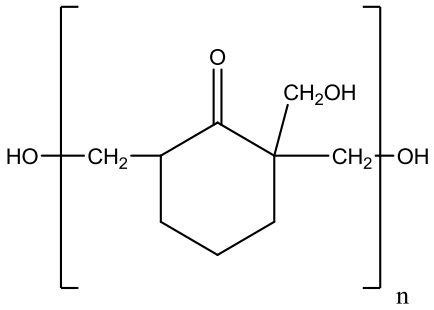

Figure 2.1 : General structure of cyclohexanone formaldehyde resin.

A reaction which has become important for the industrial production of the resin is the condensation of cyclohexanone with formaldehyde in the presence of alkalis.

In many cases, the resins are used in order to improve drying, hardness, fullness, gloss and solids content. In coatings they are used in every case only as an accompaniment to other binders, for example in alkyd/acrylic coating materials, cement paints, epoxy resin systems and marine paints. In addition to conventional printing inks, UV curing printing inks also play an increasing role. A further principal area of application is represented by adhesives and sealing compounds. Another application which has been described is in optical recording media. The broad compatibility of resins based on trimethylcyclohexanone makes them ideally suited to use in pigment pastes capable of universal application. [13]

The CFR has low molecular weight and shows unique compatibility with a great number of polymers. It is soluble in most organic solvents such as aromatic hydrocarbons, ketones, esters, alcohols, etc. Because of its good compatibility, it is usually used as a coating additive. A lot of work on modifying the CFR has been done in order to widen its application fields, however, the effects of these modifications on the application in some specific fields, such as plastic printing, etc., have not been extensively investitaged. The properties, such as solubility in solvents and compatibility with some polymers will influence the application of modified CFRs. [14]

2.3.1 Synthesis of Cyclohexanone Formaldehyde Resins

The alkali catalysed condensation polymerization of lower ketones such as methyl ethyl ketone, cyclohexanone or acetophenone with formaldehyde produces ketone/formaldehyde resins (ketone resins). When added to coating system these light, unsaponifiable hard resins improve gloss, hardness and body. [15]

2.3.2 Applications

Numerous reports about aliphatic and alicyclic ketone formaldehyde resins exist for many commodity applications like paints, foam, adhesives, and molding materials. Cyclohexanone formaldehyde resin (CFR) has good utility because it has excellent glossy and transparent properties. Due to their high compatibility and solubility with wide range of film formers, resins (CFR) play a key role in the field of coatings (paints, inks, varnish, lacquers, and light stabilizers) as a blend for the improvement of coating properties, and as an adhesive in multilayered laminated sheets. [16]

Ketonic resins play a prime role in organic coating applications, due to their excellent light resistance, high compatibility and solubility, which make it possible to blend and use them with a wide variety of resins. Ketone resin based on cyclohexanone formaldehyde (CFR), due to its hydroxy polarity, provides better wetting of pigments and surfaces, and it can thus be used in several applications. A literature survey shows that CFR resin is used as a constitute of binder to modify the coating characteristics of alkyd based coatings. [17]

Cyclohexanone formaldehyde resin, an important synthetic resin, has been widely used in coatings, inks as a multifunction additive because of its good properties.

Nowadays, UV curable coatings and inks are more and more widely used. However, the solvent resistance property of cyclohexanone formaldehyde resin (CFR) is unsatisfactory when it is used in UV curable coatings and inks, as without UV curable group in the structure of cyclohexanone formaldehyde resin, it can not be crosslinked in the system. [18]

Several patents are available where ketonic (cyclohexanone formaldehyde) resin is used as an additive to improve the coating properties of alkyd resins. [19]

Cyclohexanone formaldehyde (CF) resin have excellent compatibility with the resins used in coatings, which is able to not only make the dye to be well wetted and dispersed, but also can enhance effectively the adherence, gloss and hardness of coatings. However, CF resin also has some disadvantages such as the poor thermal stability and yellowstain resistance, and the deep color, which limits its application in coatings to a certain degree. In recent years, although much work has been carried out to improve the disadvantages of CF resin, the performance of CF resins is unsatisfied. Therefore, it is necessary to develop a new kind of polymer additive with excellent and applicable performance to replace totally or partly ketone aldehyde resins. [20]

2.4 Epoxy Resins

A The most popular epoxy monomers are those derived from the reaction of bis(4 -hydroxy phenylene) - 2,2 propane (bisphenol A) and 1 - chloroprene 2 – oxide (epichlorohydrin), in the presence of sodium hydroxide. The structure of the major product, bisphenol A diglycidyl ether (DGEBA or BADGE) and its condensed forms, is dependent upon the stoichiometry of the reactants.

Epoxy monomers containing vinyl groups, like glycidyl (meth)acrylate or glycidyl oxystyrene, can be used for the synthesis of functional oligomers. Linear or crosslinked epoxy polymers are obtained by reaction of the epoxy monomers with comonomers (hardeners) and/or initiators. Epoxy polymers can be produced by step or chain polymerizations or, eventually, by a combination of both mechanisms. [21]

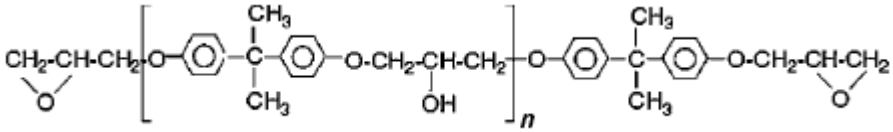

Figure 2.2 : Diglycidyl ether of bisphenol A, DGEBA.

Epoxy is perhaps the most commonly used resin for industrial protective coatings. It is derived from bisphenol-A (BPA) and epichlorhydrin (ECH). This combination of raw materials yields a series of related compounds that, prior to crosslinking, have an epoxide group at each end of the molecule, and an alcoholic hydroxyl group as a mid chain pendant. Crosslinking takes place preferentially through the terminal epoxy groups and to the midchain hydroxyl groups. [22]

The reasons for the widespread use of epoxy resin lie in the following attributes:

Easy cure

Low shrinkage

High adhesion

Thermal stability

Good chemical resistance

Versatility

Apart from the above, the epoxies also possess other properties like high mechanical strength, good electrical insulation, water resistance, serviceability at wide temperature range, and ease of handling and processing.

The epoxy resins, being thermoset in nature, cannot be used alone. They require what is called a hardener to effect the curing of the coating and conversion of the coating into a useful protective yet aesthetically appealing. [23]

Epoxy resins are generally not used alone but require a reaction partner in order to be cured (hardened). A large number of reaction partners may be used for curing at elevated or at room temperature. The cured films have high adhesion, flexibility, hardness, abrasion resistance, resistance to chemicals, and corrosion protection.

Epoxy resin types are Bisphenol A, Bisphenol F and Novolacs.

Bisphenol A Resins. Most epoxy resins are condensation products of bisphenol A and epichlorohydrin. Depending on the ratio of bisphenol A to epichlorohydrin, resins of varying chain length are obtained, which differ in molecular mass, melting point, viscosity, solubility, and content of epoxy and hydroxyl groups.

Bisphenol F Resins. Bisphenol F is produced by condensing phenol with formaldehyde in an acid medium. Bisphenol F is a mixture of isomeric and oligomeric products (novolacs). Resins produced by reaction of bisphenol F with epichlorohydrin have lower viscosities and a somewhat higher functionality (more epoxy groups) than the corresponding bisphenol A resins.

Epoxy Novolacs. Epoxy novolacs are made by condensing formaldehyde with phenolic substances in an acid medium, followed by epoxidation. Only the epoxy phenol novolac and cresol novolac resins have gained importance in the market. The high functionality of these resins allows formulation of coating systems with a high solvent resistance (high network density). The aromatic structure of the resins is responsible for the high glass transition temperature and good resistance to aqueous and acid solutions of the coatings. The chemical structure and high functionality lead to coatings with limited flexibility and a somewhat lower adhesion to metallic substrates than bisphenol A epoxy resins. [24]

2.4.1 Synthesis of Epoxy Resins

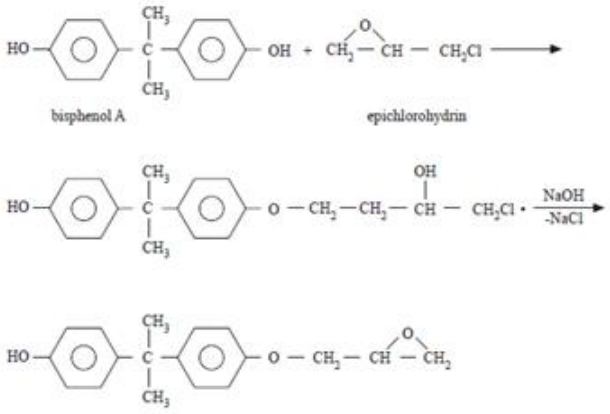

Figure 2.3 : Synthesis of epoxy resin.

The molar ratio of epichlorohydrin to bisphenol A can range from as high as 10:1 to as low as 1.2:1. This produces resins ranging from liquid to semisolid to solid and varying molecular weights and softening points. The products are oligomers or prepolymers, which are hardly used as such; they have pendant hydroxyl groups and terminal epoxy groups. The epoxy prepolymer can be cross linked or cured by reaction with a number of reagents, including primary and secondary amines. [25]

Epoxy resins are complex network polyethers usually formed in a two staged process. The first stage involves a base catalyzed step growth reaction of an excess epoxide, typically epichlorohydrin with a dihydroxy compound such as bisphenol A. This results in the formation of a low molecular weight prepolymer terminated on either side by an epoxide group.

In the second stage, a cross linked network structure is formed by curing the prepolymer with active hydrogen containing compounds. These curing agents include polyamines, polyacids and acid anhydrides, polyamides, and formaldehyde resins. Amines, preferably liquid amines like triethylene diamine, effect cure of the prepolymer by ring opening of the terminal epoxide groups.

Epoxy resins are very versatile materials with a wide range of applications. They are tough and flexible and have high tensile, compressive, and flexural strengths. Epoxy resins have excellent chemical and corrosion resistance and good electrical insulation properties. They can be cured over a wide range of temperatures with very low shrinkage. Epoxy resins have outstanding adhesion to a variety of substrates, including metals and concrete. Consequently, the major uses of epoxy resins are in protective coating applications. Other uses of epoxies include laminates and composites. Potting, encapsulation, and casting with epoxy resins are common procedures in the electrical and tooling industries. [26]

2.4.2 Curing Agents

Epoxy resins are reactive intermediates composed of mixtures of oligomeric materials containing one or more epoxy groups per molecule. To convert epoxy resins into useful products, they must be cross linked or "cured" into a threedimensional polymer network. Cross linking agents, or curing agents, function by reaction with or cause the reaction of epoxide or hydroxyl groups in the epoxy resin. The number of curing agents that have been developed over the years for

epoxy resins is overwhelming. Selection of the curing agent is as important as that of the base resin; it is dependent on the performance requirements of the film and the constraints dictated by the specific method of application. [27]

Epoxy resins must be cured with cross linking agents (hardeners) or catalysts to develop desired properties. Cross linking takes place at the epoxy and hydroxyl groups that are the reaction sites.

Aromatic amines usually require an elevated temperature cure. Epoxies cured with aromatic amines usually have a longer working life than epoxiescured with aliphatic amines. These curing agents are relatively difficult to use because they are solids and must be melted into the epoxy. However, the allowable operating temperature for epoxies cured with aromatic amines are higher than those epoxies cured with aliphatic amines.

These are widely used because the curing of the epoxies takes place at room temperature. High exothermic temperatures develop during the curing reaction that limit the mass of material that can be cured. The electrical and physical properties of these aliphatic cured resins had the greatest tendency toward degradation of electrical and physical properties at elevated temperatures. Typical aliphatic amines used include DETA and TETA.

Catalytic curing agents require a temperature of 2008F (938C) or higher to react. These epoxy formulations exhibit a longer working life than the aliphatic amine cured epoxies. The exothermic reaction may be critically affected by the mass of the resin mixture. Typical materials used include piperidine, boron trifluoride ethylamine complex, and benzyl dimethylamine (BDMA).

These curing agents are becoming more widely used because they are easy to work with, have minimum toxicity problems compared with amines, and offer optimum high temperature properties to the cured resin. Typical acid anhydrides used include nadic methyl anhydride (NMA), dodecenyl succenic anhydride (DDSA), hexahydrophthalic anhydride (HHPA), and alkendic anyhydride. [28]

2.4.3 Epoxy Acrylates

Epoxy acrylates are the reaction products of acrylic acid with various diglycidyl ethers of bisphenol A. The epoxy acrylates contain acrylate and hydroxyl functionality, but they do not contain epoxide functionality and should not be confused with the epoxides. [29]

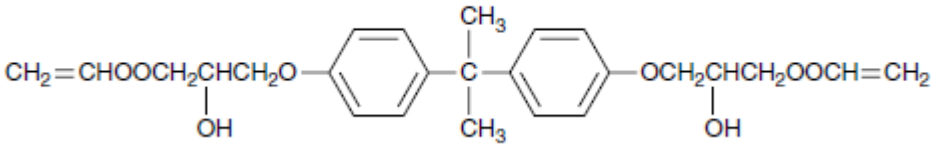

Figure 2.4 : General structure of epoxy acrylate.

Epoxy acrylic thermosetting systems to provide a combination of film hardness, resistance, gloss and color retention, and chemical resistance. [30]

2.4.4 Applications

Epoxy resins have found a wide range of applications and a steady rate of growth over the years mainly because of their versatility. Properties of the cured products can be tailored by proper selection of resin, modifier, cross linking agent, and the curing schedule.

The main attributes of properly cured epoxy systems are outstanding adhesion to a wide variety of substrates, including metals and concrete; ability to cure over a wide temperature range; very low shrinkage on cure; excellent resistance to chemicals and corrosion; excellent electrical insulation properties; and high tensile, compressive, and flexural strengths.

In general, the toughness, adhesion, chemical resistance, and corrosion resistance of epoxies suit them for protective coating applications.

For electrical and electronic applications epoxy formulations are available with low or high viscosity, unfilled or filled, slow or fast curing at low or high temperatures. Potting, encapsulation, and casting of transistors, integrated circuits, switches, coils, and insulators are a few electrical applications of epoxies.

With their adhesion to glass, electrical properties, and flexural strength, epoxies provide high quality printed circuit boards. Epoxies have been successfully used in

Europe for outdoor insulators, switchgear, and transformers for many years. In these heavy electrical applications, the advantage of cycloaliphatic epoxies over porcelain has been demonstrated.

Adhesion properties of epoxies, complete reactivity with no volatiles during cure, and minimal shrinkage make the materials outstanding for adhesives, particularly in structural applications. The most commonly known adhesive applications involve the two component liquids or pastes, which cure at room or elevated temperatures.

Epoxies are used in fiber reinforced composites, providing high strength to weight ratios and good thermal and electrical properties. Filament would epoxy composites are used for rocket motor casings, pressure vessels, and tanks. Glass fiber reinforced epoxy pipes are used in the oil, gas, mining, and chemical industries. [31]

2.5 Photopolymerization

When polymerizations are initiated by light, both the initiating species and the growing chain ends are radicals, this is radical photopolymerization. As for other polymerizations, molecules of appreciably high molecular weight can be formed in the course of the chain reaction. Playing the predominant role in technical polymer synthesis, vinyl monomers can be mostly polymerized by a radical mechanism.

Regarding initiation by light, it must be pointed out that the absorption of incident light by one or several components of the polymerization mixture is the crucial prerequisite. If the photon energy is absorbed directly by a photosensitive compound, being a monomer itself or an added initiator, this photosensitive substance undergoes a homolytic bond rupture forming radicals, which may initiate the polymerization.

Light induced free radical polymerization is of enormous commercial use. Techniques such as curing of coatings on wood, metal and paper, adhesives, printing inks and photoresists are based on photoinitiated radical vinyl polymerization. Some other interesting applications are available, including production of laser video discs and curing of acrylate dental fillings.

In contrast to thermally initiated polymerizations, photopolymerization can be performed at room temperature. This is a striking advantage for both classical polymerization of monofunctional monomers and modern curing applications.

Photopolymerization of monofunctional monomers takes place without side reactions such as chain transfer. In thermal polymerization, the probability of chain transfer is high which brings about a high amount of branched macromolecules. Thus, low energy stereospecific polymeric species, namely of syndiotactic configuration, may be obtained by photopolymerization. Another important use refers to monomers with low ceiling temperature. They can only be polymerized at moderate temperatures, otherwise depolymerization dominates over polymerization. By means of photopolymerization, these monomers are often easily polymerizable.

Radical photopolymerization of vinyl monomers played an important role in the early development of polymerization.

Photocurable formulations are mostly free of additional organic solvents; the monomer, which serves as reactive diluent, is converted to solid, environmentally safe resin without any air pollution. UV curing is often a very fast process, taking place as described previously without heating. If the polymerization mixture absorbs solar light and the efficiency of radical formation is high, photocuring can be performed with no light source but sunlight. These features make photopolymerization an ecologically friendly and economical technology, which has high potential for further development.

Photoinitiated free radical polymerization consists of four distinct steps:

1. Photoinitiation: Absorption of light by a photosensitive compound or transfer of electronic excitation energy from a light absorbing sensitizer to the photosensitive compound. Homolytic bond rupture leads to the formation of a radical that reacts with one monomer unit.

2. Propagation: Repeated addition of monomer units to the chain radical produces the polymer backbone.

3. Chain transfer: Termination of growing chains by hydrogen abstraction from various species (e.g., from solvent) and concomitant production of a new radical capable of initiating another chain reaction.

4. Termination: Chain radicals are consumed by disproportionation or recombination reactions. Termination can also occur by recombination or disproportionation with any other radical including primary radicals produced by the photoreaction.

Notably, the role that light plays in photopolymerization is restricted to the very first step, namely the absorption and generation of initiating radicals. The reactions of these radicals with monomer, propagation, transfer, and termination are purely thermal processes; they are not affected by light. [32]

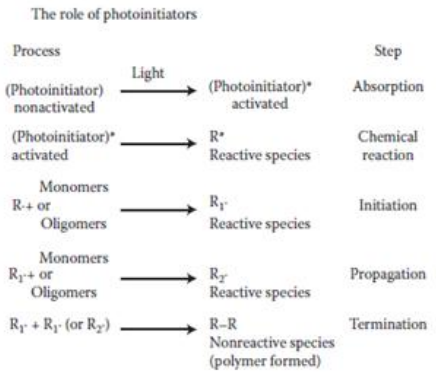

Figure 2.5 : Photopolymerization steps.

Photochemical reactions are different from thermal or electrochemical reactions in several respects.

1. Molecules have to absorb incident light to activate photochemical reactions. Thus, molecules without a chromophore cannot undergo photochemical reactions.

2. The electronic and nuclear configurations of the excited molecules are usually different from those of molecules activated by chemical or electrochemical means.

3. The products of photochemical processes are usually different from other chemical reaction products. This is due to the large excess energy and the different electronic configuration of the photochemically excited molecule compared to the ground state molecule. [33]

The absorption of UV energy by a photoinitiator results in the occurrence of a series of energetic processes. Initially a high energy singlet state is produced that may convert to a more stable, but less energetic, triplet state by intersystem crossing. Most photoinitiators produce radicals from the triplet state but a few can interact from the excited singlet state. There are also several decay processes that may occur from the excited states. The singlet state may decay to the ground state by fluorescence or convert by intersystem crossing to an excited triplet state. The triplet state may decay by phosphorescence or be quenched by monomers or oxygen, or go

on to produce radicals by various chemical mechanisms. The study of fluorescence and phosphorescence that is emitted at different wavelengths from an excited species can provide insight into the electronic transitions that are occurring and their energy levels. [34]

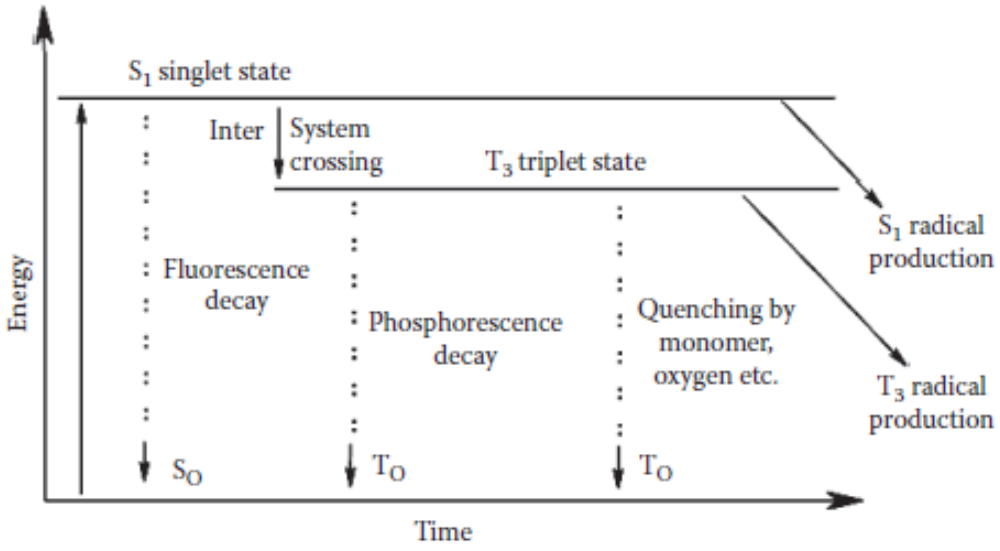

Figure 2.6 : Photoinitiators energy levels.

Several intramolecular processes are shown competing with photochemical reactions, including reemission of a photon as fluorescence or phosphorescence, radiationless decay to the ground state and crossing from one excited state to another. The ground states of almost all organic compounds have all electron spins paired. Absorption of a photon promotes an electron from the singlet state to a higher energy singlet state in the order of increasing energy above the ground state. A change in the spin state of an electronically excited molecule, called intersystem crossing, produces triplet species with two unpaired spins. A triplet state is always lower in energy than the corresponding singlet state. Singlet states may emit light and return to the ground state. [35]

Radicals can be formed by initiators. In most cases of photoinduced polymerization, initiators are used to generate radicals. One has to distinguish between two different types of photoinitiators:

Type I Photoinitiators Unimolecular Photoinitiators: These substances undergo homolytic bond cleavage upon absorption of light. The fragmentation that leads to the formation of radicals is, from the point of view of chemical kinetics, a unimolecular reaction.

Themajority of Type I photoinitiators are aromatic carbonyl compounds with appropriate substituents, which spontaneously undergo "a-cleavage," generating free radicals according to reaction. The benzoyl radical formed by the reaction depicted is very reactive toward the unsaturations of vinyl monomers.

Type II Photoinitiators Bimolecular Photoinitiators: The excited states of certain compounds do not undergo Type I reactions because their excitation energy is not high enough for fragmentation (i.e., their excitation energy is lower than the bond dissociation energy). The excited molecule can, however, react with another constituent of the polymerization mixture, the so called coinitiator (COI), to produce initiating radicals. In this case, radical generation follows second order kinetics.

Radical generation by Type II initiating systems has two distinct pathways. Hydrogen abstraction from a suitable hydrogen donor. Photoinduced electron transfer reactions and subsequent fragmentation. [36]

The role of photoinitiators is to produce the free radicals that initiate the chemical reaction. [37]

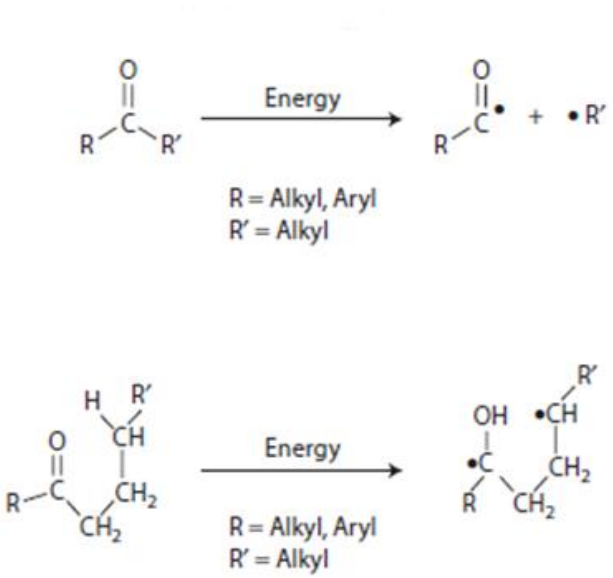

Figure 2.7 : Type I and Type II photoinitiator systems.

2.5.1 UV Curing

Besides the above noted polymerization techniques photocuring is a special process that transforms a multifunctional monomer into a crosslinked macromolecule by a chain reaction initiated by reactive species generated by UV irradiation. Three basic components are needed for photocuring:

1. The already mentioned photoinitiator;

2. A functionalized oligomer, which by polymerizing will constitute the backbone of the three dimensional polymer network formed;

3. A mono or multifunctional monomer, which acts as reactive diluent and will thus be incorporated into the network.

UV curable resins of acrylate and methacrylate monomers gained great commercial success because they offer high reactivity and the possibility of creating a large variety of crosslinked polymers with tailormade properties. On the other hand there are problems like early gelation of the irradiated sample and mobility restrictions of the reactive sites during the preceding reaction and also with increased monomer functionality.

The UV cured polymers based on the novel acrylate monomers show some advantages: completely insolubility in organic solvents which makes these very reactive photoresists well suited for imaging applications; high crosslink density; good resistance to moisture, strong acids, weathering and thermal treatment.

Photopolymerization in micellar systems is useful for the synthesis of polymers displaying high molecular weights. The model of photopolymerization used to describe a micellar polymerization does not differ from the one in bulk or solution photopolymerization. [38]

2.5.1.1 Photoinitiators

The function of a photoinitiator is:

• Absorbing the incident UV radiation

• Generation of reactive species (free radicals or ions)

• Initiation of photopolymerization

In UV curing process, photons from the UV source are absorbed by a chromophoric site of a molecule in a single event. The chromophore is a part of the photoinitiator. The light absorption by the photoinitiator requires that an emission light from the light source overlap with an absorption band of the photoinitiator. [39]

The photoinitiator is a critical component of the UV curing process. It is the additive that initiates the polymerization process to quickly reach the final cross linked product. As UV light energy is emitted, it is absorbed by the photoinitiator in the liquid, causing it to fragment into reactive species. These species can be either free radical or cationic.

Free radical initiators can be described as either hydrogen abstraction type or alpha cleavage type. While hydrogen abstraction initiators have their specific uses, especially in three or four way photoinitiator blends, alpha cleavage initiators are the most widely used. The alpha cleavage initiators have a generally higher efficiency due to their generation of free radicals via a unimolecular process. Alpha cleavage initiators need only absorb light to generate radicals; hydrogen abstraction initiators, on the other hand, require an extra step: after absorbing light, the excited state photoinitiator must find a hydrogen donating source to generate the free radicals. It is a bimolecular process.

Beyond the obvious differences in chemical structure, the alpha cleavage initiators are typically differentiated by their absorption profiles. A formulator should be interested in two different characteristics of the photoinitiator's absorption curve. The first is determining which wavelengths of light are absorbed, and the second is the strength of this absorption (molar extinction coefficients). Photoinitiators developed for curing of pigmented films typically have higher molar extinction coefficients between the wavelengths than those useful for curing clear formulations. [40]

Type I Photoinitiators are

Hydroxyacetophenones

Alkylaminoacetophenones

Benzil ketals and dialkoxyacetophenones

Benzoin ethers

Phosphine oxides

Type II Photoinitiators are

Substituted benzophenones

Thioxanthones

Anthraquinones

Benzoylformate esters

Camphorquinone [41]

2.5.1.2 Monomers and Oligomers

Acrylate/Methacrylate Systems

The most widely used UV curable radical initiated systems are based on acrylate unsaturation, with the general formula H2C=CR-COOR' (if R = H, the monomer is an acrylate, if R = CH3, it is a methacrylate). Methacrylates are less reactive than acrylates, but are less toxic and cause less skin irritation than acrylates. The curing reaction of acrylates is typical of vinyl monomers. Therefore, the degree of double bond conversion is the measure of the degree of cure. The best results are obtained when using oligomers as binders and monomers as reactive thinners. A partial list of most common acrylate oligomers follows.

Epoxy acrylates. The most widely used oligomers are aromatic and aliphatic epoxy acrylates. Epoxy acrylates are highly reactive and produce hard and chemically resistant films. The polymerization of monoacrylates produces linear polymers, whereas diacrylates produce branching, and higher functionality acrylates give rise to cross linked structures. Cured materials are useful as coatings and adhesives on rigid substrates such as metal cans and paneling, or as binders in composites. The epoxy

component contributes to adhesion to nonporous substrates and enhances chemical resistance of the film.

Urethane acrylates. Urethane acrylates are formed by the reaction of isocyanates with hydroxy functional acrylate monomers. After UV cure, they produce tough, flexible materials that exhibit good abrasion resistance.

Polyester acrylates. Acrylated polyesters are prepared by reacting the OH group of polyesters with acrylic acid or hydroxy acrylate with acid groups of the polyester structure. Polyester acrylates are often low viscosity resins requiring little or no monomer. They produce coatings and adhesives dominated by the polyester structure used in the oligomer. They are used for pressure sensitive adhesives and also for strong rigid adhesives for metal to metal bonding. Amino modified polyester acrylates show a high reactivity and low skin irritation.

Silicone acrylates. Acrylated organopolysiloxanes, which exhibit excellent release properties, are used as release coatings on papers and films. The silicone structure provides flexibility and resistance to heat, moisture, radiation degradation and shear forces.

Polyether acrylates. Polyether acrylates are produced by esterification of polyetherols with acrylic acid. They have a very low viscosity and do not require reactive thinners. Amino modified polyether acrylates have a higher reactivity and low skin irritance, similar to polyester acrylates.

Solid urethane and polyester acrylates can be used as main components of radiation curable powders. Together with suitable unsaturated polyesters, powders are formed that give low film flow temperatures and allow separating of film formation from curing. This technology has been used successfully in powder coating of wood and plastics. [42]

Reactive prepolymers used as binders are produced by acrylation of oligomers, such as epoxy resins, urethanes, polyesters, silicones, melamine derivatives, cellulose and starches. Prepolymers largely determine the basic properties of the coating. [43]

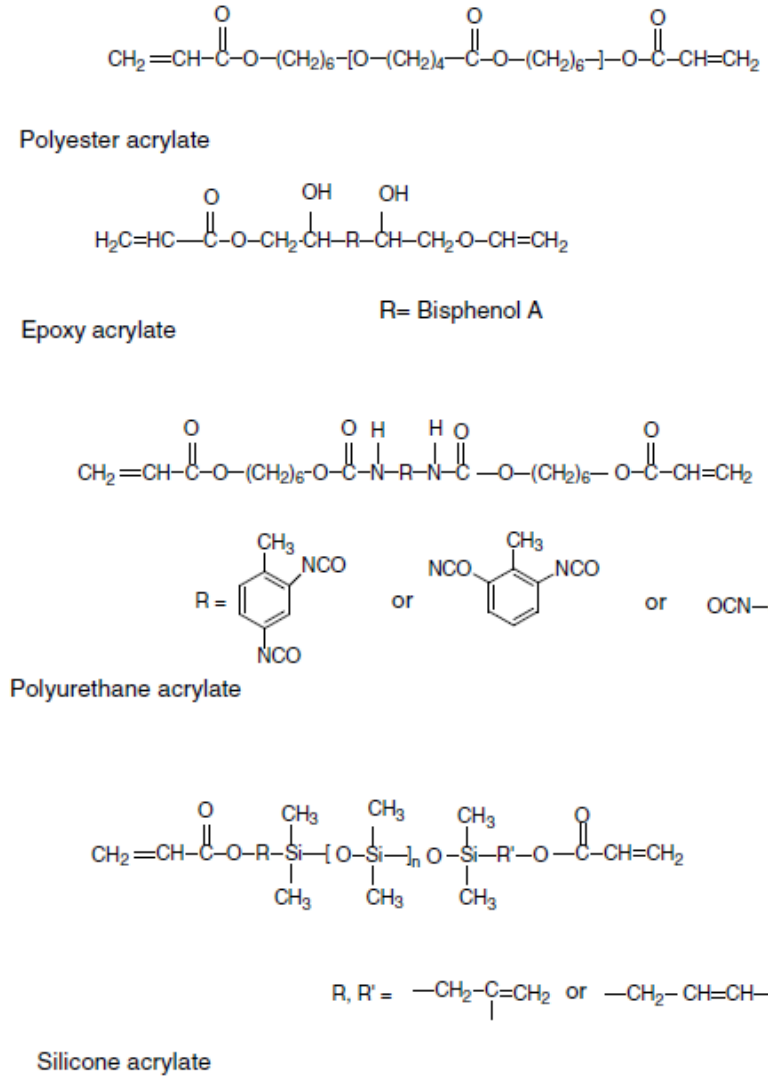

Figure 2.8 : Acrylated prepolymers.

The basic acrylic monomers or oligomers contain unsaturated double bonds (vinyl groups), and consequently cure by addition polymerization involving a free radical reaction. Free radical producing compounds such as peroxides, peracetic acids, and sulfones are added to acrylic resins to initiate polymerization. Free radical polymerization of acrylics may also be induced by exposure to UV or visible light. [44]

2.5.1.3 Reactive Diluents

In radiation curable systems, the solvent is replaced by reactive diluents (monomers) which are incorporated in the network during cross linking. These monomers have two important functions: they reduce the viscosity of the mixture and they strongly influence the physical and chemical properties of the final coating. Monomers can be divided into three groups:

1) Monofunctional monomers: improve the flexibility of the end product (e.g., isobornyl acrylate).

2) Difunctional monomers: e.g., hexanediol diacrylate (HDDA), tripropylene glycol diacrylate (TPGDA).

3) Tri or tetrafunctional monomers: increase the cross linking density of the final coating. Examples include trimethylolpropane triacrylate (TMPTA), pentaerythritol trior tetraacrylate (PETA). [45]

Monomers, also called reactive thinners, are used to reduce viscosity of the prepolymers, but also have an effect on properties of the cured film. They form a high molecular weight network with the prepolymer after curing. To attain an adequate degree of cross linking, bifunctional and polyfunctional acrylates are principally used. Monofunctional acrylates give a less reactive coating because of their volatility, odor and skin irritating effects. Currently, the following bifunctional and polyfunctional acrylates are used in industrial applications:

Tripropylene glycol diacrylate (TPGDA)

Hexanediol diacrylate (HDDA)

Dipropylene glycol diacrylate (DPGDA)

Trimethylolpropane triacrylate (TMPTA)

Trimethylolpropane ethoxytriacrylate (TMPEOTA)

Trimethylpropane propoxytriacrylate (TMPPOTA)

Pentaterythritol triacrylate (PETA)

Glyceryl propoxytriacrylate (GPTA) [46]

Diluents are low molecular weight, low viscosity, high boiling entities. Diluents, especially non reactive diluents, are similar to solvents but do not have volatility similar to solvents. There are two main types of diluents:

• Non reactive diluents

• Reactive diluents.

As the name indicates, non-reactive diluents are those without any functionality. They reduce the viscosity due to their own low viscosity and impart flexibility to a certain extent. They have high boiling points and do not evaporate easily. In most cases over a period of time these non-reactive diluents are benzyl alcohol, dibutyl phthalate, dioctyl phthalate, etc. Unlike non reactive diluents, reactive diluents contain functional group(s). They react in a similar way to resin with the curing agent used in the composition and become an integral part of they offer is permanent, so that once incorporated they remain in the cured tive diluents used in coatings. [47]

2.5.2 Applications

Radiation curing technologies provide a number of economic advantages over the usual thermal operation among them: rapid through cure, low energy requirements, room temperature treatment, nonpolluting and solvent free formulations, low costs. They use light beams to start photochemical and chemical reactions in organic materials (monomers, oligomers, polymers), to form a new polymeric material. The UV curing of coatings and varnishes on various substrates, of paints, of adhesives, of composites, etc. and the imaging area (UV curable inks, printing plates, high resolution relief imaging for microcircuits in electronics, etc.) represent a large class of industrial applications. Another area is concerned with the applications of laser induced processes in monomeric and polymeric materials to computer to plate laser writing, direct laser patterning of microcircuits, 3D machining, holographic devices, optical elements, information recording and storage, etc. Among various factors which affect the efficiency of the polymerization reaction, the photoinitiator (PI) has been recognized as a key factor that governs, e.g. in coating applications, to some extent, curing speed, through cure, tack free index, hardness, etc. [48]

2.6 Chalcones

Chalcones are α,β-unsaturated ketones consisting two aromatic rings (ring A and B) having diverse array of substituents. Rings are interconnected by a highly electrophilic three carbon α,β-unsaturated carbonyl system that assumes linear or nearly planar structure. They contain the ketoethylenic group (–CO–CH=CH–). Chalcones possess conjugated double bonds and a completely delocalized π-electron system on both benzene rings. Chalcones have crystal structure. [49]

Chalcones are 1,3-diphenyl-2-propene-1-one, in which two aromatic rings are linked by a three carbon α, β- unsaturated carbonyl system as,

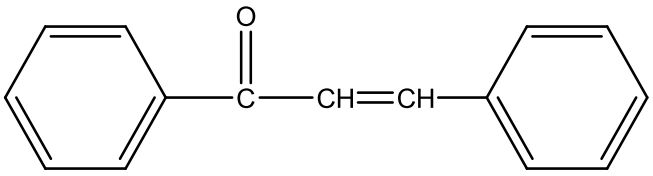

Figure 2.9 : General structure of chalcone.

Chalcones possess conjugated double bonds and a completely delocalized π-electron system on both benzene rings. Molecules possessing such system have relatively low redox potentials and have a greater probability of undergoing electron transfer reactions. [50]

2.6.1 Synthesis of Chalcones

Chalcone can be prepared by an aldol condensation between a benzaldehyde and an acetophenone in the presence of a catalyst.

The aldol condensation relies on the reactivity of a carbonyl group to build a new carbon-carbon bond. The aldol reaction is one of the most powerful methods available for forming a carbon-carbon bond. In this reaction, the conjugate base of an aldehyde or ketone adds to the carbonyl group of another aldehyde or ketone to give a β-hydroxyaldehyde or β-hydroxyketone product.

A crossed aldol condensation leads to a number of different products unless one of the carbonyl compounds involved cannot form an enolate ion which means the compound has no α-hydrogens. A good choice for such a compound is an aromatic

aldehyde. This is because only one enolate ion will form, which is from other carbonyl compound. Once formed, the nucleophilic enolate ion attacks carbonyl carbon to form a β-hydroxycarbonyl product. The β-hydroxycarbonyl product then eliminates a molecule of water to form a conjugated system composed of a double bond and the carbonyl group. The conjugation is extended through two benzene rings as well, producing a very stable product, benzalacetophenone.

There are several methods available for the synthesis of chalcones. The most widely used is the base catalyzed such as sodium hydroxide (NaOH), potassium hydroxide (KOH), barium hydroxide $Ba(OH)_2$ and lithium hydroxide ($LiOH{\cdot}H_2O$). The acid catalyzed that had been used to synthesize chalcones includes aluminum trichloride ($AlCl_3$), dry HCl, boron trifluoride etherate (BF_3-Et_2O), titanium tetrachloride ($TiCl_4$) and ruthenium trichloride ($RuCl_3$). [51]

The aldol condensation between acetophenone and benzaldehyde derivatives is an important C-C bond forming reaction which allows α,β-unsaturated ketone such as chalcones to be obtained. The classical aldol condensation reaction is routinely carried out using aqueous sodium or potassium hydroxide or ethanolic sodium ethoxide at 50^oC over a period of several hours. The benzaldehyde derivative is often used in slightly more than equivalent amounts. The extensive conjugation of the products causes them to absorb light in the visible region, lending them a yellow colour. [52]

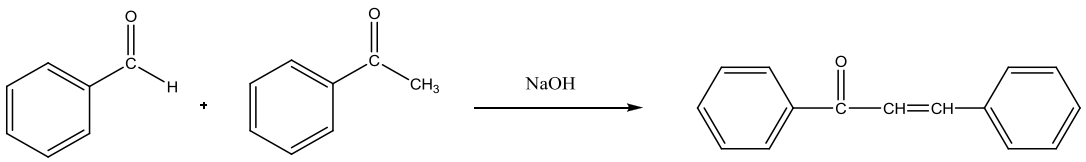

Figure 2.10 : Synthesis of chalcone.

2.6.2 Applications

Chalcones constitute an important class of natural products belonging to the flavonoid family. [53]

Among many promising photosensitive groups, a chalcone group has been well investigated and can be used in photocrosslinkable polymers because it affords high sensitivity to UV radiation. [54]

Chalcones are also found being used in the production of nematic liquid crystals, photosensitive polymers. [55]

2.6.3 Photocrosslinking Behaviour of Chalcones

Photocrosslinking technology is a first, energy saving and more efficient industrial process than heat curable process regarding low temperature and shorter time, and it can easily lead to crosslinked network structure in polyelectrolyte film. These technologies include based on the use of a self crosslinkable polymer, containing a photoinitiator system suited to absorb a light radiation of the appropriate wavelength and to produce primary radical species in order to convert a polymer into a crosslinked network. A chalcone group as a classical photosensitive unit used in photocrosslinkable polymers because it affords high sensitivity to UV radiation and chemical resistance, thermal stability of the resultant polymers. [56]

Polymers containing chalcone moieties have been widely applied because they have high sensitivity to ultraviolet (UV) radiation and good chemical stability with lower shrinkage. However, because of these photosensitive groups, the polymers have low adhesion to metal substrates when they are used in the microelectronics industry. [57]

Functionalized photocrosslinkable polymers with α,β-unsaturated carbonyl groups possess good solubility, the ability to form films, high photosensitivity, resistance towards solvents after crosslinking and thermal stability. The combination of these properties within polymers is needed for their practical use as negative photoresist materials. [58]

Photoreactive materials have recently gained a remarkable interest since the photochemical reactions in organic materials can induce many changes in properties such as solubility, optical transparency, electric constant and refractive index.

Among many photochemical reactions in organic materials, the photopolymerization by UV light exposure has been highlighted in many practical applications. [59]

A number of study on UV initiated photopolymerizations have focused on free radical polymerization of acrylate and methacrylate monomers. Most of the UV curing resins are made of acrylate monomers and their oligomers owing to their high reactivity, low cost, and high quality of the final product, which exhibit good mechanical and optical properties.

Another popular photochemical reaction conducted frequently is photocrosslinking. The photosensitivity of the materials is based mainly on the π-electron density of the photoactive chromophore (e.g. –CH=CH–). Moreover, the absorption spectrum of the chalcone group closely matches the emission spectrum from a high pressure mercury lamp so that it is possible to achieve improved photocrosslinking efficiency. [60]

3. EXPERIMENTAL

3.1 Materials

4-hydroxy acetophenone is an aromatic ketone with a hydroxyl group in para position. Its molecular weight is 136 g/mol.

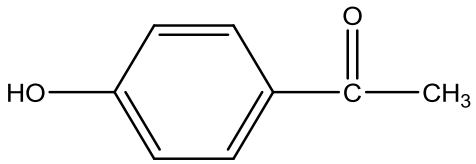

Figure 3.1 : 4-hydroxyacetophenone.

4-hydroxy benzaldehyde is an aromatic aldehyde with a hydroxyl group in para position. Its molecular weight is 122 g/mol.

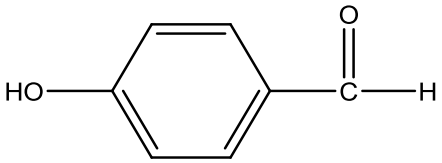

Figure 3.2 : 4-hydroxybenzaldehyde.

3,4-dihydro-2H-pyran is an organic compound to protect –OH groups of 4-hydroxy acetophenone and 4-hydroxy benzaldehyde. Its molecular weight is 84 g/mol.

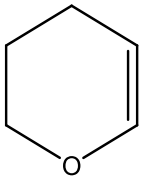

Figure 3.3 : 3,4-dihydro-2H-pyran.

Toluene-4-sulfonic acid monohydrate (p-toluene sulfonic acid) is an organic compound to remove protective pyran groups in deprotection reactions. Its molecular weight is 190 g/mol.

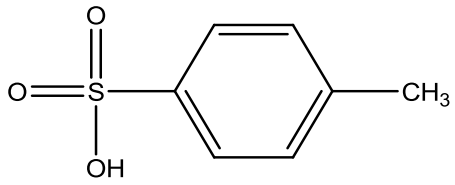

Figure 3.4 : Toluene-4-sulfonic acid monohydrate.

Cyclohexanone is used to synthesis of cyclohexanone formaldehyde resin. Its molecular weight is 98 g/mol.

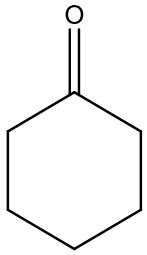

Figure 3.5 : Cyclohexanone.

Formaldehyde is used to synthesis of cyclohexanone formaldehyde resin. Its molecular weight is 30 g/mol.

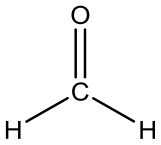

Figure 3.6 : Formaldehyde.

Acryloyl chloride is used to acrylation of –OH groups of resins. Its molecular weight is 90 g/mol.

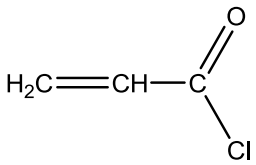

Figure 3.7 : Acryloyl chloride.

Ebecryl 605 is commercial epoxy acrylate used in film formulations as base resin.

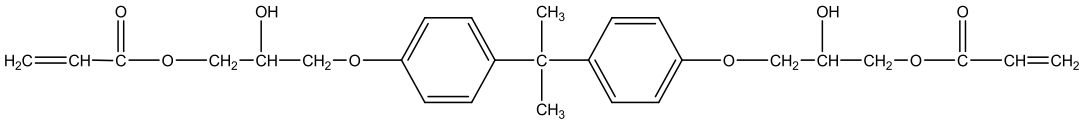

Figure 3.8 : Ebecryl 605.

Hexandioldiacrylate (HDDA) is used as reactive diluent in film formulations to reduce viscosity and component of crosslinking.

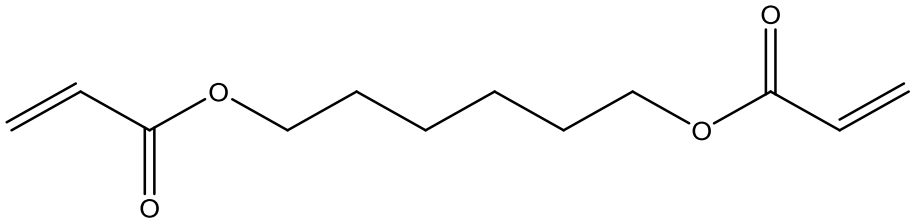

Figure 3.9 : Hexandioldiacrylate.

Dipropyleneglycoldiacrylate (DPGDA) is used as reactive diluent in film formulations to reduce viscosity and component of crosslinking.

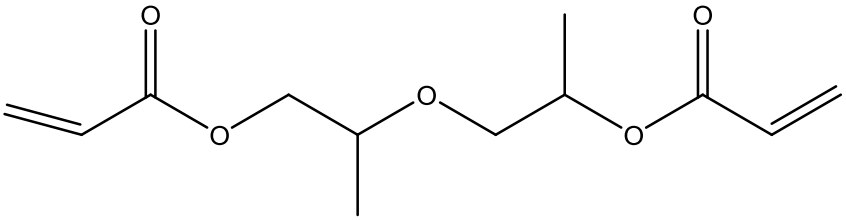

Figure 3.10 : Dipropyleneglycoldiacrylate.

Irgacure 819 is used as a photoinitiator of photopolymerization of film formulations.

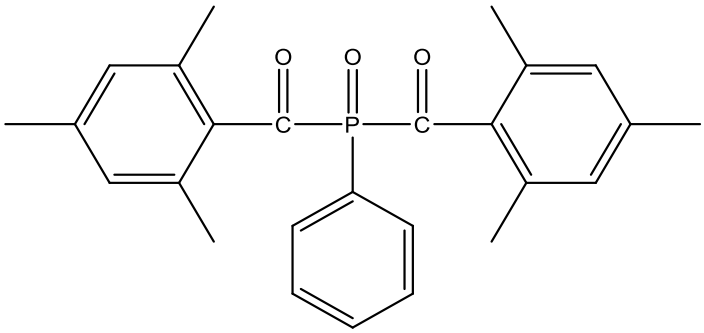

Figure 3.11 : Irgacure 819.

3.2 Equipments

3.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared analysis were performed with Thermo Scientific Nicolet IS 10 FT-IR spectrometer.

3.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR analysis were performed with Agilent VNMRS 500 MHz spectrometer.

3.2.3 Ultraviolet Spectroscopy (UV)

UV Spectroscopy analysis were performed with Shimadzu PharmaSpec UV-1700 UV-Visible Spectrometer.

3.2.4 Thermogravimetric Analyser (TGA)

Thermogravimetric analysis were performed with Thermal Analysis TGA Q50 instrument.

3.2.5 Contact Angle

Contact angles of samples were measured with KSV CAM 100 instrument.

3.2.6 Gloss

Gloss of samples were measured with BYK Gardner (Micro-TRI) gloss meter with 20^{o} and 60^{o}.

3.2.7 Pendulum Hardness

Pendulum hardness of samples were measured with BYK Gardner Konig Pendulum Hardness instrument.

3.2.8 Tensile Test

Tensile modulus, tensile strength and elongation at break values of samples were measured with Zwick Z010 Universal Tensile Tester instrument.

3.3 Synthesis

3.3.1 Synthesis of 4-tetrahydropyran-2-yloxyl acetophenone

4-hydroxyacetophenone was protected with 3,4-dihydro-2H-pyran. According to this reaction, 36.7 mmol (5 g) 4-hydroxyacetophenone and 1.47 mmol (0.37 g) PPTS were dissolved in 100 ml CH_2Cl_2 and stirred for 30 minutes. After that 73.45 mmol (6.7 ml) 3,4-dihydro-2H-pyran was added dropwise into the mixture. Reaction mixture was stirred for 4 hours at room temperature.

Mixture was washed with distilled water for 2 times and once with saturated sodium chloride aqueous solution. Solvent was evaporated and product was dried in vacuum evaporator. Yield of the reaction is 70 %. Completion of reaction in Figure 3.12 was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

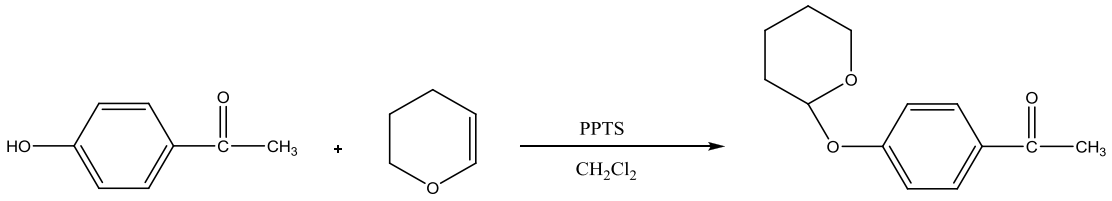

Figure 3.12 : Synthesis of 4-tetrahydropyran-2-yloxyl acetophenone.

FT-IR spectrum of 4-hydroxyacetophenone in Figure 3.13 shows characteristic broad band peak of –OH group at 3295 cm^{-1}. 4-tetrahydropyran-2-yloxyl acetophenone FT-IR spectrum in Figure 3.14 shows that characteristic broad band peak of –OH group diseppeared, $-CH_2$ and -C-O-C- peaks of tetrahydropyranyl ether group occured at 2940 and 1107 cm^{-1}. FT-IR results show that protection of –OH groups was achieved.

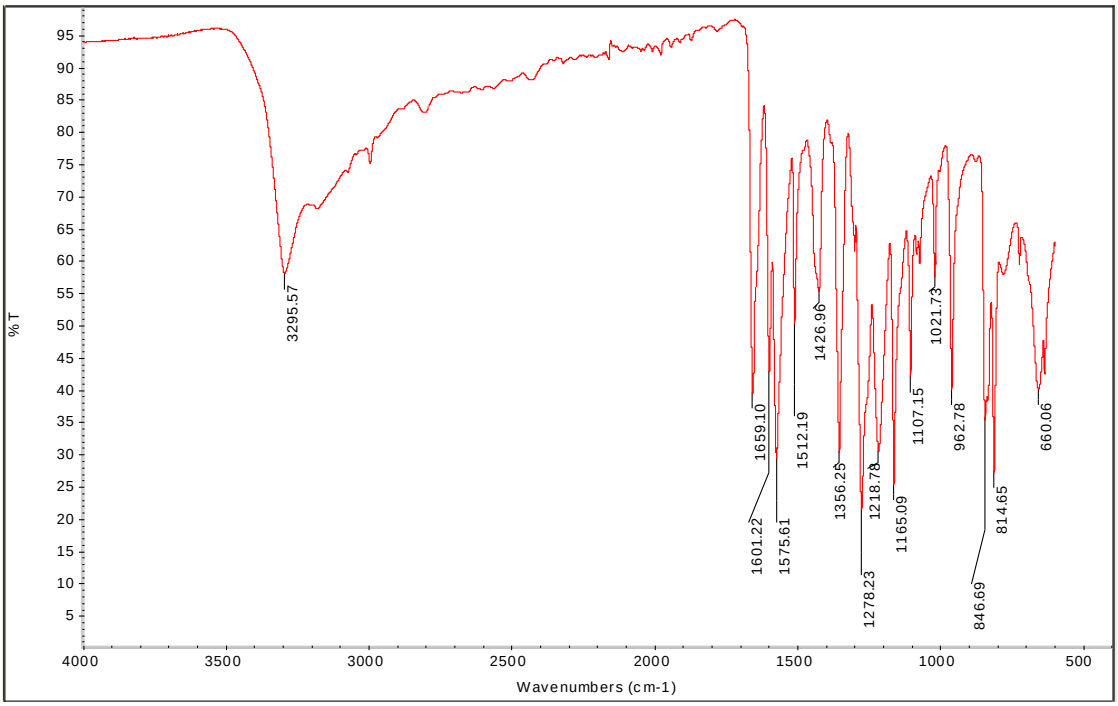

Figure 3.13 : FT-IR spectrum of 4-hydroxyacetophenone.

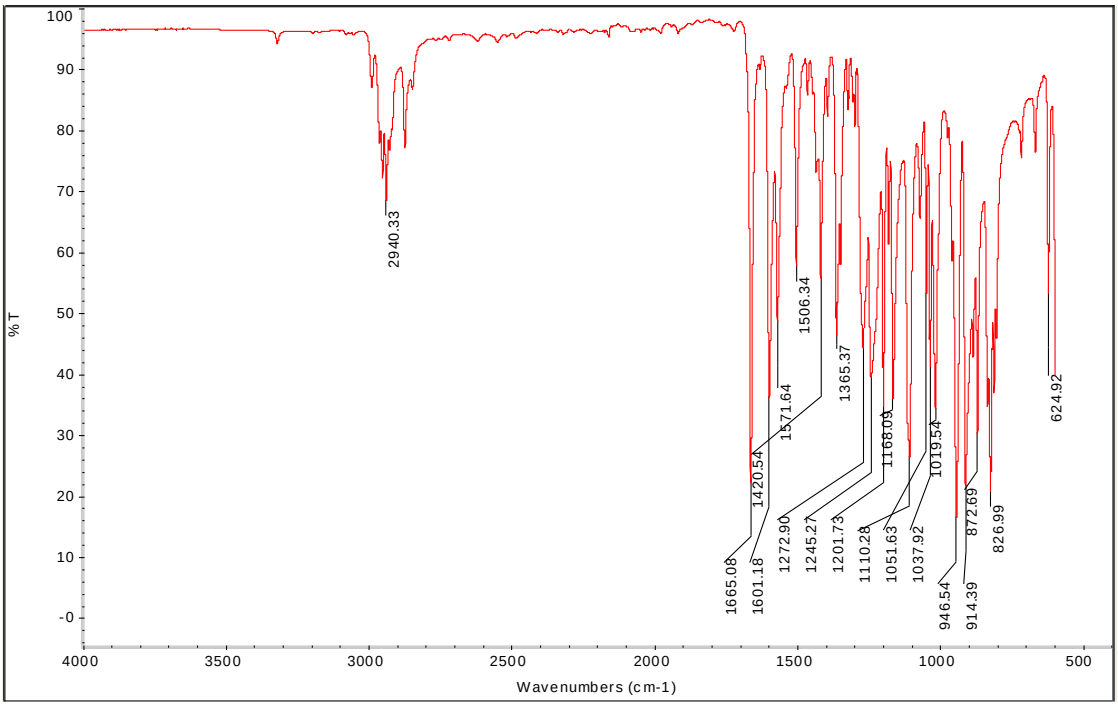

Figure 3.14 : FT-IR spectrum of 4-tetrahydropyran-2-yloxyl acetophenone.

^{1}H-NMR spectrum of 4-hydroxyacetophenone in Figure 3.15 shows –OH group signal at 10 ppm. After protection in Figure 3.16, -OH group signal disappeared, methylenic and etheric protons of tetrahydropyranyl ether group occured between 1-4 ppm and 5-6 ppm respectively.

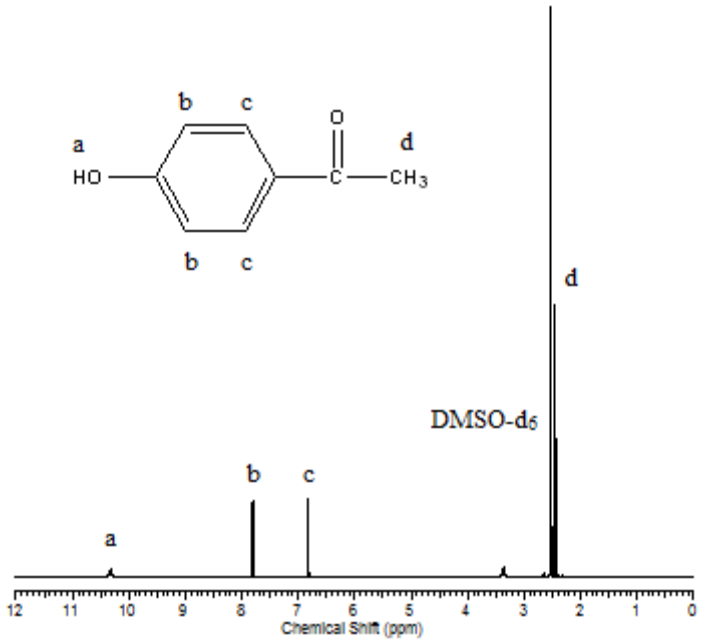

Figure 3.15 : ^{1}H-NMR spectrum of 4-hydroxy acetophenone.

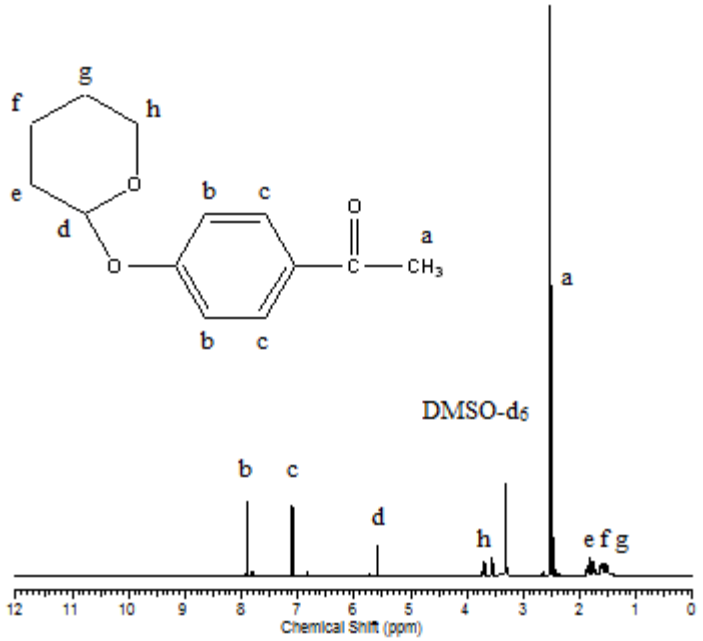

Figure 3.16 : ^{1}H-NMR spectrum of 4-tetrahydropyran-2-yloxyl acetophenone.

3.3.2 Synthesis of 4-tetrahydropyran-2-yloxyl benzaldehyde

4-hydroxybenzaldhyde was protected with 3,4-dihydro-2H-pyran. According to this reaction, 40.95 mmol (5 g) 4-hydroxybenzaldehyde and 1.64 mmol (0.41 g) PPTS were dissolved in 100 ml CH_2Cl_2 and stirred for 30 minutes. After that 82 mmol (7.45 ml) 3,4-dihydro-2H-pyran was added dropwise into the mixture. Reaction mixture was stirred for 4 hours at room temperature.

Mixture was washed with distilled water for 2 times and once with saturated sodium chloride aqueous solution. Solvent was evaporated and product was dried in vacuum evaporator. Yield of the reaction is 70 %. Completion of reaction in Figure 3.17 was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

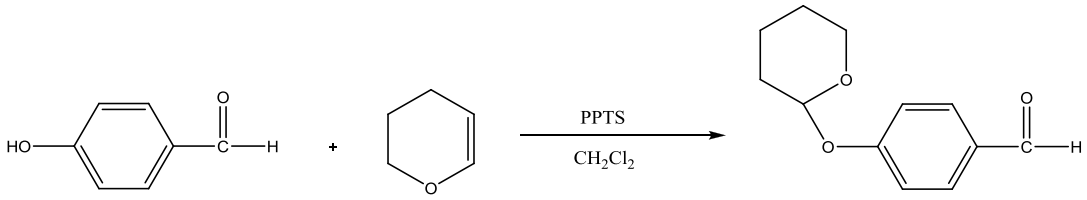

Figure 3.17 : 4-tetrahydropyran-2-yloxyl benzaldehyde.

FT-IR spectrum of 4-hydroxybenzaldehyde in Figure 3.18 shows characteristic broad band peak of –OH group at 3157 cm^{-1}. 4-tetrahydropyran-2-yloxyl benzaldehyde FT-IR spectrum in Figure 3.19 shows that characteristic broad band peak of –OH group diseppeared, $-CH_2$ and -C-O-C- peaks of tetrahydropyranyl ether group occured at 2943 and 1116 cm^{-1}. FT-IR results show that protection of –OH groups was achieved.

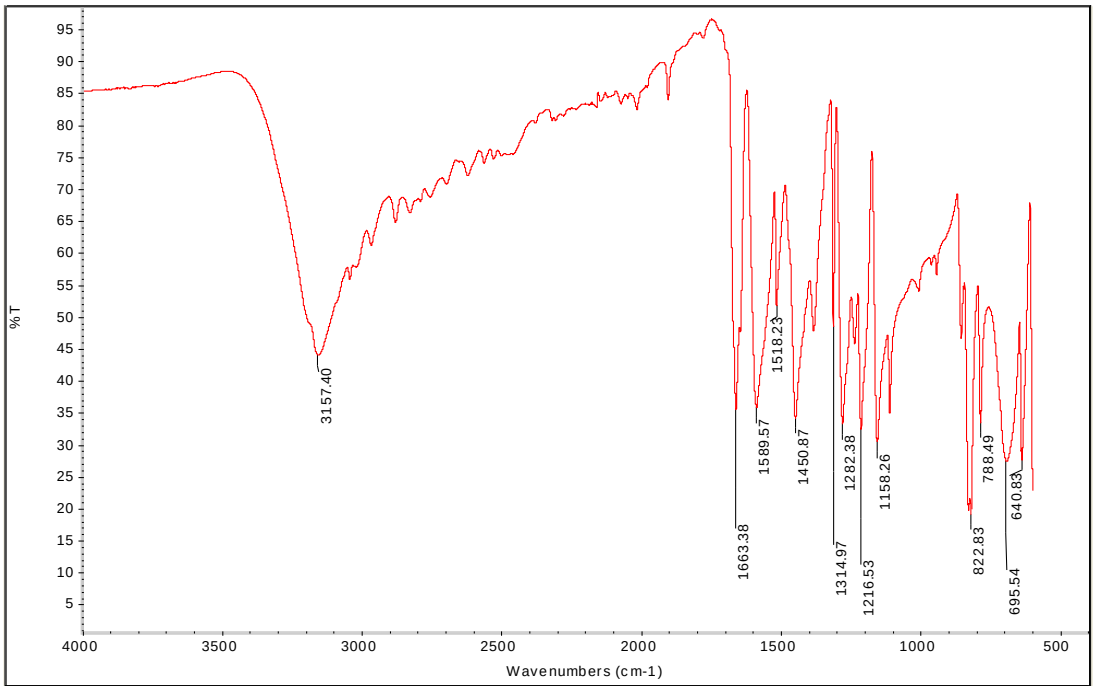

Figure 3.18 : FT-IR spectrum of 4-hydroxybenzaldehyde.

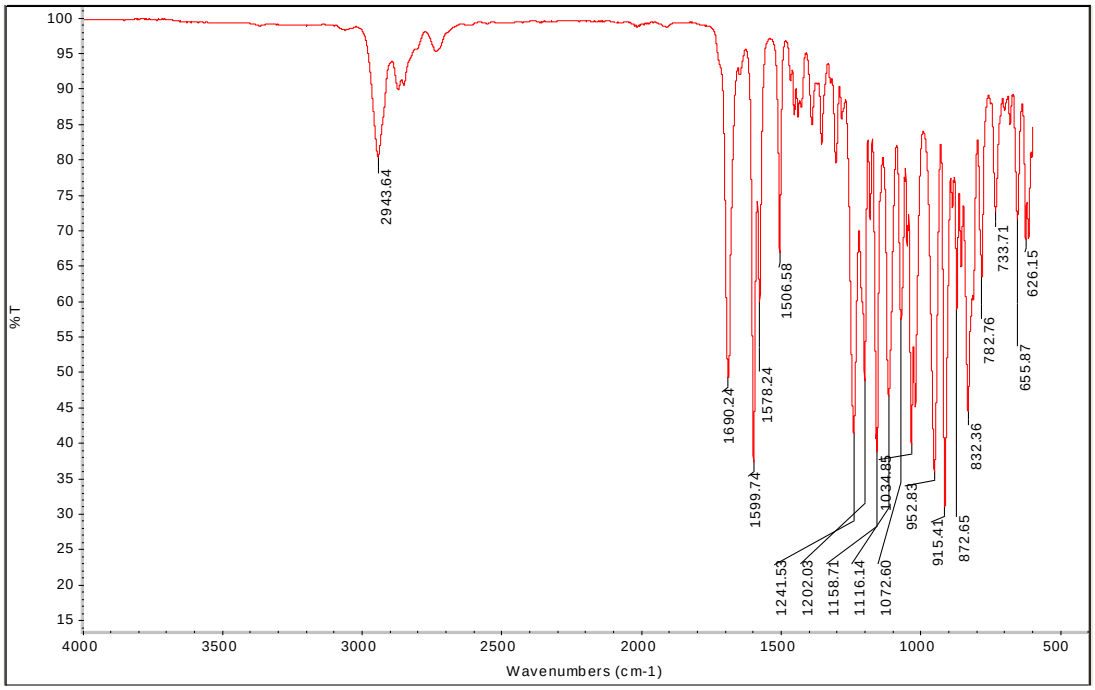

Figure 3.19 : FT-IR spectrum of 4-tetrahydropyran-2-yloxyl benzaldehyde.

^{1}H-NMR spectrum of 4-hydroxybenzaldehyde in Figure 3.20 shows –OH group signal at 10 ppm. After protection in Figure 3.21, -OH group signal disappeared, methylenic and etheric protons of tetrahydropyranyl ether group occured between 1-4 ppm and 5-6 ppm respectively.

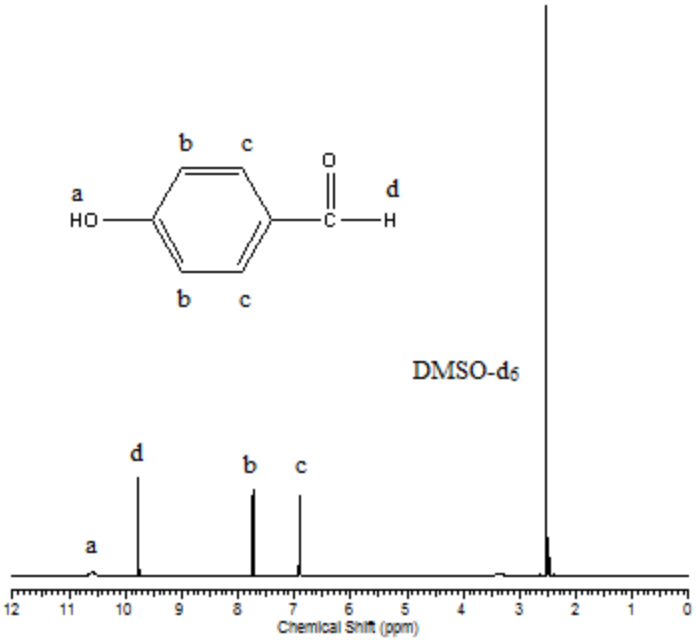

Figure 3.20 : ^{1}H-NMR spectrum of 4-hydroxy benzaldehyde.

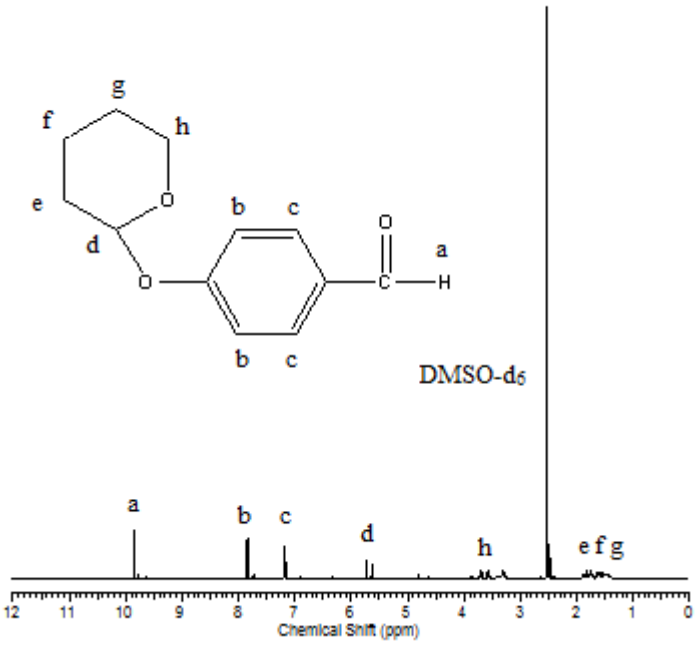

Figure 3.21 : ^{1}H-NMR spectrum of 4-tetrahydropyran-2-yloxyl benzaldehyde.

3.3.3 Synthesis of 4,4'-dihydroxychalcone

37.35 mmol (8.22 g) 4-tetrahydropyran-2-yloxyl-acetophenone was dissolved in 100 ml ethanol at 45^{o}C. 37.35 mmol (7.69 gr) 4-tetrahydropyran-2-yloxyl-benzaldehyde was added into the mixture. After that 40 % NaOH aqueous solution (3.74 gr) was added dropwise into the solution with constant stirring. Mixture was stirred at room temperature for 12 h. Product was filtered and dried in vacuum evaporator. Yield of the reaction is 70 %.

Completion of reaction was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques. For deprotection, 2.06 mmol (3.9 g) p-toluene sulfonic acid monohydrate was dissolved in 100 ml ethanol at 50^{o}C. 2.06 mmol (8.41 g) protected chalcone and 10 ml distilled water was added into the mixture and stirred for 4 hours at 50 ^{o}C.

After stirring, 50 ml distilled water and 25 ml of 5 % $NaHCO_3$ aqueous solution was added to the mixture. Product was filtered and dried in vacuum evaporator. Finally, 4,4'-dihydroxychalcone was obtained . Yield of the reaction is 50 % and the melting point of the product is 205^{o}C. Completion of reaction in Figure 3.22 was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

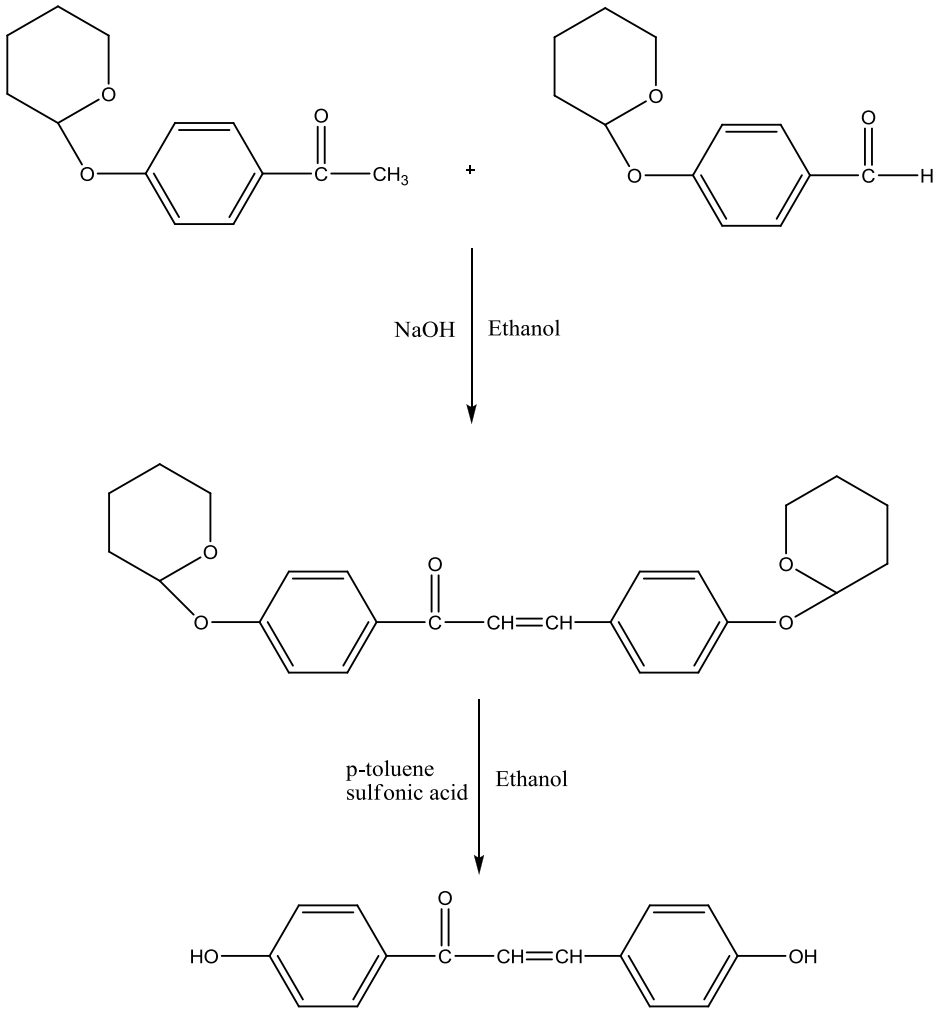

Figure 3.22 : Synthesis of 4,4'-dihydroxychalcone.

FT-IR spectrum of protected chalcone in Figure 3.23 shows that there is no characteristic –OH group peak at 3300 cm^{-1} region. –C=C– double bond and –C=O group peak observed at 1591 and 1651 cm^{-1} respectively. -CH_2 and -C-O-C- peaks of tetrahydropyranyl ether group occured at 2940 cm^{-1} and 1106 cm^{-1} respectively.

After deprotection in Figure 3.24, characteristic –OH group peak observed at 3289 cm^{-1} –C=C– double bond and –C=O group peak observed at 1600 and 1641 cm^{-1} respectively.

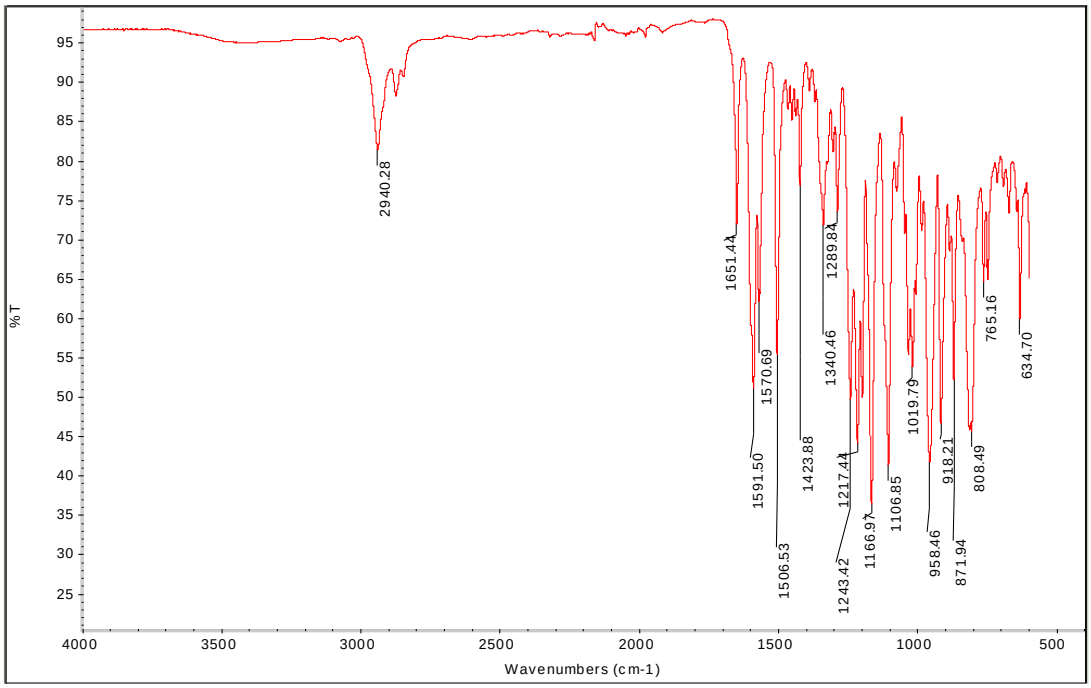

Figure 3.23 : FT-IR spectrum of protected chalcone.

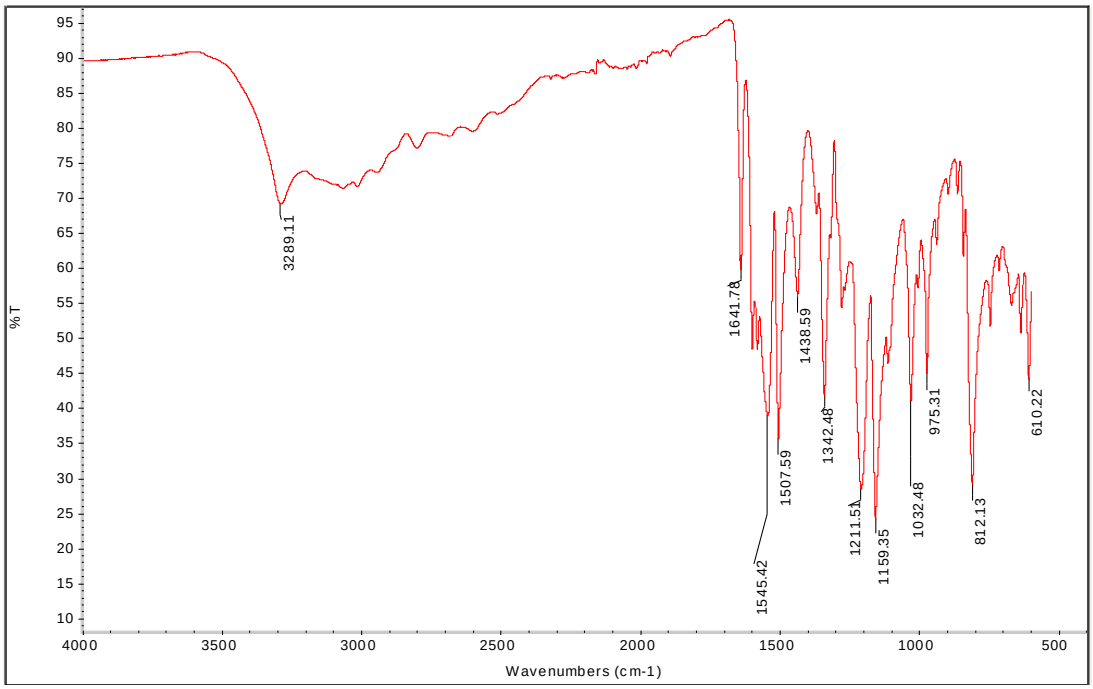

Figure 3.24 : FT-IR spectrum of 4,4'-dihydroxychalcone.

^{1}H-NMR result of protected chalcone in Figure 3.25 shows that there is no –OH group signal. Aromatic protons signals observed between 6-8 ppm, etheric protons signals between 1-4 ppm and –CH=CH– protons signals between 5-6 ppm. After deprotection in Figure 3.26, –OH group signal was observed at 10 ppm.

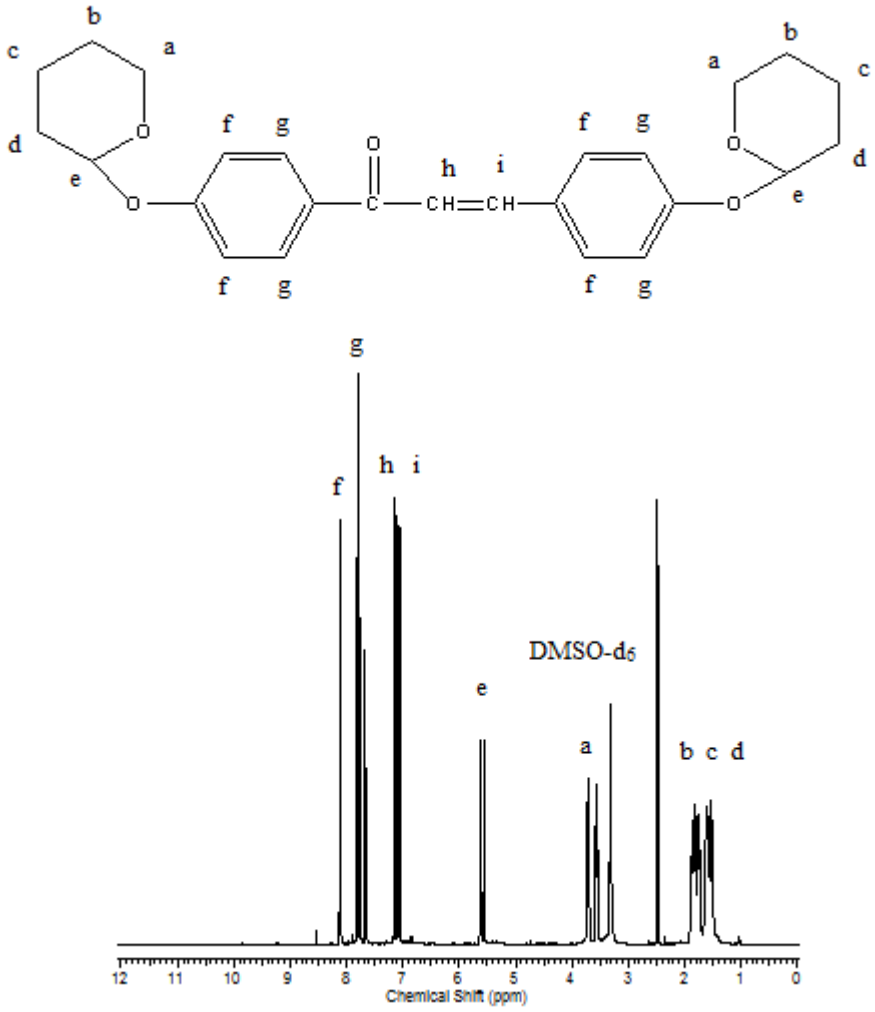

Figure 3.25 : ^{1}H-NMR spectrum of protected chalcone.

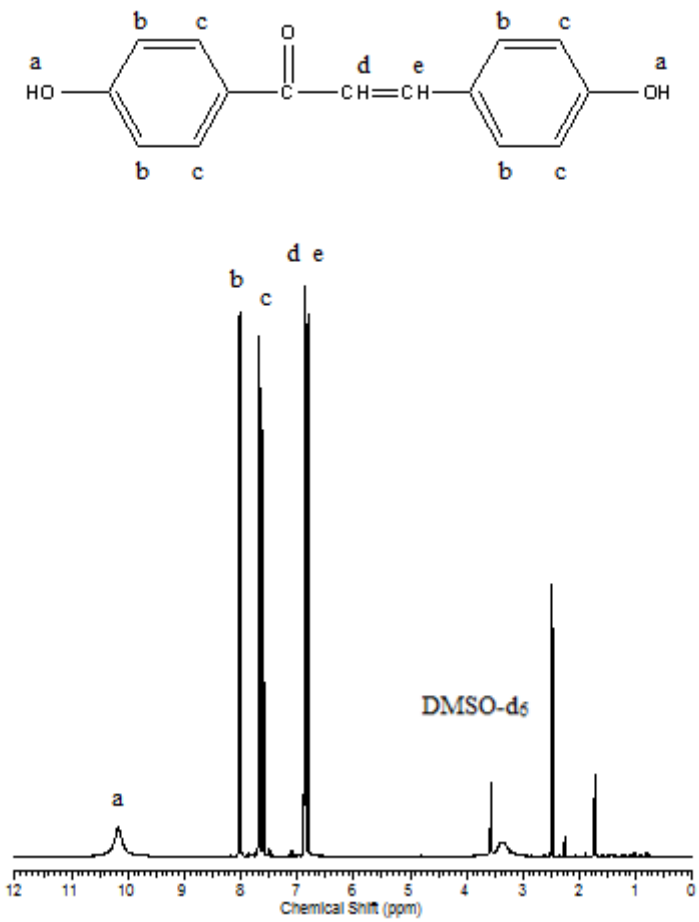

Figure 3.26 : ^{1}H-NMR spectrum of 4,4'-dihydroxychalcone.

3.3.4 Synthesis of Cyclohexanone Formaldehyde Resin

0.1 mol cyclohexanone, 0.02 mol cyclohexane, 0.08 mol formaldehyde (% 37 aqueous solution) was stirred until system reached 60^{o}C. When system reached this temperature 0.1 mol formaldehyde (% 37 aqueous solution) was added. pH of the mixture should be 11. To get basic conditions % 20 NaOH aqueous solution was added to the reaction mixture. Reaction mixture was stirred for 4 h at 80^{o}C. At the end of the reaction, resin washed with water, filtered and dried in vacuum evaporator. Yield of the reaction is % 90. Completion of reaction was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

3.3.5 Synthesis of Chalcone Modified Cyclohexanone Formaldehyde Resin

0.1 mol Cyclohexanone, 0.02 mol cyclohexane, 0.08 mol formaldehyde (% 37 aqueous solution), 0.01 mol 4,4'-dihydroxychalcone was stirred until system reached 60^{o}C. When system reached this temperature 1 mol formaldehyde (% 37 aqueous solution) was added. pH of the mixture should be 11. To get basic conditions % 20 NaOH aqueous solution was added to the reaction mixture. Reaction mixture was stirred for 6 h at 80^{o}C. At the end of the reaction, resin washed with water, filtered and dried in vacuum evaporator. Yield of the reaction is % 70. Completion of reaction was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

3.3.6 Synthesis of Acrylated Cyclohexanone Formaldehyde Resin

0.01 mol cyclohexanone formaldehyde resin dissolved in 100 ml chloroform. 0.09 mol triethylamine was added to the mixture at 0-5^{o}C. 0.09 mol acryloyl chloride was added to the resin mixture dropwise at 0-5^{o}C, stirred for 1 hour on ice bath and kept in room temperature for 1 day.

Reaction mixture was washed with HCl, saturated K_2CO_3, saturated sodium chloride solution and distilled water. Chloroform was evaporated and resin dried in vacuum evaporator. Yield of the reaction is % 70. Completion of reaction was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

3.3.7 Synthesis of Acrylated Chalcone Modified Cyclohexanone Formaldehyde Resin

0.01 mol chalcone modified cyclohexanone formaldehyde resin dissolved in 100 ml chloroform. 0.09 mol triethylamine was added to the mixture at 0-5^{o}C. 0.09 mol acryloyl chloride was added to the resin mixture dropwise at 0-5^{o}C, stirred for 1 hour on ice bath and kept in room temperature for 1 day.

Reaction mixture was washed with HCl, saturated K_2CO_3, saturated sodium chloride solution and distilled water. Chloroform was evaporated and resin dried in vacuum evaporator. Yield of the reaction is % 60. Completion of reaction was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

3.4 Preparation of Formulations

Film formulations were prepared according to Table 3.1. In formulations commercial epoxy resin, reactive diluents, photoinitiators and modified resins were used in indicated amounts.

Table 3.1 : Film formulations.

Sample	Ebecryl 605 (%)	ACFR (%)	ACMCFR (%)	HDDA (%)	DPGDA (%)	Irgacure 819 (%)
F1	50	-	-	10	38	2
F2	45	5	-	10	38	2
F3	40	10	-	10	38	2
F4	45	-	5	10	38	2
F5	40	-	10	10	38	2

3.4.1 Preparation of Test Samples

3.4.1.1 Free Films

Free film samples were prepared with a teflon mould with dimensions of 1 mm x 10 mm x 50 mm. Formulations were prepared according to the table, mixed homogeneously and kept in vacuum oven for 1 hour to remove air, then poured on the teflon mould. The mould were placed in EMA Curing instrument and passed several times. Cured films were kept at room temperature for a couple of days before performing tests. Thermal, stress-strain test, gel content, solvent resistance tests were applied on these films.

3.4.1.2 Coated Plexiglass Plates

1 g of formulation were placed on plexiglass surface and samples were cured in EMA Curing instrument and passed several times. Coated samples were kept at room temperature for a couple of days before performing tests. Contact angle, gloss, pendulum hardness, pencil hardness tests were applied on these coated samples.

3.5 Analysis

Following tests were applied to investigate effect of acrylated cyclohexanone formaldehyde resin and acrylated chalcone modified cyclohexanone formaldehyde resin on characteristic, thermal and mechanical behaviours of films and coated samples.

3.5.1 FT-IR Analysis

Completion of reactions were checked by FT-IR. FT-IR was used to investigate characteristic peaks of synthesized products.

3.5.2 NMR Analysis

Completion of reactions were checked by ^{1}H-NMR.^{1}H-NMR was used to investigate characteristic signals of synthesized products.

3.5.3 UV Analysis

UV Spectroscopy technique was used to determine chromofore groups of synthesized products and the formation of cyclobutane rings through [2+2] cycloaddition of the carbon-carbon double bond in the chalcone units.

3.5.4 Thermogravimetric Analysis

TGA was used to determine weight loss temperatures and char yields of cured films.

3.5.5 Gel Content Test

Gel content measurement was done to get polymerization degree of cured films. Cured film samples were weighed and put in the Soxhlet extractor and extracted for 6 hours with acetone. Films were dried until getting constant weight. Gel content of cured film was calculated with this equation.

$$\text{Gel content (\%)} = (m_2/m_1)*100$$

m_1= Initial weight of film

m_2= Residual weight of film

3.5.6 Solvent Resistance Test

Solvent resistamce test were done to get resistance of films to various solvents. Solvent resistance of cured films were determined with various solvents for one day. After that cured films were dried until getting constant weight. Solvent resistance of cured film was calculated with this equation.

$$\text{Weight loss (\%)} = (m_1-m_2)/m_1*100$$

m_1= Initial weight of film

m_2= Residual weight of film

3.5.7 Contact Angle Test

Contact angle instrument was used to investigate wetting behaviour of coated samples whether products are hydrophilic or hydrophobic.

3.5.8 Gloss Test

Gloss instrument was used to determine light reflecting properties of coated samples.

3.5.9 Pendulum Hardness Test

Pendulum hardness test was used to determine hardness behaviour of coated samples against applied force.

3.5.10 Pencil Hardness Test

Pencil hardness test was used to determine scratch behaviour of coated samples against applied force.

3.5.11 Tensile Loading Test

Tensile loading test was used to determine mechanical behaviours of cured films against applied force.

4. RESULTS AND DISCUSSION

In this thesis, cyclohexanone formaldehyde resin was modified with 4,4'-dihydroxychalcone and subsequently acrylated to obtain UV curable properties. Modified resin were employed as an oligomers on UV curable film formulations which contain epoxy resin, photoinitiator and reactive diluent.

Thermal and mechanical properties of cured and coated films were investigated with further tests.

4.1 Synthesis of Cyclohexanone Formaldehyde Resin

Cyclohexanone formaldehyde resin was synthesized according to procedure meentioned in section 3.3.4. Cyclohexanone and formaldehyde were reacted to obtain cyclohexanone formaldehyde resin. Completion of reaction in Figure 4.1 was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

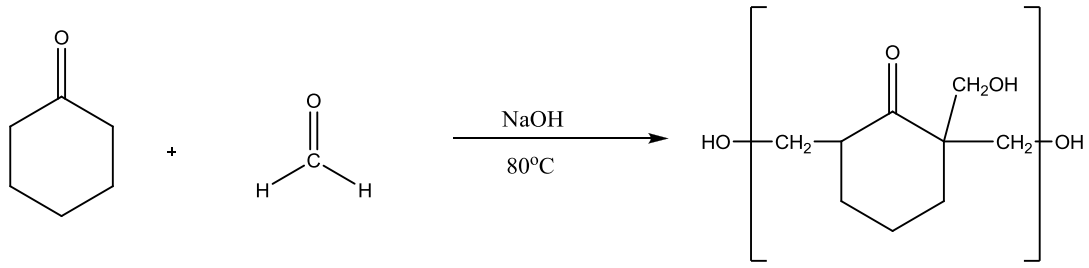

Figure 4.1 : Synthesis of cyclohexanone formaldehyde resin.

FT-IR spectrum of CFR in Figure 4.2 shows characteristic –OH group peak at 3380 cm^{-1}, -CH_2 peaks at 2929 and 2861 cm^{-1} and carbonyl group peak at 1697 cm^{-1}.

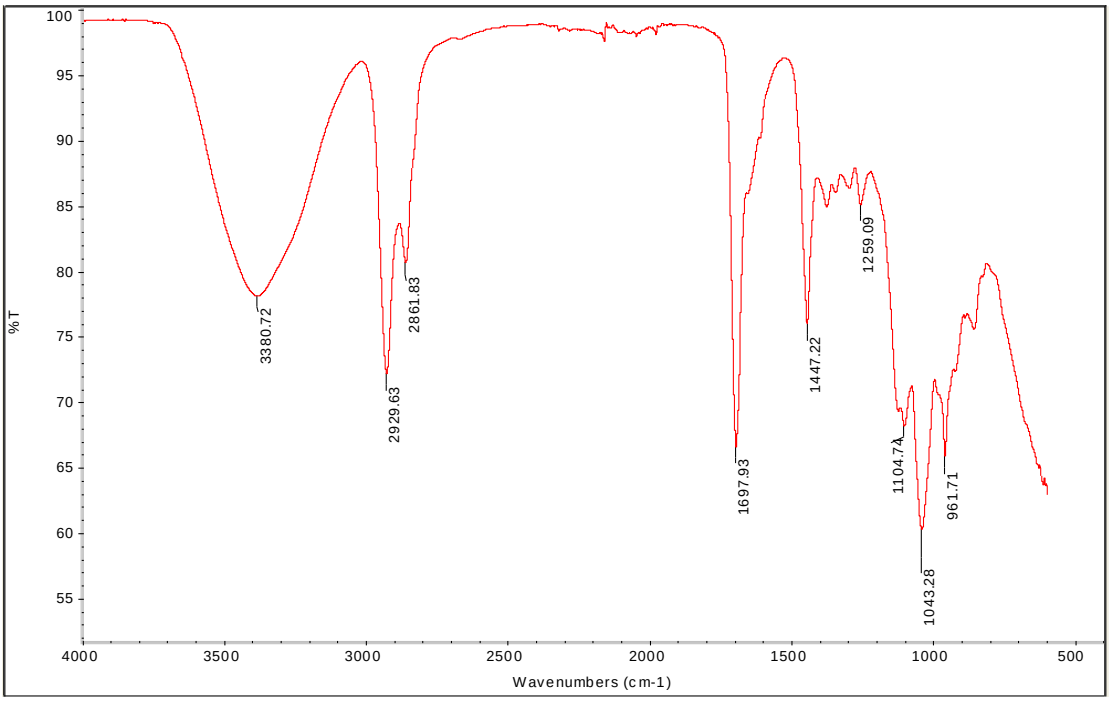

Figure 4.2 : FT-IR spectrum of CFR.

^{1}H-NMR result in Figure 4.3 shows signal originated from –CH_2 protons between 1-3 ppm, -CH_2OH protons between 3-5 ppm.

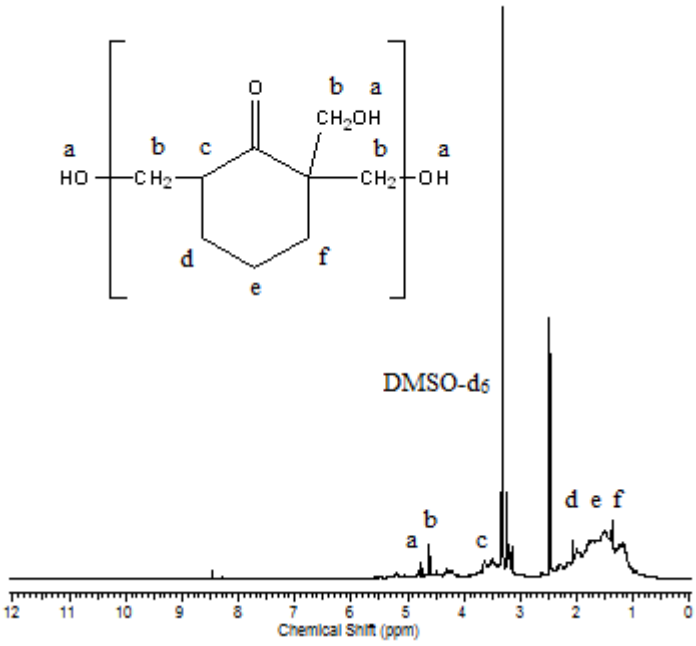

Figure 4.3 : ^{1}H-NMR spectrum of CFR.

4.2 Synthesis of Chalcone Modified Cyclohexanone Formaldehyde Resin

Chalcone modified cyclohexanone formaldehyde resin was synthesized according to procedure mentioned in section 3.3.5. Cyclohexanone, formaldehyde and chalcone were reacted to obtain chalcone modified cyclohexanone formaldehyde resin. Completion of reaction in Figure 4.4 was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

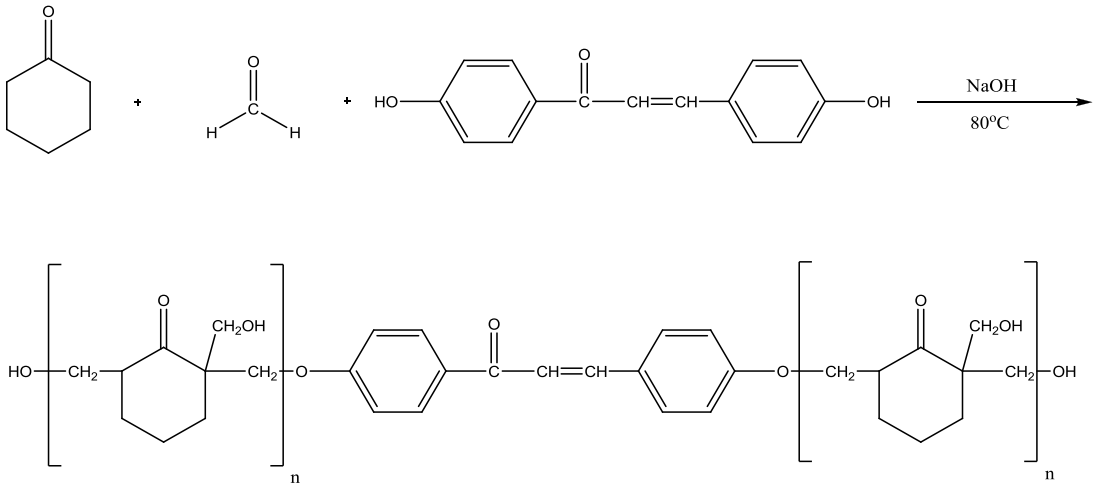

Figure 4.4 : Synthesis of chalcone modified cyclohexanone formaldehyde resin.

FT-IR spectrum of CMCFR shows in Figure 4.5 characteristic –OH group peak at 3390 cm^{-1}, -CH_2 peaks at 2929 and 2862 cm^{-1}, carbonyl group peak at 1707 cm^{-1}, –C=C– bond at 1600 cm^{-1} and aromatic group peak at 1577 cm^{-1}.

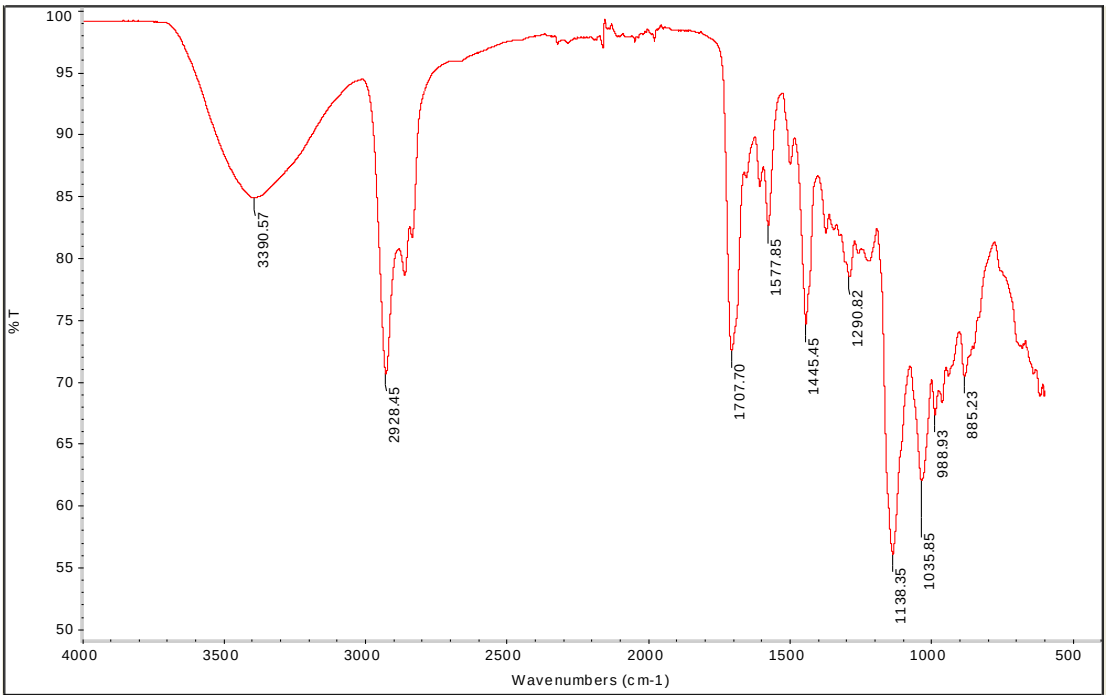

Figure 4.5 : FT-IR spectrum of CMCFR.

^{1}H-NMR result shows in Figure 4.6 signals originated from –CH_2 protons between 1-3 ppm, -CH_2OH protons between 3-4 ppm, olefinic and aromatic protons between 6-8 ppm corresponds to chalcone units.

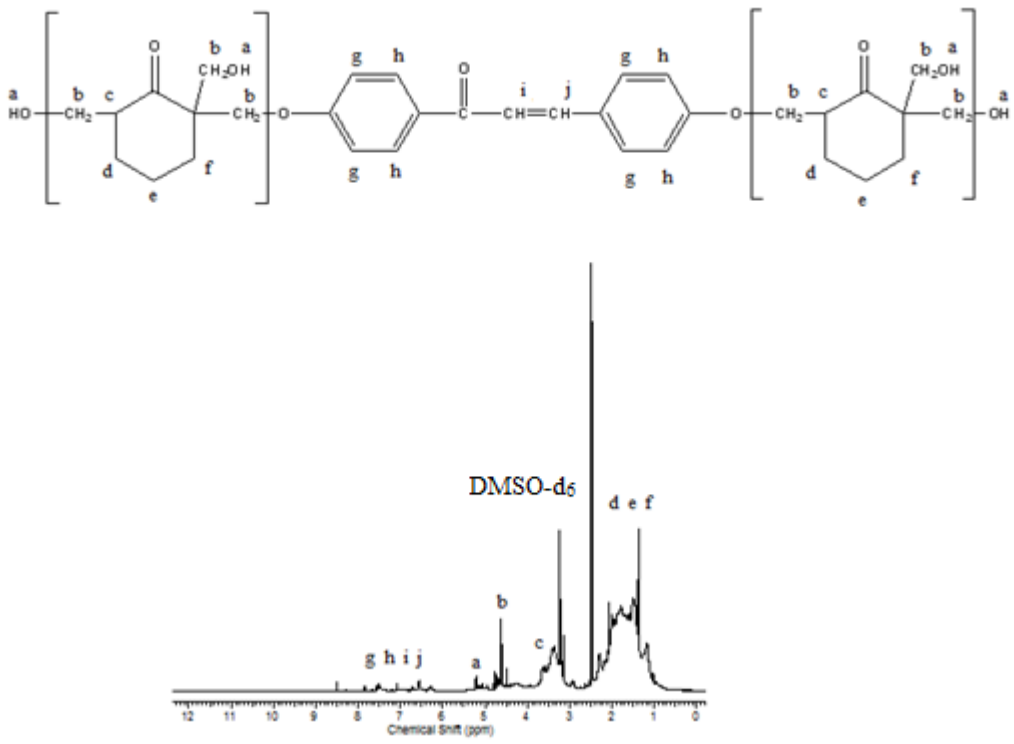

Figure 4.6 : ^{1}H-NMR spectrum of CMCFR.

4.3 Synthesis of Acrylated Cyclohexanone Formaldehyde Resin

Acrylated cyclohexanone formaldehyde resin was synthesized according to procedure meentioned in section 3.3.6 Cyclohexanone formaldehyde resin and acryloyl chloride were reacted to obtain acrylated cyclohexanone formaldehyde resin. Completion of reaction in Figure 4.7 was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

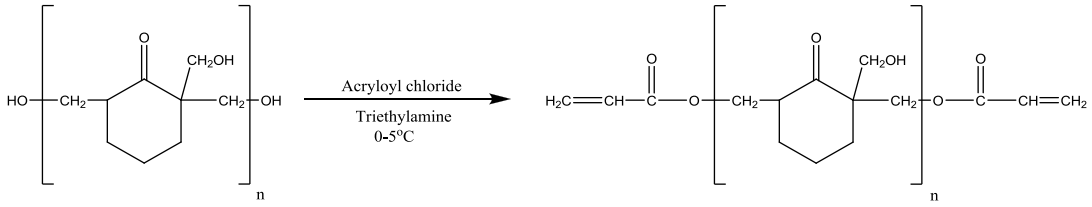

Figure 4.7 : Synthesis of acrylated cyclohexanone formaldehyde resin.

Acrylation reaction was followed with FT-IR spectrum in Figure 4.8 by decrease in –OH group peak of CFR at 3300 cm^{-1}. As a result of acrylation –C=C– peak observed at 1633 cm^{-1}.

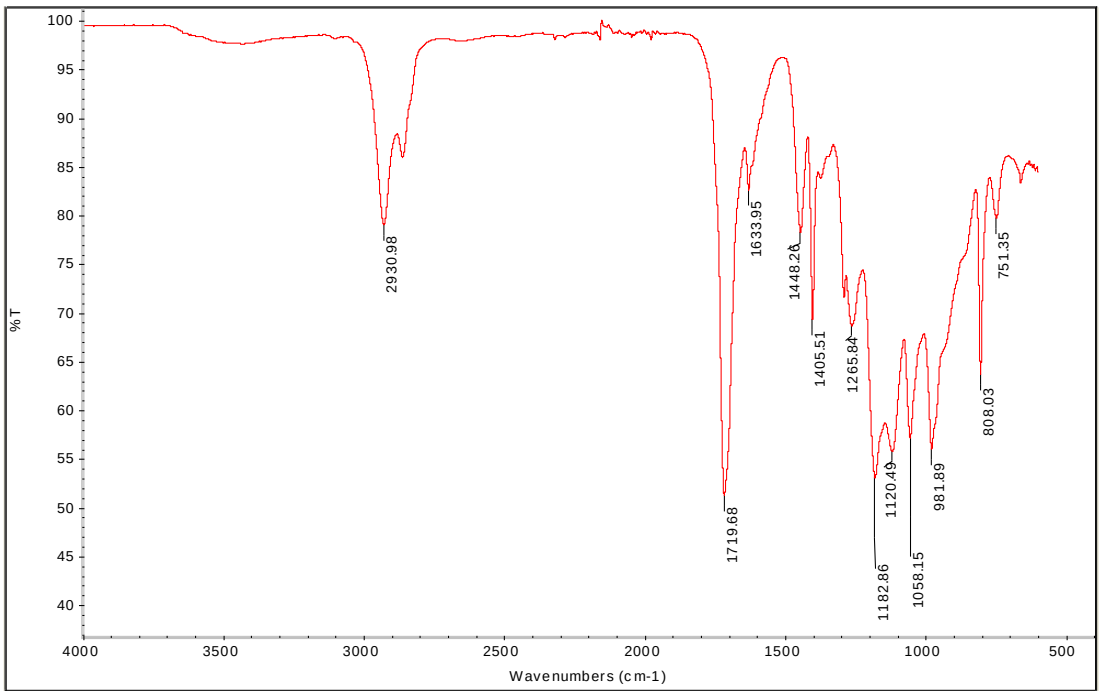

Figure 4.8 : FT-IR spectrum of ACFR.

^{1}H-NMR result shows in Figure 4.9 characteristic olefinic protons occured between 5-6 ppm. A significant decrease in –OH group signal between 3-4 ppm was also observed.

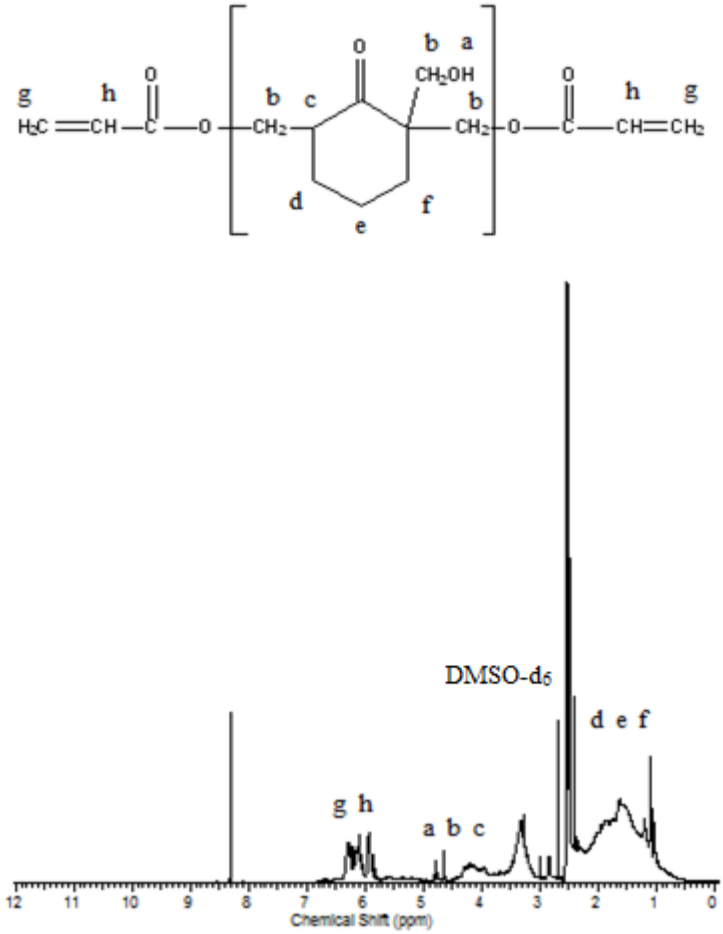

Figure 4.9 : ^{1}H-NMR spectrum of ACFR.

4.4 Synthesis of Acrylated Chalcone Modified Cyclohexanone Formaldehyde Resin

Acrylated chalcone modified cyclohexanone formaldehyde resin was synthesized according to procedure meentioned in section 3.3.7. Chalcone modified cyclohexanone formaldehyde resin and acryloyl chloride were reacted to obtain acrylated chalcone modified cyclohexanone formaldehyde resin. Completion of reaction in Figure 4.10 was checked by both FT-IR and ^{1}H-NMR spectroscopy techniques.

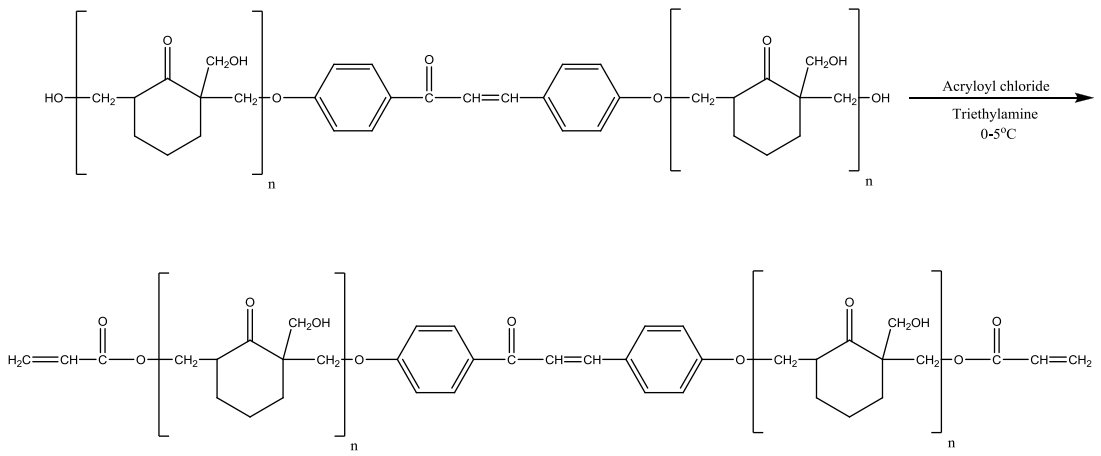

Figure 4.10 : Synthesis of acrylated chalcone modified cyclohexanone formaldehyde resin.

Acrylation reaction was followed with FT-IR spectrum in Figure 4.11 by decrease in –OH group peak of CMCFR at 3300 cm^{-1}. As a result of acrylation –C=C– peak observed at 1633 cm^{-1}.

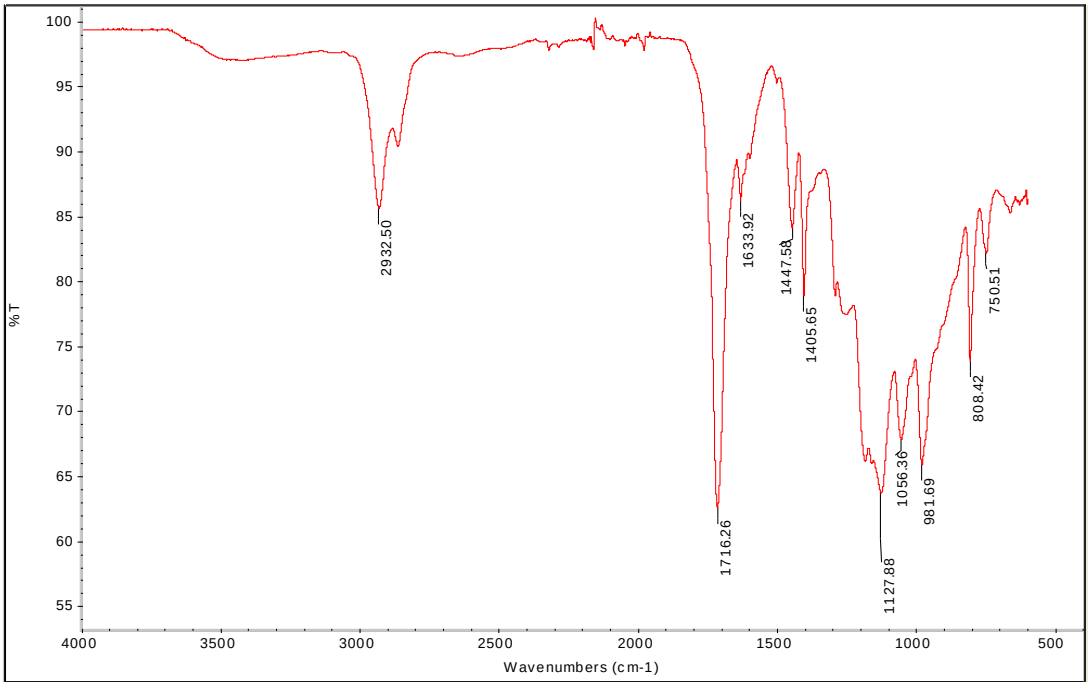

Figure 4.11 : FT-IR spectrum of ACMCFR.

^{1}H-NMR result shows in Figure 4.12 characteristic olefinic protons of vinyl and chalcone between 5-6 ppm, aromatis protons of chalcone observed between 6-8 ppm respectively. A significant decrease in –OH group signal between 3-4 ppm was also observed.

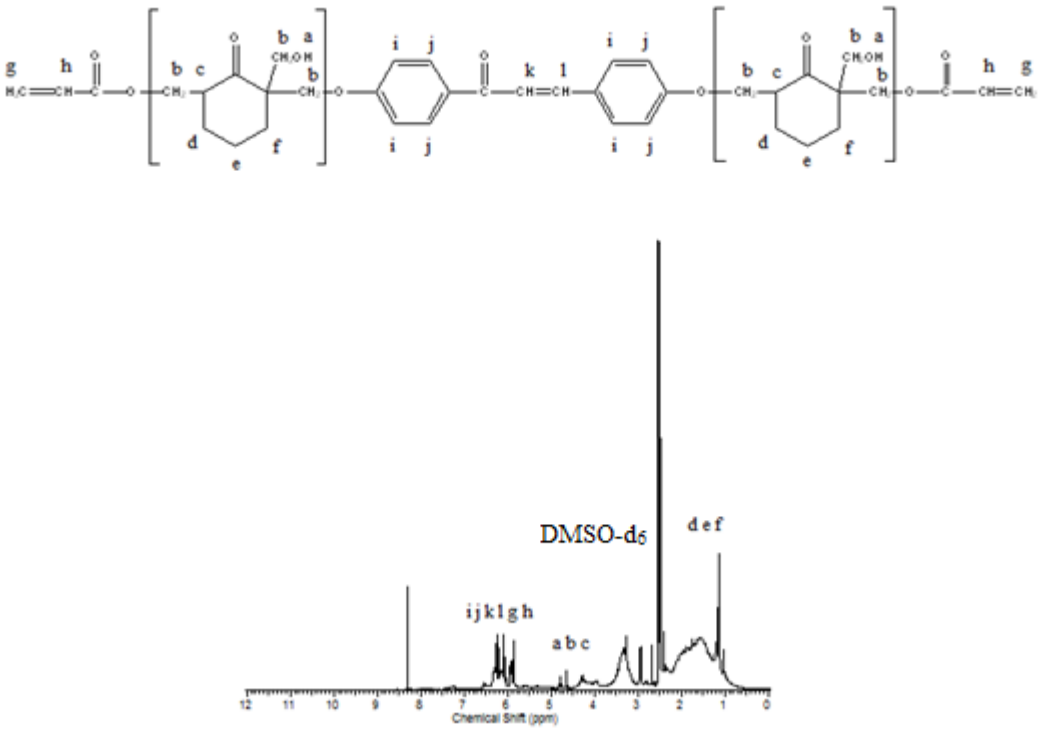

Figure 4.12 : ^{1}H-NMR spectrum of ACMCFR.

4.5 Photoreactivity Behaviour of Chalcone Modified Cyclohexanone Formaldehyde Resin

Changes in UV absorption of the CMCFR were followed by UV spectroscopy. The absorbance change at 332 nm was monitored during UV irradiation in Figure 4.13 as a result of cyclic structure formation.

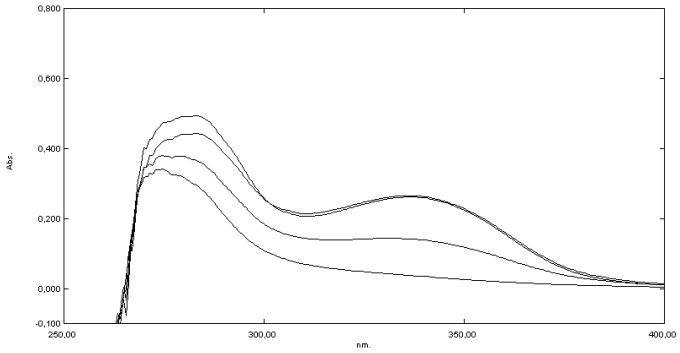

Figure 4.13 : UV spectra change of chalcone modified cyclohexanone formaldehyde resin during UV irridation.

Decrease in the absorbtion band at 332 nm was evident, which is attributed to the formation of cyclobutane rings through [2+2] cycloaddition of the carbon-carbon double bond in the chalcone units in Figure 4.14 upon UV irridation.

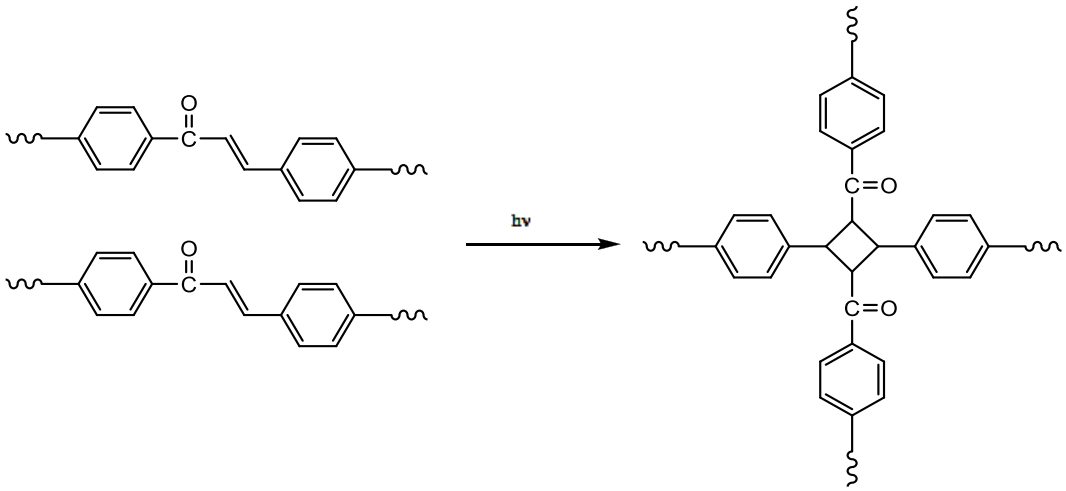

Figure 4.14 : Photocrosslinked –C=C– bond during UV irridation.

These results prove successful incorporation of chalcone moiety into the resin structure and resulting resins are expected to undergo cycloaddition reactions in Figure 4.15 via carbon-carbon double bond of chalcone units.

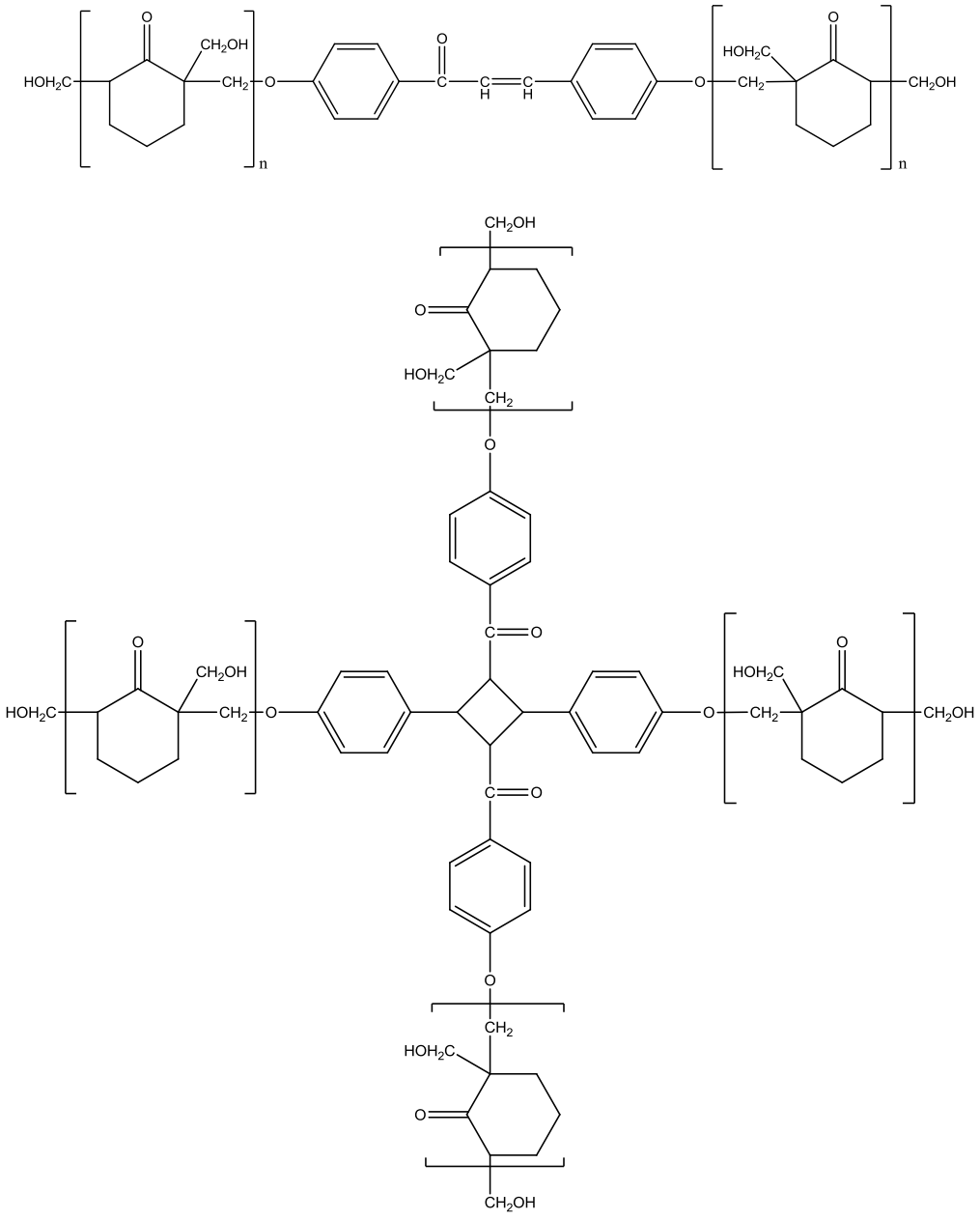

Figure 4.15 : Cyclic structure formation of cyclohexanone formaldehyde resin during UV irridation.

4.6 Film Formation

Films were prepared according to procedure mentioned in section 3.4. Further test were performed to the cured and coated films.

4.6.1 Thermogravimetric Analysis

Thermogravimetric analysis were performed in nitrogen atmosphere with heating rate of 20^{o}C/min between 30^{o}C and 800^{o}C. TGA results were listed in Table 4.1

Table 4.1 : TGA results of cured films.

Sample	% 5 Weight loss temperature (^{o}C)	% 50 Weight loss temperature (^{o}C)	Residue (%)
F1	363	432	8,1
F2	362	430	5,5
F3	357	430	6,1
F4	362	432	7,1
F5	357	430	6,2

TGA results show that both ACFR and ACMCFR resins don't have significant effect on % 5 and % 50 weight loss temperature on films. Char yield of cured films were decreased with increase in both resins content.

4.6.2 Gel Content

Gel content test was performed to measure polymerization degree of films. Gel content results were listed in Table 4.2.

Table 4.2 : Gel content results of cured films.

Sample	Gel Content (%)
F1	100
F2	98,5
F3	96,1
F4	98,8
F5	98,6

Gel content results indicate that increase in acrylated ACFR content in formulations resulted with decrease in polymerization degree of films. On the other hand, incorporation of ACMCFR in formulations resulted higher polymerization degree of films due to the cyclobutane ring formation. Unreacted part of the cured films are under % 4.

4.6.3 Solvent Resistance

Solvent resistance results show resistance behaviours of films against solvents. Solvent resistance and appearance results were listed in Table 4.3 and Table 4.4.

Table 4.3 : Solvent resistance results of films.

	Weight loss (%)				
Solvent	F1	F2	F3	F4	F5
Xylene	< 1	< 1	< 1	< 1	< 1
Chloroform	-	-	-	-	-
Asetic Acid	< 1	< 2	< 1	< 1	< 1
Methanol	< 1	< 1	< 1	< 1	< 1
NaOH	< 1	< 1	< 2	< 1	< 1
HCl	< 1	< 1	< 1	< 1	< 1

Table 4.4 : Appearance results of films.

	Appearance				
Solvent	F1	F2	F3	F4	F5
Xylene	Good	Good	Good	Good	Good
Chloroform	Brittle	Brittle	Brittle	Brittle	Brittle
Asetic Acid	Good	Good	Good	Good	Good
Methanol	Good	Good	Good	Good	Good
NaOH	Good	Good	Good	Good	Good
HCl	Good	Good	Good	Good	Good

Solvent resistance results show that cured films don’t have resistance against chloroform but have resistance to other solvents and chemicals.

4.6.4 Contact Angle

Contact angle result show wetting behaviour of coated samples whether products are hydrophilic or hydrophobic. Contact angle results were listed in Table 4.5.

Table 4.5 : Contact angle results of coated films.

Sample	Water Contact Angle (^{o})
F1	68
F2	64
F3	66
F4	64
F5	65

Contact angle results show that all of cured films show hydrophilic behaviour due to the having polar groups in the structures.

4.6.5 Gloss

Gloss result show light reflecting properties of coated samples. Gloss results were listed in Table 4.6.

Table 4.6 : Gloss results of coated films.

	Gloss (^{o})	
Sample	20^o	60^o
F1	152	150
F2	154	155
F3	157	158
F4	155	154
F5	151	152

Incorporation of thermoplastic resin into the formulation improve gloss results of samples. Gloss results shifted to higher values with increase in ACFR content. According to the increase in ACMCFR in the formulation, gloss values were not improved as much as ACFR based formulations.

4.6.6 Pendulum Hardness

Hardness of a coating depends mainly on chain flexibility of the molecules and crosslinking density. Pendulum hardness test shows surface hardness in combination with surface friction. Pendulum hardness results were listed in Table 4.7.

Table 4.7 : Pendulum hardness results of coated films.

Sample	Pendulum Hardness
F1	86
F2	84
F3	83
F4	84
F5	88

Pendulum hardness values of coated films were decreased with increase in ACFR in the formulation due to the thermoplastic behaviour. Due to the photocrosslinking behaviour, ACMCFR based formulations showed nearly same pendulum hardness values compared to epoxy film.

4.6.7 Pencil Hardness

Pencil hardness test measures the surface hardness in combination with surface scratch. Pencil hardness results were listed in Table 4.8.

Table 4.8 : Pencil hardness results of coated films.

Sample	Pencil Hardness
F1	6H
F2	6H
F3	5H
F4	6H
F5	6H

Pencil hardness of coated films were decreased according to increase in ACFR content in the formulation because of its thermoplastic behaviour. As a result of photocrosslinking behaviour of chalcone units, pencil hardness values of ACMCFR same as epoxy film.

4.6.8 Tensile Loading

Mechanical properties were seriously affected by the crosslink density and chemical composition of the polymeric films. Tensile test results were listed in Table 4.9.

Table 4.9 : Tensile test results of cured films.

Sample	Modulus (MPa)	Tensile Strength (MPa)	Elongation At Break (%)
F1	870	32	5
F2	844	24	4
F3	645	19	6
F4	850	28	5
F5	861	32	5

Modulus of cured films were decreased with increase in ACFR content in the formulations. ACFR showed thermoplastic behaviour and increased flexibility of cured films. On the other hand, modulus of cured films were increased with increase in ACMCFR content in the formulations. Films became harder due to the cyclobutane ring formation of chalcone units of ACMCFR.

5. CONCLUSIONS

In this thesis, UV curable cyclohexanone formaldehyde resins, ACFR and ACMCFR having 4,4'-dihydroxychalcone moiety in the structure were synthesized and characterized by FT-IR and ^{1}H-NMR spectroscopic techniques. ACFR and ACMCFR were incorporated as an oligomer in UV curable coating formulations to introduce the benefits of thermoplastic resins and UV active chalcone groups into UV curing technology. The coating performances and thermal properties of UV cured films were evaluated.

Thermal properties of films were analysed by TGA. Results show that incorporation of ACFR and ACMCFR resins don't have significant effect on weight loss temperature of UV cured films. Residue of cured films were decreased with increasing resin content in UV curable formulations.

Mechanical properties of UV cured films were seriously affected in the presence of resins. Due to the thermoplastic behaviour of ACFR, decrease in modulus and tensile strength values were recorded compared to that of neat epoxy resin based films. On the other hand, due to the photocrosslinking behavior and rigidity of chalcone units of ACMCFR, modulus and tensile strength values of films were found to be in the same order with neat epoxy resin based films.

Pendulum hardness results are affected by nature of material and crosslink density of materials. Because of thermoplastic behaviour of ACFR, pendulum hardness values decreased. Due to the increasing crosslinking density and rigidity of chalcone groups of ACMCFR, pendulum hardness results were found nearly same as epoxy film.

Pencil hardness results indicated that an increase in ACFR content in formulation resulted lower pencil hardness values due to the thermoplastic behavior of ACFR. In the case of ACMCFR, pencil hardness values were found quite close to that of neat

epoxy film due to the contribution of chalcone groups on photocrosslinking efficiency and rigidity. .

The gel content values of UV cured films including ACFR and ACMCFR resins were found over 95% indicating the formation of network structure.

UV cured films showed good resistance to all chemicals and solvents except for chloroform.

Contact angle results indicated that all of the samples have hydrophilic behavior.

Gloss values shifted to higher values with increasing ACFR content, but ACMCFR based resin did not have a significant affect on the gloss values.

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