İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF MODIFIED EPOXY ACRYLATE RESIN

M.Sc.Thesis by
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Department: **Polymer Science and Technology**

Programme: **Polymer Science and Technology**

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

MODİFİYELİ EPOKSİ AKRİLAT SENTEZİ

YÜKSEK LİSANS TEZİ
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FOREWORD

This study has been carried out in POLMAG Laboratory (Polymeric Materials Research Group), Faculty of Science and Letters, Istanbul Technical University.

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December, 2010 Ömer Faruk VURUR

Polymer Science & Technology Department

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ABBREVIATIONS

T **:** Terephthalic acid modified epoxy acrylate
Si-T **:** Terephthalic acid modified epoxy acrylate with VTS
UA-T **:** Terephthalic acid modified epoxy acrylate with urethane acrylate
UA **:** Urethane acrylate
VTS **:** Vinyl trimethoxysilane
IPDI **:** Isophorone diisocyanate
HEMA **:** 2-Hydroxy ethyl methacrylate
UV **:** Ultra Violet
NMR **:** Nuclear Magnetic Resonance
TGA **:** Thermal Gravimetrical Analysis
FT-IR **:** Fourier Transform Infrared
DPGDA **:** Dipropyleneglycoldiacrylate
DBTL **:** Dibutyl Tinlaurate
HDDA **:** 1,6-hexanedioldiacrylate

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SYNTHESIS OF MODIFIED EPOXY ACRYLATES

SUMMARY

In recent years, UV curable coating techniques have attracted great attention due to its advantages over thermal curing techniques. The UV curing system is a high-speed process where UV light induces the polymeric film formation leading to a fast transformation of the wet film into the solid film. UV-curing formulations provide some benefits such as fast cure response,excellent chemical resistance, good weathering characteristics, and broad formulating latitude. In the field of UV curing industries, epoxy and epoxy acrylate derivatives have been widely used as coatings, structural adhesives and advanced composite matrices. Epoxy resins are a major class of commercial resins and they are characterized by the possession of more than one 1,2-epoxy groups per molecule, which are the active centers of the resin. What distinguishes epoxy resins from the other polymers is their excellent chemical and solvent resistance, good thermal and adhesion properties, versatility in cross-linking. Besides organic–inorganic hybrid materials have gained considerable attention recently because of its superior mechanical properties, thermal stability, and optical properties. Of particular interest is the acrylic–silica hybrid which has found great use in the optical membrane application. While acrylics provide easy processibility and optical transparency, silica particles provide hardness and scratch resistance. However, the incompatibility between the acrylics and the silica causes poor dispersion of silica particles in the acrylics matrix and makes a direct blending of acrylics and silica particles impossible. Therefore, significant efforts have been devoted to forming chemical bonding between the acrylics and silica particles. Because the sol-gel processes, which involve an in situ formation of bonded silica particles via the reaction of tetraethylorthosilane with preformed acrylic polymers containing alkoxysilane functional groups, often require a significant amount of effort to eliminate the byproducts (water or alcohol) and a prolonged time to reach the desired extent of reaction, attempts on using acrylic monomers with preformed silica particles which have been functionalized with compatible and copolymerizable organic species have been made.

In this study, diglycidyl ether of bisphenol A (DGEBA) epoxy resin was reacted with various amounts of terephthalic acid and acrylic acid. The formed resin was used for preparing three different formulations, coated and cured by UV light. The characterizations of coatings were performed by spectroscopic tools and the thermal and mechanical properties of the formulations were investigated.

MODİFİYELİ EPOKSİ AKRİLAT SENTEZİ

ÖZET

Son yıllarda UV kürlenebilir kaplama teknikleri avantajlarından dolayı termal kürlenebilir tekniklerine göre daha büyük bir ilgi çekmektedir. UV kürlenebilir sistemi; UV ışının ıslak filmden katı filme hızlı bir dönüşüme yol açan polimerik film oluşumuna neden olduğu hızlı bir işlemdir. UV kürlenebilir formülasyonlar hızlı kürlenme, mükemmel kimyasal direnç, iyi şartlanma özellikleri ve geniş formule edilebilir kapsamı gibi bazı faydalar sağlarlar. UV ile kürleme endüstrisinde epoksi ve epoksi akrilat türevleri kaplamalar, yapı yapıştırıcıları, ileri komposit materyalleri olarak geniş bir çerçevede kullanılmaktadır. Epoksi reçineler ticari reçinelerin büyük bir sınıfıdır ve reçinenin aktif merkezi olan her moleküldeki birden fazla epoksi grubuna sahip olma özelliği ile tanımlanır. Epoksi reçineleri diğerlerinden ayıran şey mükemmel kimyasal ve solvent direncidir, iyi ısısal ve yapışma özellikleri, çapraz bağlanmada çeşitliliğidir. Bunun yanı sıra organik-inorganik hibrid materyaller süper mekanik özellikler, ısısal kararlılık ve optiksel özelliklerinden dolayı büyük bir ilgi kazanmaktadır. Asıl ilgi de optiksel membran uygulamasında büyük bir kullanım barındıran akrilik-silika hibrid materyalidir. Akrilikler kolay işlenebilirlik ve optiksel geçirgenlik sağlıyorken, silika partikülleri sertlik ve çizilme direnci sağlar. Ama silika ve akrilikler arasındaki uyumsuzluk akrilik malzemesindeki silika partiküllerinin kötü dispersiyonuna neden olur ve silika ve akriliklerin direkt bir karşımını imkansız kılar. Bu yüzden akrikler ve silikalar arasındaki kimyasal bağların oluşumuna önemli eforlar harcanılmaktadır. Alkoksisilan grubu taşıyan öncül akrilik polimerlerle tetraetilortosilanın reaksiyonu vasıtasıyla bağlı silikanın yerinde oluşumunu gerektiren solgel işlemleri, istenilen reaksiyon derecesine ulaşmak için uzatılmış zaman ve alkol su gibi ürünleri yok edebilecek önemli eforları gerektirdiğinden dolayı uygun ve kopolimerize edilebilir organik türlerle fonsiyonlaştırılmış öncül silika partiküllerle akrilik monomerlerini kullanma girişimleri yapılmaktadır.

Bu çalışmada digilisidileter bisfenol A epoksi reçine tereftalik asit ve akrilik asitin değişen oranlarıyla reaksiyona sokuldu. Oluşan reçine üç farklı formülasyon hazırlamada kullanıldı, kaplandı ve UV ışığıyla kürlendi. Kaplamanın özellikleri spektroskopik aletlerle ölçüldü ve formülasyonların ısısal ve mekanik özellikleri incelendi.

1. INTRODUCTION

Early surface coatings were limited mainly to air drying systems which film formed by either evaporation of solvent, to leave a dried film of the natural resin or oxidative crosslinking of any unsaturation present in vegetable oil based binders. French polish, based upon shellac is an example of the first type of coating, whilst alkyds or oleoresinious based systems are example of the latter.

Today coatings can be divided into thermoplastic and thermoset. Thermoplastic systems primarily film form by the evaporation of solvent. As a general rule, thermoplastic coatings are based on high molecular weight polymers. Solutions of high molecular weight thermoplastic resins are normally too high in viscosity for the desired applications solids, hence dispersions of thermoplastic resins are frequently used.

The natural resins were used in the protective surface coatings industry in the past but the use of natural resins has decreased in the USA since about 1930, when they were replaced by synthetic resins.The one type of synthetic resin is epoxy resin. Epoxy resins only became commercially avaliable in about 1947 [1]. Epoxy resins are commercially used in coating and various applications. The largest single use in coatings, where high chemical and corrosion resistance and adhesion are important. The presence of unsaturation at the end of the polymer backbone as a result of the reaction with acid functional acrylic monomers hs shaped epoxy resins for the radiation curing industry. Terminal unsaturated double bonds are the reactive sites for coatings and paints [2-6]. Unsaturated monofunctional and multifunctional acrylated monomer and acrylated oligomers having epoxy backbone are capable of a rational designed formulation that provides good coating properties after curing. In general, the cure process is radical and results in three dimensional network formation. The curing process is the faster and depends on the radiation dose and the time of radiation. UV curing, i.e., the process of photoinitiated conversion of polymeric materials from a liquid to a solid is a popular alternative to conventional thermal curing. UV curing process has attractive advantages over thermal curing.

Their major advantages are high speed process, low energy consumption due to the operation at room temparature, and enviromental friendliness by avoiding solvent exposure [7-9].

This thesis will concern the preparation of bifuctional resin formed by reaction between epoxy acrylate oligomer and terephthalic acid at different modification ratio. The modified resin is crosslinked by photo polymerization and characterized by thermal and mechanic analaysis. The coating performance is also examined.

2. THEORETICAL PART

2.1 Epoxy Resins

2.1.1 Introduction

Epoxy resins are organic compounds with more than one epoxide (IUPAC: oxirane) group per molecule which are used to obtain prepolymers. The term ‘resins’ is now generally accepted although misleading since the compounds refferred to are low molecular mass or oligomeric compounds. Polymerization by polyaddition is based on the characteristic behaviour of epoxide groups to react with suitable reaction partners by addition. The reactivity and functionality of the di-, tri- and tetra-epoxide compounds (epoxy resins) and crosslinking compounds (curing agents) must however correspond to each other.Epoxy resins can also be crosslinked directly by polymerization of the epoxide groups. The designations ‘resin’ and ‘curing agent’ or ‘hardener’ are historical in origin but are totally irrelevant from a scientific viewpoint. Epoxy resins systems (resin/hardener combinations) are used primarily to obtain crosslinked polymers which are also usually termed ‘epoxy resins’ but, correctly, should be described by detailing the crosslinking components. The use of diepoxide compounds with bifunctional addition components results in linear, soluble strcture. Adding small amounts of trifunctional components leads to branched soluble structure. Because of the numerous possibilities of combining resin and curing agent structures (known technically as formulation), the properties of epoxy resin systems are particularly easy to adjust, firstly as far as viscosity and rheological characteristics during processing, and secondly, as far as properties of the end product are concerned (tailor-made plastics). The range of applications can be considerably expanded by judicious addition or incorporation of additives such as fillers, reinforcements, flame retardants, flexibilizers and pigments. In contrast to the soluble melt-processable thermoplastics, crosslinked epoxy resins can not be shaped by heat. Their industrial application must therefore be performed in the non-crosslinked state (in sollution if necessary) and the crosslinked state achieved by heat treatment or suitably extended curing times at ambient temperature [10].

Although the first products that would now be called epoxy resins were synthesized as early as 1891 it was not until the independent work of Pierre Castan in Switzerland and Sylvan Greenlee in the United States that commercial epoxy resins were marketed in the 1940s, although similar resins had been patented in the 1930s. The earliest epoxy resins marketed were the reaction products of bisphenol A and epichlorohydrin (Figure 2.1.) and this is still the major route for the manufacture of most of the resins marketed today, although there are many other types of resin available [11].

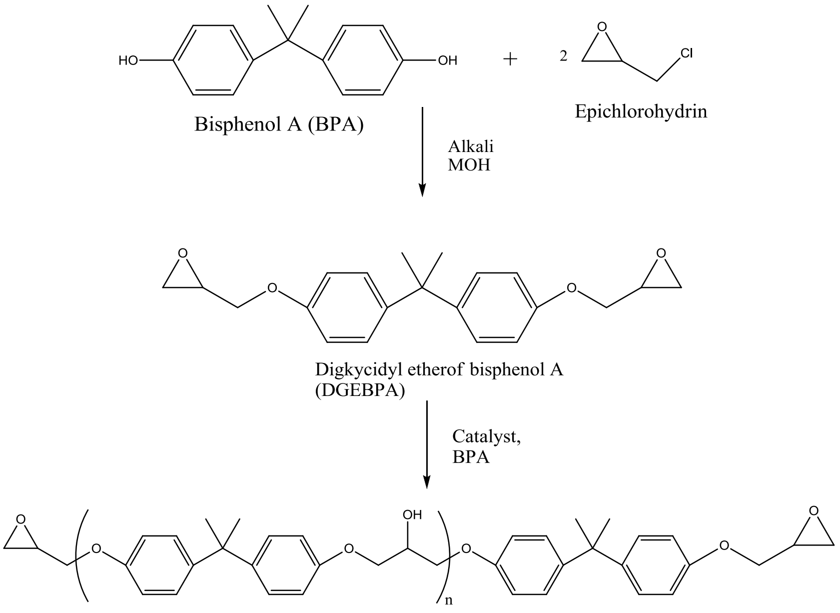


Figure 2.1: Reaction of bisphenol A and epichlorohydrin

Epoxy resins are synthetic and are not the lowest cost resins potentially avaliable for most applications. Thus they most confer a property or properties to the final product which justifies their additional cost. In almost all cases they impart outstanding chemical /corrosion resistance to the cured film. If this is not required then the formulator can consider other lower cost options. Protective coatings are an area in which it is difficult to math the performance of epoxy resins at similar cost, particularly when the value of the article being protected is considered. Epoxy resins are commercially avaliable either as solids or liquids. Generally the higher the molecule weight the higher the melting point. Grades of liquid epoxy resins vary in viscosity. It is possible to obtain epoxy resins dissolved in organic solvents or containing reactive diluents to reduce viscosity. Waterbased emulsions of some epoxy resins are also commercially available. Epoxy resins are not only used simply as epoxy resin with a curing agent, but they frequently modified by further chemical reaction prior to incorporation in the coating formulation. The main objective is to give an overview of the relevance of epoxy resins to the coatings industry. Only minimal details of production processes wil be given to enable the reader to understand something of the limitations of the manufacture of the resins [12].

The cure of epoxy resins involves the formation of a rigid three-dimensional network by reaction with hardeners which have more than two reactive functional groups, that is, functionality is $f > 2$. Often $f > 4$ for common hardeners for bisphenol A epoxy resins which often have an effective functionality of two, but may be higher when the cure temperature is high enough for the secondary hydroxy groups to react.The cure of epoxy resins is complicated and it is useful to visualize the process in several stages, although except for gelation, the process is continuous. Initially there is reaction between epoxy and hardener reactive groups so that somewhat larger molecules are formed. As cure proceeds, larger and larger molecules are formed but it should be noted that the average molecular size is still small even when half the reactive groups have reacted. When the molecular size increases as cure progresses, some very highly branched molecules are formed and then more and more highly branched structures develop. The critical point is gelation when the branched structures extend throughout the whole sample. Prior to gelation the sample is soluble in suitable solvents but after the gel point the network will not dissolve but swells as it imbibes solvent. At the gel point small and branched molecules are present which are soluble, hence the curing sample contains sol as well as gel fractions. The gel initially formed is to continue until most of the sample is connected into the three-dimensional network so that the sol fraction becomes small and for many cured products it has to be essentially zero [13].

The cured epoxy systems have one main drawback, their considerable brittleness. For instance, cured epoxy systems typically display a low fracture toughness below 1.0 MPa·m1/2 and have poor resistance to crack propagation . This inherent brittleness has limited the applications of the epoxy resins in fields requiring high impact and fracture toughness. Therefore, in the past several decades, much attention has been focused on improving the fracture resistance of epoxy resins. It is widely believed that the brittleness of epoxy resins is associated with their highly cross-linked structures, which absorb insignificant amounts of energy during the fracture process. The cured epoxy resins have fracture energies (GIC = 100 to 200 J/m2) two orders of magnitude lower than many thermoplastics and other high-performance materials [14-17]. Most of the research has been focused on improving the fracture properties of epoxy resins by either reducing the crosslinking density of the epoxy network or modifying commercially available epoxy resins with secondary components. This review will focus on the second approach: modifying epoxy resins using secondary components/modifiers to improve their toughness. The research on reducing the crosslinking density of the epoxy network will be briefly discussed. The fracture behavior of epoxy resins is a complex phenomenon; and it can be affected by many factors such as the properties of the modifiers, the compatibility between the dispersed modifier phase and the epoxy matrix phase, and the curing conditions. In the past decades, many researchers have studied how these parameters influence the properties of toughened thermosetting materials. Several toughening theories or models based on thermoplastic and rubber-toughened thermoset resins have been established in order to explain the increased fracture toughness and to predict the extent of toughness improvement.

2.1.2 The Chemistry of The Epoxy Group

The geometrical structure of the epoxy ring is planar, with bond angles and lengths determined from electron diffraction and microwave spectroscopic measurements which have been discussed by Lwowski, Lewars and Peters. The differences in bond angle from dimethyl ether are considerable, and there must be considerable ring strain due to angular distortion from the tetrahedral carbon angle of 109°. The dipole moment of simple ethers is 1.1 to 1.3 D and that for ethylene oxide is 1.82 and 1.91 D in benzene solution and the vapour phase respectively. The ionization potential of the oxygen 2pл lone pair in ethylene oxide is 10.6 to 10.8 eV which is rather higher than that of dimethyl (10.0 eV) and diethyl (9.5 eV) ethers which has compared with the ionization energies of other simple oxygen compounds. The electronic structure of three-membered rings poses difficult problems since with a C-O-C or C-C-C bond angle of about 60° the ‘normal’ sp^3 hybridization with linear bonds between the ring atoms is impossible. The bonding in cyclopropane has been discussed extensively and Halton [18-19] in an interesting review of ring strain in cyclic molecules considered the latest evidence. The bonding in cyclopropane is abnormal with the interbond angle compressed to about 60° which is required for ring formation with the nuclei ‘moving ahead’ of the bonding electron density with the formation of a ‘bent’ or so-called ‘banana’ bond. The geometry of the epoxy ring is similar to that of cyclopropane but because of the electronegativity of the heteroatom the internal ring bond angles and lengths are not equal. Parker and Isaacs discussed the various structures that have been proposed for ethylene oxide. It has been suggested that the carbon atoms are trigonally hybridized, that is sp^2, and that one such orbital from each carbon atom overlaps with an oxygen atomic orbital to form a molecular orbital which occupies the centre of the ring. It is possible that the presence of the ‘central’ ring orbital accounts for conjugation of the epoxy ring with other delocalized electrons, which is shown by bathochromic shifts in UV (electronic) spectra [20] and NMR ring currents. Of course such conjugation does not prove that the electrons in the unsubstituted compounds are delocalized, and there has been dispute regarding the possibility of ring currents in these compounds . Although the strain energies of cyclopropane and the epoxy ring are very similar, 27.43 and 27.28 kcal/mole respectively, it may be that the bonding is very different. For instance, from the NMR data compiled by Lwowski [21] the chemical shifts and coupling constants for the epoxy ring are different from those for cyclopropane. The many industrial applications of epoxy resins require the formation of three-dimensional networks by reaction with suitable polyfunctional hardeners. Many of these curing reactions depend on the reactivity of the epoxy ring, which is very much more reactive than the ‘normal’ non-cyclic ethers, R-OR’, where R and R’ are alkyl or aryl groups. In normal ethers the oxygen link is resistant to attack by alkalis, ammonia or amines. Epoxy resins will react with some aliphatic amines at room temperature; these amines may be used as curing agents at ambient temperatures. This increased reactivity of cyclic ethers is due to the ring strain.

The chemistry of the epoxy ring has been reviewed comprehensively by Parker and Isaacs and a more recent discussion is that of Lewars [22]. The literature of heterocyclic chemistry including that of the epoxy ring has been listed periodically; initially references to epoxy resins were listed but not recently. However, these annotations are a useful source of reference to information on the reactions of the epoxy group.

The original discovery of the parent compound ethylene oxide, or oxirane, is attributed to Wurtz who in 1859 published details of its synthesis from ethylene chlorohydrin by reaction with aqueous alkali (Figure 2.2.).

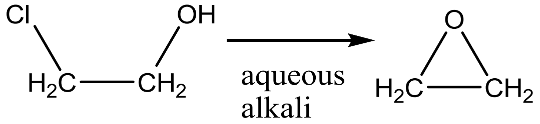


Figure 2.2: Ethylene chlorohydrins reaction

This method is general for the synthesis of epoxy compounds but ethylene oxide is now manufactured by direct oxidation of ethylene with air or oxygen and a silver catalyst. Some of the early history of the synthesis and chemistry of epoxy compounds has been discussed by Malinovskii with especial reference to early Russian work. The synthesis of epoxy rings has been discussed in detail by Gritter and Lewars and epoxy resins by Tanaka [23-24]. There are many methods for the synthesis of epoxy rings. Although not the only ones, the most important routes for the manufacture of epoxy resins are reaction of a halohydrin with hydroxyl compounds, and the oxidation of unsaturated compounds with a peracid. The first method is similar to the original synthesis of ethylene oxide by Wurtz and may be illustrated by the reaction of epichlorohydrin with hydroxyl compounds, such as phenols or aliphatic alcohols.

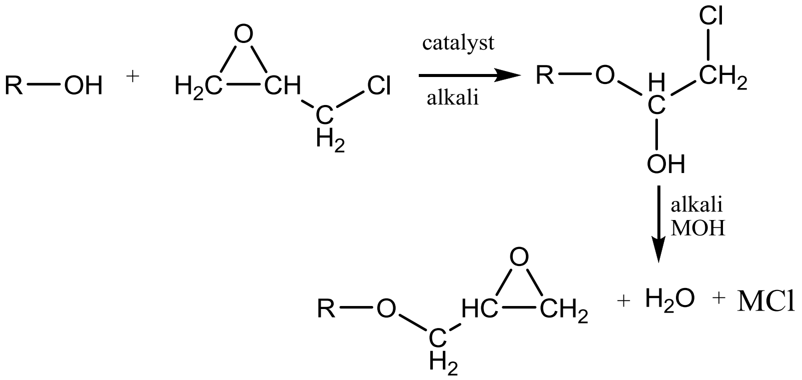


Figure 2.3: Method for synthesis of epoxy rings

MOH could be sodium or potassium hydroxide and has to be used in stoichiometric concentration to neutralize the halogen acid, HC1 in this case, that is produced when the epoxy ring is formed. Unsaturated compounds can be oxidized to yield epoxy groups by the use of peracids such as peracetic acid (Figure 2.4.).

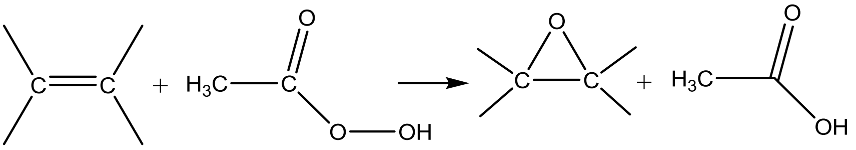


Figure 2.4: Oxidation reaction with peracid

The reactions that are most important for the synthesis and cure of epoxy resins involve either electrophilic attack on the oxygen atom or nucleophilic attack on one of the ring carbon atoms. For the unsymmetrically substituted epoxy compound, which occurs in most epoxy resins, several factors determine ring opening reactions, such as, the nature of the reagent or catalyst which may be either electrophilic or nucleophilic, the influence of the substituent and the relative steric hindrance at the two carbon atoms. With the general reagent HR’, two possible products of ring opening may be produced:

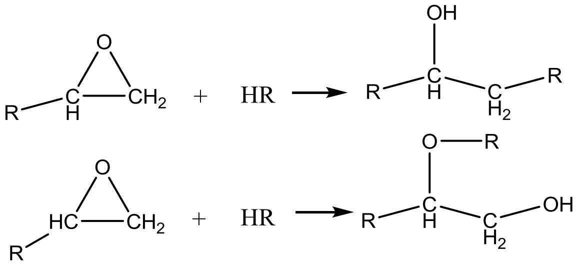


Figure 2.5: Ring opening of epoxy- 1

a secondary alcohol or primary alcohol or a mixture (Figure 2.5). When HR' is an amine, carboxylic acid or thiol, the 'normal' product, a secondary alcohol, is usually formed (Figure 2.6).

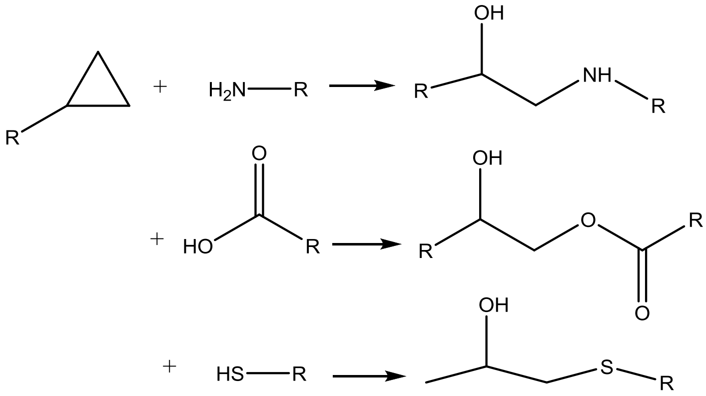


Figure 2.6: Ring opening of epoxy- 2

In these reactions the attacking group donates a pair of unshared electrons to the atom with the lowest electron density, that is, the methylene group which is also less sterically hindered and hence the product is the secondary alcohol. A mechanism for the base catalyzed addition is regarded as 'borderline' S_N2.

2.1.3 The Synthesis of Epoxy Resins

2.1.3.1 Direct Methods

2.1.3.1.1 Using Peracids

The epoxidation cycloolefinic intermediates with peracids or acetaldehyde-monoperacetate is in industrially important because it produces completely halogen free epoxy resins. These are in particular demand in the electrical and electronics sector. The rate of epoxidation depends strongly on the structure of the olefins and of the peracid, the reaction medium and temperature. Catalayst play little or no role. Direct preparation of glycidyl compounds from allyl compounds is also of potential interest. However, the formation of allyl radicals and their oligomerization into undesirable by-products must be taken into account. While, for example, reaction of bisphenol A diallylether (2,2-bis-(4-allyl-phenyl)-propane) with perpropionic acid results in only medicore yields (approx. 50%) of the diglycidyl ether, cycloalkyl and arylalkyl-allyl ethers as well as allyl esters give yields of at least 80% of the corresponding glycidyl compounds [25-30].

2.1.3.1.2 Using Hydrogen Peroxide

Unsaturated alcohols, such as tetrahyrobenzyl alcohol (4-hydroxymethyl-cyclohexane), cyclopentenaol (3-hyroxy-cyclopentene) and allyl alcohol, have been epoxidized in aqueous solution by hydrogen peroxide in the presence of tungstate (or Mo-, V-copmounds) . Epoxidations with alkaline hydrogen peroxide are successful only with olefins with conjugated electron-attracting substituents such as carbonyl or nitrile groups. The prerequisites are the opposite to those for epoxidation with organic peracids. None of these structure is of technicak importance. Epoxidation with hydrogen peroxide in the presence of nitriles via the intermediate iminopercarboxylic acid has proved particularly effective for allyl compounds

(Figure 2.7). In contrast to per-acid epoxidation, this process has the advantage of not requiring an acid medium thus avoiding the formation of undesired acid adducts. The disadvantage is the formation by a radical mechanism of allyl oligomers which can be separated only by expensive processes which lead to loss of material.

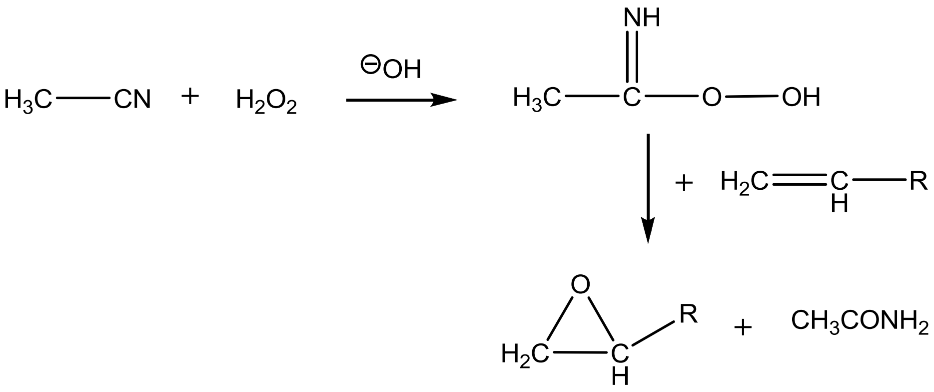


Figure 2.7: The synthesis of epoxy via hydrogen peroxide

2.1.3.1.3 Using Oxygen

The oxygen epoxidation methods with and without metal catalysts (Ag-, Mo-, W-compounds) used successfully with low molecular olefins (ethylenei propylene) is of only limited (low yields) use for higher homologs of this series of olefins or those compounds with functional groups (ethers, esters, amides).

2.1.3.1.4 Using Halogen Hydrins

The epoxidation of olefins with hypohalogenous acid HOX occurs via the following reaction mechanism (Figure 2.8).

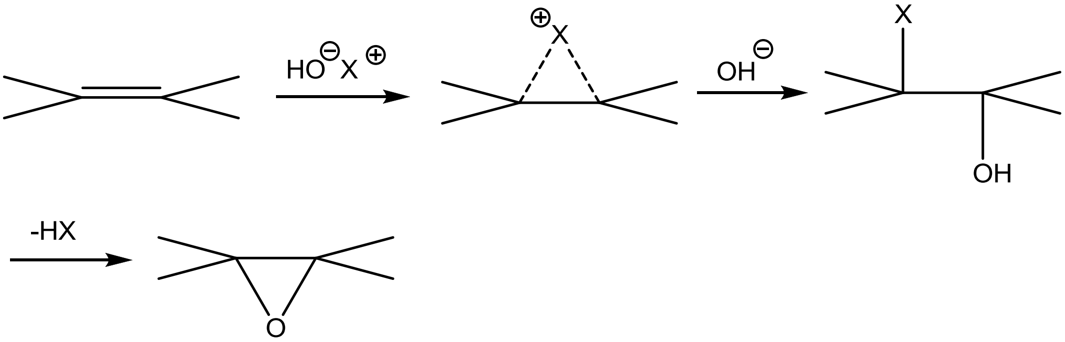


Figure 2.8: The epoxidation with hypohalogenous acid

The hypohalogenous acids are generally used in the form of an aqueous solution of the halogen. The industrial preparation of glyceroldichlorohydrin and epichlorohydrin from allyl chloride is based on this process. The process is not used products are formed which are difficult to separate. In the case of substituted olefins, as e.g. endomethylen-tetrahyrobenzene derivatives, steric hindrance affects synthesis and addition reactions [31-36].

2.1.3.2 Indirect Methods

Only the common methods of synthesis with preparative or technical advantages are considered here. These are the adddition of compounds with active hyrogen atoms to:
a) Epichlorohydrin with the formation of a chlorohydrin derivative which can be converted into the corresponding glycidyl compounds by splitting off hyrogen chloride, and
b) Di, tri- or poly-epoxide compounds by reaction of only one epoxide group per molecule.

2.1.3.2.1 Synthesis via Chlorohydrins

Pratically all compounds with active hydrogen atoms can be converted into epoxide compounds using epichlorohydrin. This process is of industrial importance. It is based on the particular characteristic of epichlorohydrin to have potentially a new epoxide group in the chlorohydrin group formed. The purity of the resulting products depends, however, to a large extent on the mole ratio of the compound used to that of epichlorohydrin and on the reaction conditions. If the addition of the epichlorohydrin and the conversion of the intermediate chlorohydrin into the epoxide compound are combined in a single reaction step, certain amounts of so-called advancement products can be also result. The only case where this is acceptable is in the preparation of bisphenol A diglycidylether. Separation of the required low molecular main product by crystallization or destillation is costly, even if feasible, and entails significant losses of material by thermally induced side reactions.

Glycidyl Compounds Based on Bisphenol A

Bisphenol A diglycidylether is not only of historical but also of industrial importance as it comprises more than 85% of the volume of epoxy resin produced. However, numerous other bis- and poly-phenols can be converted to into glycidyl ethers by the same process. The synthesis of the low molecular, liquid bisphenol A diglycidylether runs as shown in Figure 2.9. Depending on the reaction conditions and the mole ratio of the components, epoxide compounds of general formula in figure 2.10 are formed in the reaction mixture. Industrially, 6.6 mol epichlorohydrin is used for 1 mol bisphenol. In the product, the quantity ratio I:II:III comes up 2.43:0.23:0.02; the epoxide equivalent of the product mixture is approx. 185 to 190 [37-38].

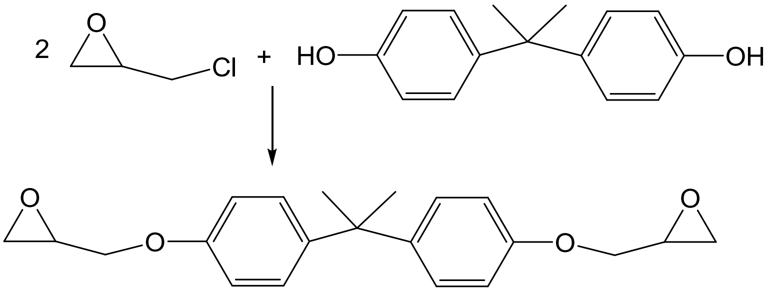


Figure 2.9: The synthesis of the low molecular, liquid bisphenol A diglycidylether

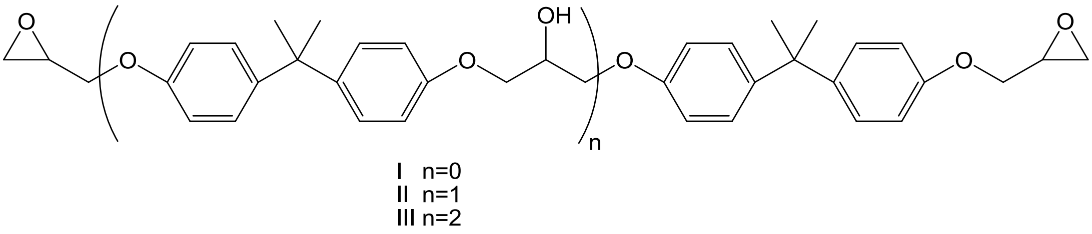


Figure 2.10: The general formula of bisphenol A diglycidylether

The advanced products II and III are also diglycidyl compounds. Their functionality and reactivity, but not their molacular mass, are equal to those of the simple low molecular diglycidylethers. Consequently, in industrial production, the epoxide content and the molecular weight distribution have to be kept constant by sophisticated processes. The synthesis of advances epoxy resins, preferably carried out with bisphenols, is used industrially with bisphenol A for targetted adjustment of the average molecular mass. The Taffy and Advancement Processes are suitable for this. In the Taffy Process, The charge is such that the epichlorohydrin/ bisphenol A ratio will yield a resin with the required value of the degree of polymerization $1 < n < 4$, so that the upper limit for the average molecular weight produced is about 1500. A stoichiometric amount of caustic soda in aqueous solution is added with stirring and the reaction temperature raised to 45-50°C. As the molecular weight increases the reaction temperature is raised to 90-95°C for about 80 min with maybe increased pressure and more vigorous agitation. At the end of the reaction period the product is in a water resin emulsion plus an alkaline brine. The epoxy resin is recovered by separating the phases, washed with water to remove inorganic salts and the water removed by drying at temperatures of up to 1300C and under vacuum. For purification of the resin dissolution in an organic solvent may be advantageous and removal of water may be assisted by the use of methyl isobutyl ketone. However, it is then essential that the level of solvent remaining in the resin is minimized. The recovery of the resin in this process is a major disadvantage especially because of the large amounts of brine that have to be removed. These problems are not encountered in the fusion or advancement process. In the Taffy process integral values of n, the degree of polymerization, are usually produced with n values of (0),1,2,3 whereas in the advancement process n is even numbered. A typical product with a weight per epoxide (wpe) ca. 500 and $n = 2$ has a softening point of about 70°C and the practical limitation for this process is $n = 3.7$ and a softening point of 95-100°C. These resins will not crystallize as will DGEBA as mentioned previously and the determination of their softening point [11].

Glycidylation of Carboxylic Acids, Amines, Alcohols, and Heterocyclics

The glycidylation of carboxylic acids, amines, alcohols, and heterocyclics with active N-H hydrogen atoms is performed advantageously in two reaction steps. As described in reaction figure 2.11, a quantitative addition of epichlorohydrin to the H-active compound occurs in a first step with the help of quaternary ammonium compounds. In the second step, the epichlorohydrin is dehalogenated by adding dropwise equimolar amounts of concentrated aqueous sodium hyroxide and simultaneously distilling off azeotropically the added and generated water and excess epichlorohydrin.

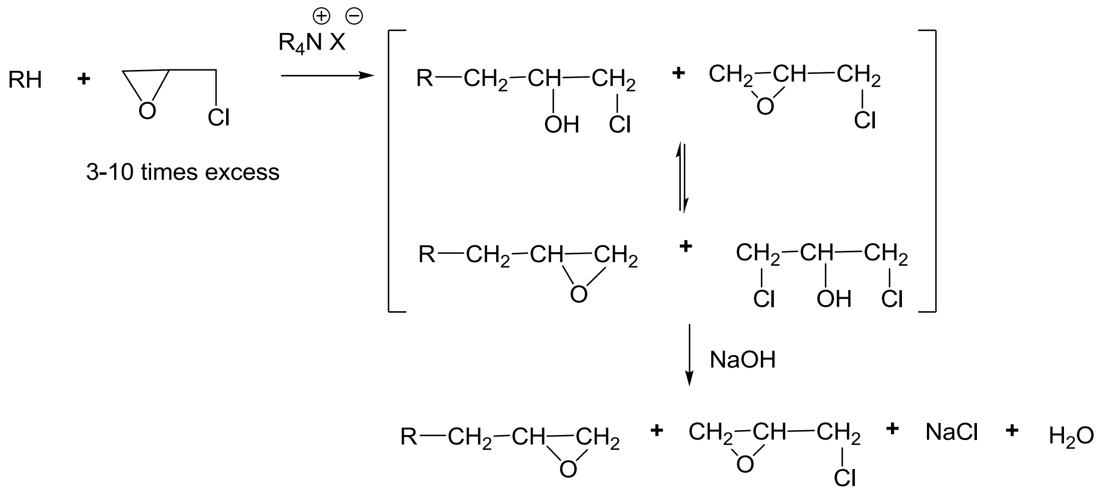


Figure 2.11: The epoxy synthesis with glycidylation

This process reduces the manyfold side and advancement reactions which might appear with dicarboxylic acids and amines. Moreover, starting and end products sensitive to bases are protected by gradual hydrogen chloride elimination from rearrangement and saponification reactions. This is particularly important for glycidyl ester, glycidylized oligoesterdicarboxylic acids and cyanuric acid. The behaviour or aromatic and aliphatic amines differs during the glycidylation with epichlorohydrin. Steric hindrance can also greatly reduce the reactivity of the NH group. Since bases initiate dehydrohalogenation, the formation of mixtures of N-glycidyl compounds, ammonium halogenides and amine-chlorohydrin derivatives can be expected, particularly with aliphatic amines, after addition of the first molecule of epichlorohydrin. These diverse side reactions, influenced in part by equilibria, can be repressed but not prevented by performing the reaction under cooling conditions. Here too, two step epoxidization process with phase transfer catalysts such as ammonium salts and excess epichlorohydrin, has proved uself. In case of, glycidyl formaiton must be completed with alkali hydroxide. For glycidylation of primary and secondary alcohols. Lewis acid catalysts (tin tetra chloride, boron trifluoride etherate) generally effect the addition of the epichlorohydrin in the first stage. Ammonium compounds are also suitable. Under the given conditions as in all glycidylation reactions of H-active compounds, the secondary hydroxyl group of the chlorohydrin, freshly formed according to Figure 2.12, Equation C, undergoes further reaction with epichlorohydrin according to Equaiton D.

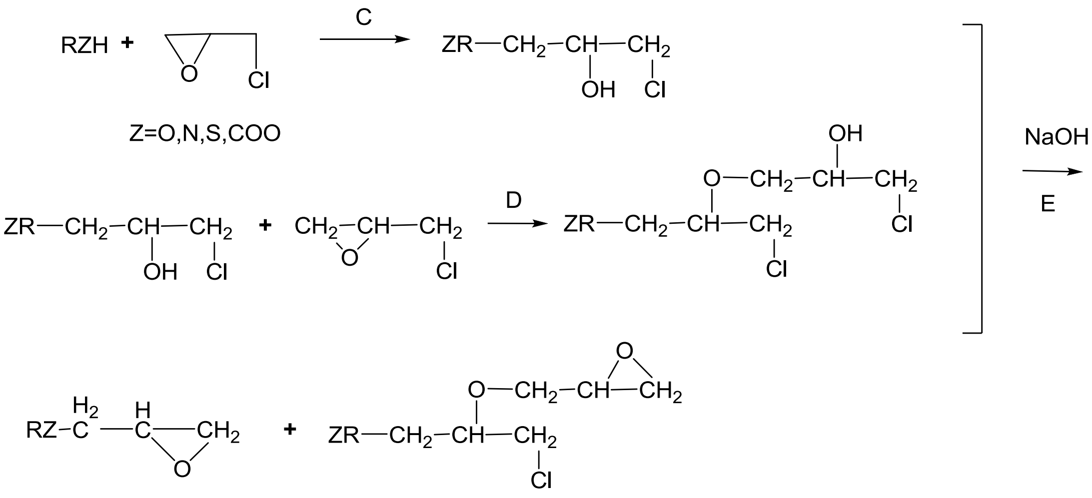


Figure 2.12: The glycidylation reactions of H-active compounds

However during dehalogenation according to Figure 2.12, Equation E, only the halogen of the halogenhydrin is easily eliminated with the liberation of hydrogen chloride. The products obtained from this synthesis thus contain chlorine. Efforts to circumvent this problem have so far been successful. Tertiary alcohols cannot be glycidylized in this way. The most important heterocyclic glycidyl compound is triglycidyl isocyanurate. It is manufactured from cyanuric acid by the usual process with epichlorohydrin and quaternary ammonium compounds as catalysts. The widely prepared glycidylized hydantoin compounds have not been accepted in surface protection [31-35].

2.1.3.2.2 Addition of Active Hydrogen Compounds to Epoxide Compounds

The comporatively uniform course of phenols to glycidyl compounds also opens the way for the use of diglycidyl compounds of any structure in the Advancement reaction with bisphenol A. This presupposes, however, that both glycidyl groups exhibit the same reactivity. Dicarboxylic acids and aromatic amines can be used with di-, tri- and tetra-glycidyl compounds to manufacture fusible, soluble preadducts which still possess free terminal epoxide groups as shown in Figure 2.13:

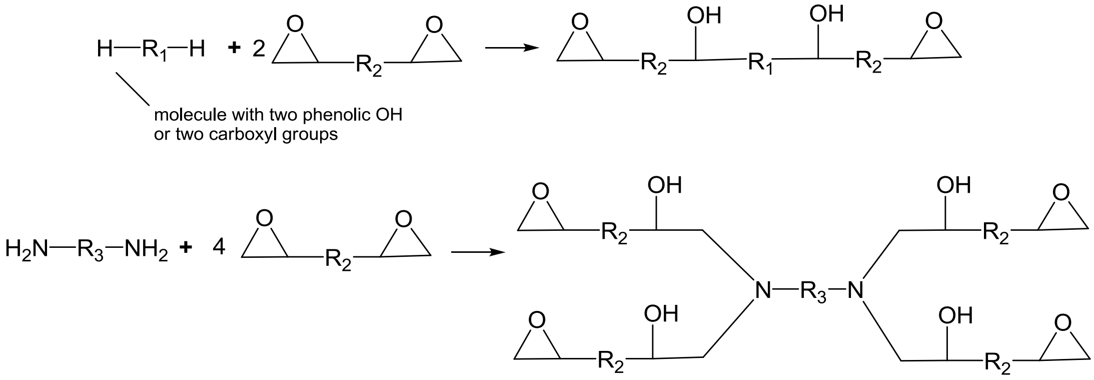


Figure 2.13: Addition of Hydrogen to Epoxy Groups

In principle, all compounds with active hydrogen atoms of general formula H-R_3-H can be used to obtain preadducts with epoxide compounds. With the exception of phenol addition, small amounts of more complex structures have to be expected because addition reactions also occur on the newly formed, free secondary hydroxyl groups. This leads to higher molecular epoxide compounds structures of the formula shown in Figure 2.14.

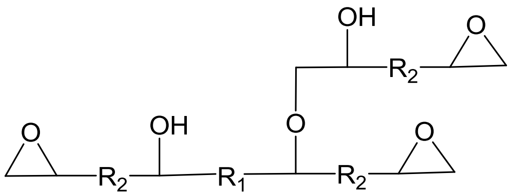


Figure 2.14: The epoxide compounds structures

To prevent all crosslinking, these reactions re allowed to proceed with an excess of 20 to 100% of epoxide equivalent per active hydrogen equivalent. This type of chain extension and structure variation is exploited commercially in a huge variety of ways, the preadducts are not isolated but reacted and crosslinked with curing agents by the user. The development of such systems has required detailed investigation of the course of the reactions, the shelf-life and the behaviour of the curing agents during mixing. Reproducibility is strongly dependent on reaction parameters which have to be determined previously and then adhered to. This is also true of industrial processing to the cured material. An analogous method of manufacturing preadducts with cycloaliphatic epoxide compounds is reliable only with dicarboxylic acids.

2.1.3.2.3 Phenoxy Resins

From the previous discussion it would appear that if side reactions are suppressed it should be possible to produce high molecular weight resins from DGEBA and bisphenol A when there is exact stoichiometric equivalence, i.e. epoxy-hydroxyl group ratio is unity, and reaction conditions such that $p \rightarrow 1$, where p is the probability that an epoxy or hydroxyl group has reacted. Thermoplastic resins with average values of n of about 100 and average molecular weights of maybe 30 000 to 45 000 are available. These resins may not have terminal epoxy groups, but each repeat unit has a secondary hydroxyl group which is reactive, with, for example, isocyanates. Phenoxy resins are available in solution for coating applications which harden when the solvent evaporates. Granular resins may also be used for extrusions and injection mouldings [39].

2.1.3.2.4 Resins from Other Phenolic Compound

Any multifunctional, $f \geq 2$, phenolic compound is a potential starting material for the manufacture of epoxy resins. Although many have been studied, only a few have any commercial significance and these are 'formulated' to meet specific requirements. Also, some monofunctional phenols have been reacted with epichlorohydrin to produce monofunctional reactants for use as modifying diluent agents. The dihydric phenol which is produced by reaction of phenol with formaldehyde is called bisphenol F.

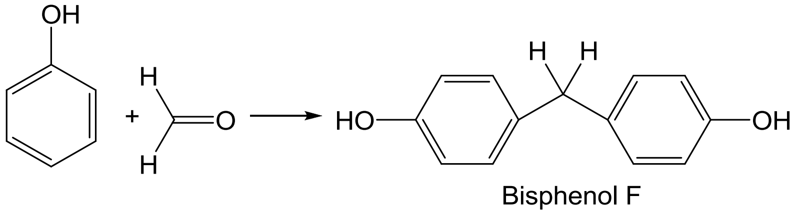


Figure 2.15: Sythesis of bisphenol F

Resins can be manufactured from bisphenol F by similar methods to those used for bisphenol A and epichlorohydrin with a catalyst such as NaOH. These resins have lower viscosities than the equivalent DGEBA. Phenolic 'novolac' resins are manufactured by the reaction of phenol with formaldehyde with P/F of = 0.8 with the use of an acid catalyst. These novolac resins may be represented by the idealized structure [40],

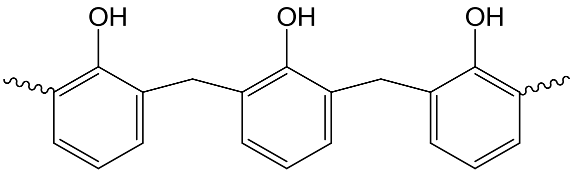


Figure 2.16: Novolac resin

with n depending on reaction conditions and P/F ratio. Not all the substitution is in the ortho position but the reactivity of the ortho position is higher than that of the para because of the 'activating' effect of the phenolic group. The reaction conditions used to manufacture epoxy-novolacs is similar to those used with BPA resins and the idealized structure of the product is

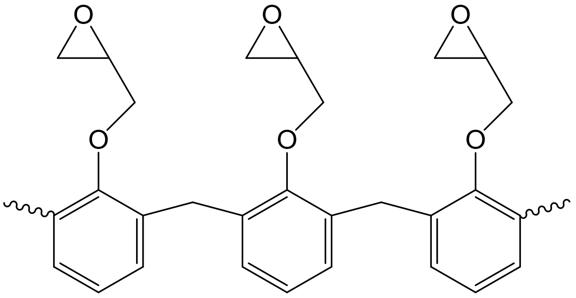


Figure 2.17: Epoxy-novolac

There are considerable 'variants on a theme' with this type of resin; use of excess epichlorohydrin minimizes the reaction of phenolic hydroxyl with the epoxy groups attached to the novolac resin and limits the amount of branching that can occur. Also it is essential that all phenolic hydroxyl groups have reacted because their presence would adversely affect the storage life of the resin and also volatiles would be formed during cure. The epoxy novolacs have improved thermal and chemical resistance compared to the BPA resins. It is possible to partially esterify novolac resin before reaction with epichlorohydrin or esterify afterwards for ester coating applications. Also the novolacs may be based on chlorinated phenols to obtain improved flame resistance.

2.1.3.2.5 Other Resins Derived from Epichlorohydrin

Many compounds with reactive hydrogen atoms will react with epichlorohydrin and these have been evaluated as potential resins. Formally many react similarly to phenols but there are important differences. For instance, the chlorohydrin formed by reaction of epichlorohydrin with a secondary alcohol is much more sensitive to alkali than aromatic ether-chlorohydrin and hence caustic alkali cannot be used as a catalyst or for dehydrochlorination. A Lewis acid, such as BF_3 or $SnCl_4$, is used to catalyse the reaction between epichlorohydrin and the hydroxylic compounds. Caustic alkali would also catalyse the epoxy-epoxy reaction which leads to polymerization of the product. Aluminates affect dehydrochlorination without catalysing further side-reactions. Resins have also been prepared from cycloaliphatic alcohols such as hydrogenated bisphenol A, tetracyclohexylethane and hydrogenated novolacs. Glycidyl esters are manufactured from acids, such as phthalic and hydrogenated phthalic acids. The viscosities of these esters are lower than bisphenol A type resins but have similar reactivities. Also, bisphenol A type epoxy resins can be reacted with fatty acids to produce vehicles for surface coatings. Other chlorohydrins than epichlorohydrin could be used to produce epoxy resins. Methylepichlorohydrin, derived from isobutylene, has been used to manufacture resins by reaction with bisphenol A and also polybasic acids and novolac phenolic resins [41].

2.1.3.3 Oxidation of Unsaturated Compounds

The oxidation of unsaturated compounds has been studied extensively with a variety of reagents of which the most important for the synthesis of epoxy resins are organic peracids and their esters. Preparation of the peracid in situ often offers advantages. Numerous peracids, aliphatic, aromatic and cycloaliphatic have been luated. Peracetic acid is widely used, either in aqueous, or non-aqueous media homogeneous or heterogeneous phase systems. It has high epoxidation efficiency and stability at ambient temperatures but there are handling hazards and reaction mixtures can be potentially explosive. A major advantage of the peracid route for the synthesis of epoxy intermediates is that since no species containing chlorine are involved in these synthesis the resins do not contain hydrolysable chlorine, and they are also low in ash and ionic content. Thus these resins have better weathering and ageing properties than 'conventional' epoxy resins and find application where 'good' electrical properties are required. However, some impurities are formed during oxidation with per acetic acid.

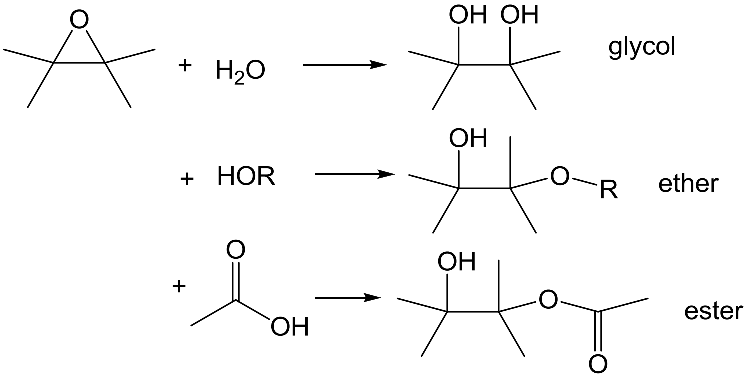


Figure 2.18: Epoxy reactions

These reactions can be minimized by the use of peracetic acid in which the sulphuric acid used in its synthesis is neutralized. With this reagent natural oils can be epoxidized but it is not satisfactory for the production of compounds with more reactive epoxy groups, even when reaction temperatures are kept low and reaction times short. However, the hydroxyl groups formed are reactive and can be employed in the cure of these resins. The epoxidation of unsaturated compounds with a peracid is used in the manufacture of cycloaliphatic epoxy resins. Not only are these resins free of hydrolysable chloride and inorganic salts (ash) they do not contain aromatic compounds and hence are more stable to UV exposure than the bisphenol A derived epoxy resins. The presence of aromatic rings in BPA resins increases the UV absorption of the resins and also degradative processes occur by the formation of conjugated structures [42]. The starting materials for the production of cyclo-aliphatic resins may be synthesized by Diels-Alder addition of unsaturated compounds. This can be illustrated by the dimerization of butadiene to yield vinyl cyclohexene which can then be epoxidized with a peracid. Other epoxy products can be produced by peracid epoxidation, such as epoxidation polyolefins, oils and fatty acid esters. The last are used as plasticizers and stabilizers for polyvinyl chloride compositions.

2.1.4 Types of Application for Epoxy Resins

2.1.4.1 Curing at Room Temperature

The worldwide consumption of epoxy resin for room-temperature curing systems was about 250 000 t at the beginning of the 1990s.Of this 170 000 t (25% of total world epoxide production) was used for surface protection systems. The rest was distributed between adhesives, tooling resins, potting compounds and polymer concrete. This clearly shows the importance of ‘ambient curing’ in the field of epoxy resin. With this background it is also easy to understand the importance of the polyamines which, expect for isocyanates, are the only crosslinking partners for epoxy resins at room temperature. While about 90 000 t of epoxy resins are used fort he formulation of two-pack paints for maintenance and in naval work (these are mainly solvent-based although nowadays the solvent is often water), 80 000 t are used fort he formulation of the solvent-free or low solvent (high build or high solids) coatings for application in thick layers as paints or flor covering. Depending on the type and amount of solvent, two-pack coatings are applied in thicknesses of from 40 to 30 μm whereas solvent-free coatings are applied in thicknessses of 300 to 1000 μm. Floor screed are applied between 2 and 10 mm thick depending on the degree of filling, method of application and purpose.

Solvent-Free Coatings

Only low molecular, liquid bisphenol A and bisphenol F epoxy resins or their mixtures are suitable for formulating solvent-free coatings. Bisphenol A epoxy resins have the highest viscosity of these epoxide types and show the strongest tendency to crystallize. This tendency to crystallize can be reduced or (as long as the proportion of bisphenol F is sufficiently high) completely suppressed. As these mixtures also have a lower viscosity than the unmodified bisphenol A epoxy resins, they are favored for application in the building sector. Bisphenol F epoxy resins have a higher epoxide content and a a higher epoxide functionality than the bisphenol A resins. Optimally formulated and cured bisphenol F epoxy resins are therefore characterized by the best resistance to chemicals, exceeded only by the high viscosity epoxidized novolaks. Of course the higher the epoxide functionality of these resins, the lower their flexibility. For flexibility and adhesive strength, bisphenol A epoxy resin is optimal. The relativelty high viscosity of bisphenol A and bisphenol F epoxy resins necessitates the use of reactive diluents to improve their processability. Because they contain reactive epoxy groups, reactive diluents take part in the curing and thereby affect the properties of both the liquid and the cured coating. The amount of reactive diluent should therefore be kept as low as possible so as not to impair unacceptably the chemical and mechanical strengths of the cured coating. In generali it is not advisable for the reactive diluent to exceed 25% w/w of the epoxy resin. This is especially true if the diluent has a monoglycidyl group which, while it effects flexibility, leads to chain termination expect with anhyride crosslinking. The following generalizations can be made:

a) Aliphatic monoglycidyl compounds cause the greatest reduction in viscosity of an epoxy system. This effect and the reactivity of the resin system are reduced with increasesing molecular mass. They improve the flexibility of the cured film but simultaneously reduce resistance to solvents.

b) Aliphatic diglycidylethers lower the viscosity of the epoxy resin less than monoglycides. Di functional diluents give rise to the best reactivity, flexibilty and solvent resistance. Reactivity and solvent resistance decrease with increasing chain length while the flexibility increases. All aliphatic diglycidylethers reduce resistance to acids in proportion to the number of aliphatic ether linkages.

c) Aromatic monoglycidylethers reduce the viscosity least but do noticeably reduce the reactivity and flexibility of the binder. On the other hand, aromatic monoglyicidylethers hardly affect the water and acid resistance of the binder system [43].

The sole curing agents for solvent free coatings and floorings ar polyamines, however, these are only used in unmodified form in exceptional cases. Usually reaction products with monomeric or dimeric fatty acids, mono or di-epoxides or methylol compounds are used. Depending on the field of application they often need additional physical modification, for example, by the addition of nonreacting plasticizer. The curing component exerts a substantial influence on the properties affecting not only curing but also resistance and applications. Aliphatic amines, particularly the alkyl amines, confer high reactivity on the coating compounds and the cured films are very resistant to solventt. In contrast, polyamidoamines produce films with high flexibiltiy and good adhesion. Cycoaliphatic polyamines are noticeably slower to react than aliphatic ones and must therefore be modified and accelerated. They confer hardness, attractive film appearance and high gloss on the epoxy resin coating. Conqeusently, these systems are preferred for decorative wall and flor coverings. While resistance to water, alkali, and acids is generally satisfactory, resistance to solvents does not always meet the Standard deamnded by the end user. The pot life of solvent free epoxy systems is very short and therefore presents problems, especially whent the temperature of the surroundings is 25^0C or above. Low air or substrate temperatures also cause problems as the viscosity increases as the temperature is lowered. Such coatings should therefore be applied wherever possible with heatable, two component airless equipment. It has proved impossible to reduce the high reactivities of the amines or to adjust them to suit application. The most succesful attempts have involved (partial) reaction of the amines with acrylonitrile [44] to produce partially cyanoethylated amine sor reaction with ketones to form ketimines [45]. This type of modification increases the pot life and the curing time. However, curing below room temperature is rendered difficult or impossible and the chemical and physical properties of the cured systems are noticeably poorer. While the cyanoethylated amines cıre without by-products, ketimines liberate the ketone, which in practice is usually methylisobutyl ketone. This ‘unmasking’ of the amines demands temperatıres of at least 25^0C and Access of moisture. Values of about 70% relative humidity guarantees good curing. It is clear that he film thickness of such systems is restricted to about 150 µm. If this is exceeded, the upper zone of the coating cures but the material close to the substrate remains liquid for a long time, as in the case of solvent based paints when applied too thick. Because of the short distance between the epoxide groups in the resin and the high content of reactive hydrogen in low molecular amine curing agents, these systems cure to close meshed Networks. While this favors high resistance to solvents and low water permeability, flexibility is impaired. To obtain sufficient flexibility, either flexibilizing liquid extenders or substances which affect either the resin or the curing agent so that the crosslinking density is lowered must be added to these systems. To affect the epoxy resin, long chained, aliphatic glycidylethers or blocked isocyanate perpolymers are often used, these can be cured with amines. Prereaction of epoxy resins with carboxyl functional substances results in flexibilizing resins which can be crosslinked with amines in the usual way. The curing agents can be also modified usually with polyamidoamines, polyoxyalkyl amines, polyurethane amines and the amino functional polybutadiene-acrylonitriles. These can be used either alone or in mixtures with aliphatic or cycloaliphatic amines. In all cases, whether modification is made to the resin or curing component, the chemical resistance, particularly to acids and solvents reduced.

Solvent Based Coatings

While solvent based, two-pack paints are mainly made from bisphenol A epoxy resins with average molecular mass of ca. 1000, high solids formulations primarily use types with average molecular mass of 500. However, high molecular resins are necessary if short dust dry times are required. This results in lower solids content, increased pot life and somewhat improved flexibilityi When formulating coatings which must have high resistance to solvents, epoxidized novolaks are added to low molecular bisphenol A solid resins to improve solvent resistance by raising the network density. Aromatic hydrocarbons, mixed with alcohols which should be as non water miscible as possible, are used as solvents for 2-pack coating which cure at room temperature. Crosslinking of these resins is preferably performed with polyamidoamines especially if high flexibility and optimum adhesion are demanded. Better compatibility and superior film appearance are obtained without prereacting of the resin and the hardener during 10 to 20 minutes by using polyamidoamines-epoxy resin preadducts which are commercially avaliable as a 60% solution in xylene/butanol. Coatings based on polyamidoamines and/or their adducts are mainly used fort he formulation primers for steel concrete. Such combinations have also proved effective as one coat paints where there are no great demands on chemical resistance. For a more functional coating with high chemical and mechanical resistance, amine adducts are usually used either as ‘in situ’ products or in isolated form. This type of paint has a shorter pot life and faster curing but a somewhat lower flexibility and adhesion. In general, two-pack paints cured with polyamidoamines have a somewhat improved weathering resistance to those based on amine adducts. However all aromatic epoxy resins have no good weathering resistance. When exposed to light and moisture, these resisns have a tendency to yellow, to become matt and to chalk, aromatic epoxy resins ar therefore preferably used fpr tp interior applications. Light and weather resistant epoxy resin systems can be made by combination of non aromatic glycidylethers or preferably with diglycidylesters and with carboxy functional acrylates [46] or polyesters as crosslinker. These are new developments but curing at room temperature is not yet satisfactory, to obtain sufficient film hardness the systems need post curing at 50-80^{0}C. Because such systems hava different structures compared with conventional aromatic epoxy resin/polyamine systems, they have different reactivities and product profiles. Carboxy functional acrylate /epoxy resin systemts have also recently become avaliable in water thinnable form. These and the corresponding solvent based systems, are used as paints for machines. They are also used as refinishes in tropical and subtropical areas because of their simple processability and favorable curing requirements. Higher molecular bisphenol A epoxy resins with molecular weights between 3000 and 50 000 can be crosslinked with isocyanates via urethane bridges, they can be viewed as polyhydroxy compounds because of their large number of hydroxyl groups. The epoxide groups which are also present are very reactive and undergo uncontrollable addition with hydroxyl groups. Epoxy resin/isocyanate ombinations are characterized by high reactivity and exceptional solvent resistance. In shop primers or for formulation of solvent resistant coatings for storage tanks or in the ship building industry, aromatic isocyanates are almost exclusively used as they are more reactive adn more resistant to chemicals than the aliphatics. Esters, ketones and aromatic hydrocarbons are the preferred solvents for such systems.

Waterborne Coatings

Low molecular liquid bisphenol A and bisphenol F epoxy resins and low molecular epoxidized novolaks are made water thinnable by the addition of non ionic emulsifiers such as those based on polyethlene oxide. Epoxy resins can be produced by partial reaction of epoxide groups of there resins with water soluble polyols. These are usually cured with water soluble polyamidoamines or polyimidazoline adducts. Such systems can be processed as thixotropically adjusted two pack coatings. The main use of waterborne epoxy resin systems are for coating concrete and other mineral substrates, as these systems tolerate the residual moisture of the substrate. As water evaporates more slowly than solvent, there are limits to the ability to cure at low temperatures. Also it must be noted that coatings baed on waterborne epoxy resin systems dont cure sufficiently at high relative humidity so that, especially in closed spaces, there must be adequate ventilation. High molecular epoxy resins, although not fully solvent free but with the advantages of long pot life, short dust free drying time and better adhesion and flexibility, can be manufactured as waterborne systems as described above. Because of their relatively low reactivity compared with the low molecular epoxy resins, these resins can also be combined with water soluble polyamine adducts resulting in coatings systems with improved solvent resistance. It is a characteristic of all waterborne systems that, if cured at room temperature, they have no long term resistance to acids. This can be traced back to the water incorporated in the film on curing in the presence of polyamine curing agent segments. If however these coatings are crosslinked at temperatures over 100^0C, they resistant to acids [47]. Water thinnable epoxy resins, formulated from liquid, semi solid or solid bisphenol A, bisphenol F or novolak epxoy resin, can also be cured with water thinnable acrylates containing carboxy or amino funtions at temperatures between 20 and 80^{0}C. The films show good flexibility and somewhat improved light and weathering resistance. Optimal light and weathering resistance can only be obtained with non aromatic epoxy resins, these have been considered earlier in the discussion of solvent containing, two pack coatings. While the use of waterborne epoxy systems causes no problems in coating concrete and similar mineral substrates, coating of steel sheet and particularly sand blasted steel requires corrosion inhibitors to be added to the formulation.

2.1.4.2 Curing at Elevated Temperature

Solvent based finished for cans, tubes, tanks, drums, industrial goods of all types and automobiles were, and occasionally still are, cured at temperatures over 140^{0}C. Due to environmental reasons and partly because of quality improvements, the paint industry and raw materials industry have been working for 15 years to replace the large amounts of solvents by waterborne or, better, solvent free paints. Bisphenol A epoxy resins are well suited for chemical modification because the epoxide and hydroxyl groups have different reactivity, they are now used in applications which were previously reserved for other binders. This is particularly true fort he automotive industry which used over 50 000 tonnes of epoxy resins per year at the beginning of the 1990s for cataphoresis, primer surfacer, and coating of small parts. The extended use of powder coatings has also caused the demand for epoxidized resins to grow strongly in the past 20 years. Because of this, the demand for other heat curable binders which were previously much used in solvent based industrial finishes but could not be formulated as powder coatings, has decreased. It is estimated that, world wide, demand for powder coatings will increase by 7 to 12% up to the year 2000 and will penetrate further into industrial coating applications for solvent based, hot cure systems. Some 80 000 tonnes of epoxy resins are currently used in the manufacture of powder coatings. Consumption of epoxy resins in can coatings is just as great. In contrast to the automotive industry, epoxy resins have been used since many years in the coating of tubes and cans. Here too, the trend is towards low solvent or solvent free resin systems.

Solvent Based Coatings

Heat-Curing epoxy resin esters; these are obtained by reacting solid epoxy resins based on bisphenol A with fatty acids, these can be nın drying (saturated or mono unsaturated fatty acids suh as coconut, castor or lauric acids) or drying (fatty acids with two or more unsaturated groups such as lineolic and linolenic acids). The degree of esterification distinguishes between short oil, medium oil, long oil epoxy esters. These products are usually crosslinked with urea formaldehyde resins (for primers) or melamine formaldehyde resins (for top coats) with a w/w ester/amino resin ratio between 75:25 and 70:30. Curing temperature is between 120 and 180^{0}C. Short and medium oil epoxy esters are especially suited for stoving coatings. They are characterized by high hardness and good chemical and mechanical resistance. The long oil esters are particularly used for high quality, anti rust coatings or for high duty external paints and coatings.

Industrial finishes and packaging lacquers; Because of their low cost and outstanding properties, heat curing formulations of bisphenol A diglycidylether with molecular mass 1000 and higher with amino and phenolic resins are widely used as industrial finishes and coatings for packaging. In industrial coatings, butylated urea formaldehyde, butylated and methylated melamine formaldehyde and butylated benzoguanamine formaldeyde resins are used as curing agents and crosslinked at temperatures between 160 and 200^{0}C with elimination of corresponding alcohols and formation of ether bridges. These paint films are characterized by good chemical resistance, outstanding adhesion and impact strength and good flexibility with high surface hardness. As for the epoxy resin esters described above, the urea resin combinations are mostly used as primer or one coat systems in the packaging sector, while the melamine and benzoguanamine combinations find their main application as finishing agent. Compared with epoxy resin esters, these systems have higher chemical resistance and mechanical strength but are inferior in substrate tolerance and gloss. Higher molecular epoxy resins can also be cured with blocked din d tri isocyanates. The curing temperature must lie clearly above the deblocking temperature of the isocyanate to obtain high quality paint films. Crosslinking is achieved by addition of free hydroxyl groups of the epoxide to the isocyanate group while the blocking agent evaporates. These coatings are also characterized by high hardness, good flexibility and excellent resistance to a large number of solvents and chemicals. Butylated phenol, alkylphenol and bisphenol A formaldehyde resins have achieved great importance as curing agents for packaging finishes. Depending on the desired property spectrum, the epoxide etherified resol ratio is between 80:20 and 60:40, stoving is at temperatures over 200^0C. Curing can be accelerated by acids. Crosslinking occurs mainly by reaction of hydroxyl groups of the epoxy resin with the partly etherified methylol groups of the phenolic resin with elimination of water and/or alcohols. The epoxide groups also react with the phenolic hydroxyl groups of the curing agent. The cured coatings are characterized by extremely high resistance to acid solutions and fodostuffs. Phenolic resins tend to yellow on stoving and for about the last 20 years relatively low molecular polyesters with carboxy and anhydride end groups have been used as crosslinkers alonside phenolic resins. This type of system cures to a practically colorless finish and can therefore be pigmented without andy problem. White pigmented they are important as internal can coatings, the films are taste free and also aesthetically more pleasing than the yellow phenolic resin coatings [48].

2.1.4.3 Radiation Curing

Crosslinking of epoxy resins using UV light is used at present mainly in the field of microelectronics. However it is perfectly feasible for this to be extended to surface protection, for example, for image structured surfaces or generally where crosslinking by light has advantages from the point of view of design or processing. All epoxy resins can be crosslinked with the currently avaliable cationic photoinitiators so far no anionic ones have been reported. In practice only cycloaliphatic epoxy resins are used. The choice of structure must be appropriate to the demands of the application. The resin must contain about 1 to 4% w/w of suitable photoinitiator. Under UV light photolysis of the initiator occurs in the film layer and lewis or bronsted acids are formed which start the polymerization. With the formation of low molecular oligomers, the glass transition temperature of the crosslinked system rises above room temperature and thereby becomes frozen in. These structure can therefore be stored at room temperature as latent reactive systems and later be fully crosslinked at a higher temperature. Aryldiazonium saltsa are no longer used as photoinitiators because of their poor stroge stability in the dark and the poor film quality caused by the liberation of nitrogen. Diarylammonium saltsa are also seldom used and have been replaced by the far more effective triarylsulfonium salts. Arene ferrocene complexes are another group of good photoinitiators. With electron beam curing, the crosslinking of the films occurs by a free radical mechanism, epoxy resins are especially suitable fort his because of the strain in the oxiran rings. Copolymers of acrylic aicd glycidyl ester or methacrylic acid ester with acrylic acid alkylesters are mainly used [49-50].

2.1.5 Epoxy Acrylate

Epoxy acrylates are dominant oligomers in the radiation curable coatings market. In most cases epoxy acrylates do not have any free epoxy groups left from their synthesis but react through their unsaturation. Within this group of oligomers, there are several major subclassifications: aromatic difunctional epoxy acrylates, acrylated oil epoxy acrylates, novolac epoxy acrylate, aliphatic epoxy acrylate, and miscellaneous epoxy acrylates.

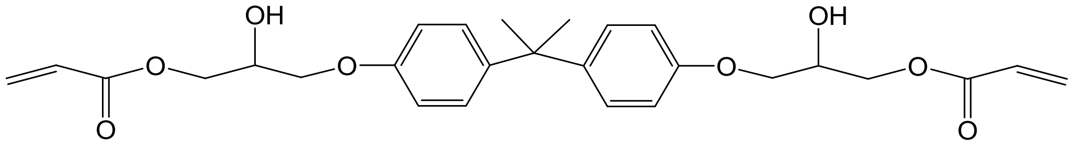


Figure 2.19: Epoxy acrylate

Aromatic difunctional epoxy acrylates have very low molecular weight, which gives them attractive properties such as high reactivity, high gloss, and low irritation. Common applications for these resins include overprint varnishes for paper and board, wood coatings for furniture and flooring, and coatings for compact discs and optical fibers. Aromatic difunctional epoxy acrylates have limited flexibility, and they yellow to a certain extent when exposed to sunlight. The aromatic epoxies are viscous and need to be thinned with functional monomers. These monomers are potentially hazardous materials. Acrylated oil epoxy acrylates are essentially epoxidized soy bean oil acrylate. These resins have low viscosity, low cost, and good pigment wetting properties. They produce relatively flexible coatings. Acrylated oil epoxy acrylates are used mainly in pigmented coatings or to reduce cost. Epoxy novolac acrylates are specialty products. They are mainly used in the electrical / electronics industry because of their excellent heat and chemical resistance. However, they provide rigid coatings with relatively high viscosity and high costs. Aliphatic epoxy acrylates comprise several varieties. They are available difunctional and trifunctional or higher. The difunctional types have good flexibility, reactivity, adhesion, and very low viscosity. Some difunctional types can be diluted with water. The trifunctional or higher types have moderate viscosity and poor flexibility but excellent reactivity. Aliphatic epoxy acrylates have higher cost than the aromatic epoxy acrylates and are generally used in niche applications. Miscellaneous epoxy acrylates consist mainly of oligomers with fatty acid modification. They provide good pigment wetting properties and higher molecular weight but lower functionality than other aromatic epoxy acrylates. They are used in printing inks and pigmented coatings.

2.2 Hybrid Materials

Hybrid inorganic–organic materials are not just physical mixtures of inorganic and organic moieties. They can be defined as nanocomposites with organic and inorganic components that are intimately mixed on a molecular level. The general concept is to combine the properties of organic groups, biomolecules and polymers (functionalization, ease of processing at low temperatures, toughness) with properties of glass- or ceramic like materials (hardness, chemical, and thermal stability), in order to generate new and synergetic properties not accessible otherwise. Hybrids are typically either homogeneous systems derived from monomers or miscible organic and inorganic components, or heterogeneous systems (nanocomposites) in which at least one of the components' domains has dimensions ranging from some Å to several nanometers. The properties of the final materials certainly depend to a large degree on the chemical nature of the compounds, however, the synergistic effects arising from the combination of the different moieties cannot be underestimated. Therefore, one key aspect in the synthesis of hybrid inorganic–organic materials is the deliberate positioning of the various species in the network and the design of the nature, the extent and accessibility of the interface between the various parts. One very prominent natural inorganic–organic nanocomposite material is nacre with its alternating layers composed of calcium carbonate and an organic polymer. Hybrid inorganic–organic materials are typically divided into different classes: Class I materials are typically composed of organic or inorganic moieties embedded in an inorganic or organic matrix, respectively, by only weak chemical bonding (hydrogen, van der- Waals or sometimes ionic bonds). In class II materials, the different components are linked on a molecular level by strong bonds (covalent or iono-covalent bonds). (For further information see also the excellent review articles and the special issue devoted to Hybrid Materials in J. Mater. Chem. İn 2005 and references herein). In the synthesis of hybrid inorganic–organic materials with an inorganic backbone in general, but also more specifically for porous materials, the sol–gel process plays an essential role, due to its mild processing conditions (metal-organic precursors, organic solvents, low processing temperatures, processing variability of the colloidal state). It allows not only the intact integration of a large variety of organic functionsinto an inorganic framework (due to the low temperatures) but also for homogeneous mixing of all components on a nanometric level. There is a wide range of possibilities to vary the composition and structure and thus the properties of the materials, starting from the chemical composition, the ratio of the inorganic to organic components, the structure and distribution of the building blocks. The ability to entrap molecular species (class I) has been largely used to prepare functional materials applicable in catalysis, optical, electrochemical, and other applications. For porous materials simple entrapment of functional molecules inside the matrix always bears the risk of leaching of the active compound. Therefore, for many applications, covalent bonding to the backbone greatly enhances the lifetime and stability of the material. Siloxane-based class II materials can be easily synthesized due to the high hydrolytic stability of the Si–C(sp 3) bond. A large variety of organo-substituted silanes of the general formula R′–Si(OR) 3 or the corresponding bridged species (RO) 3 Si–R′–Si(OR) 3 are available, where R′ can be almost any organofunctional group (e.g., an alkyl group, a polymerizable group, a group that complexes metal centres, an organic dye, etc) (Fig. 2.20). The chemical synthesis pathway that is used to design a given hybrid network structure is one of the most important parameters in the preparation process. General strategies towards the synthesis of hybrid materials are discussed in detail in several review articles and references herein). With respect to porous hybrid matrices many of these synthetic approaches can be used, but in many cases have to be adapted to the specific porous host material. Chemical modification of porous materials in principle, and covalent modification by organic entities in particular, can be achieved at various stages of the preparation process.

a) Post-synthesis modification of the final dried porous product by gaseous, liquid or dissolved organic or organometallic species.

b) Addition of molecular, but non-reactive compounds to the precursor solution.

c) Liquid-phase modification in the wet nanocomposite stage or – for mesostructured materials or zeolites – prior to removal of the template.

d) Co-condensation reactions by the use of organically substituted co-precursors.

e) Application of “single source precursors” in which the organic entity is an integral part of the network-forming species.

These approaches open the door to a large variety of porous hybrid materials that benefit from the properties of both parts by the combination of inorganic and organic building blocks. The purpose for is to improve the spectrum of properties without deteriorating the existing positive characteristics by modifying porous materials by organic groups. The favorable physical and derived properties of porous materials are a consequence typical of the highly porous structure. Therefore, any chemical modification of the material must retain this structure. In the case of crystalline microporous materials, the crystallinity and stability of the material should remain unchanged, and for mesostructured porous materials, the periodicity of the structure must be retained. For example, unmodified M41S silica-based materials are hydrophilic, which is undesired for many applications. The material can be rendered hydrophobic by the introduction of hydrophobic organic groups, e.g., methyl or phenyl groups (vide infra). The organic groups can selectively be placed on the internal and/or the external pore surfaces or even within the pore walls. The organic modification in principle permits a very selective fine tuning of material properties, including potential interaction to guest molecules. In addition, surface reactivities can be altered, the surface can be protected by organic groups from chemical attack, and bulk properties, e.g., mechanical or optical properties can be modified. This flexibility in choosing organic, inorganic, or even hybrid building blocks allows control over the materials properties to optimize them for each desired application [51].

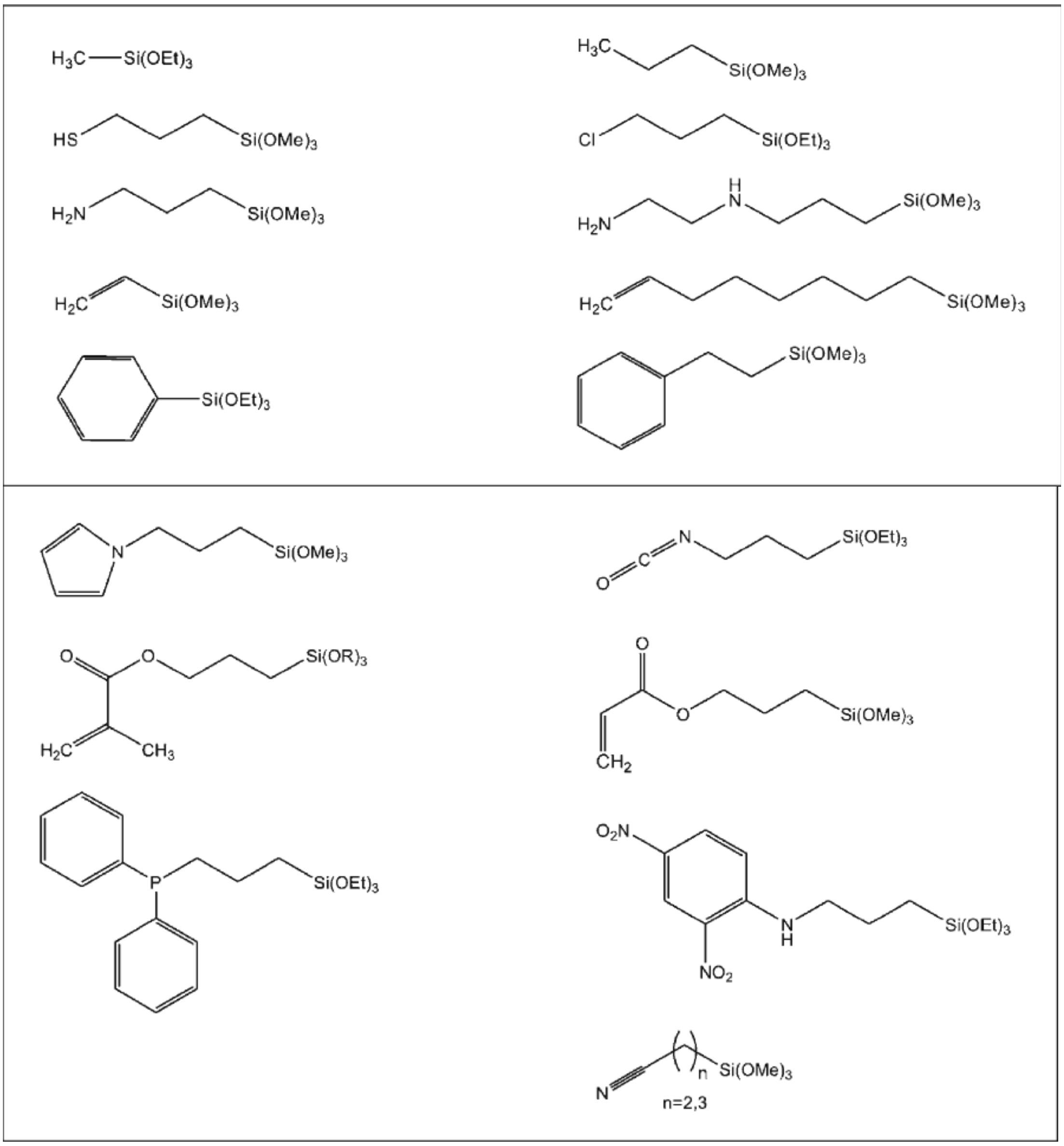


Figure 2.20: Selection of representative organofunctional silanes available for the preparation of inorganic–organic hybrid materials (APTS= aminopropyl-trialkoxysilane).

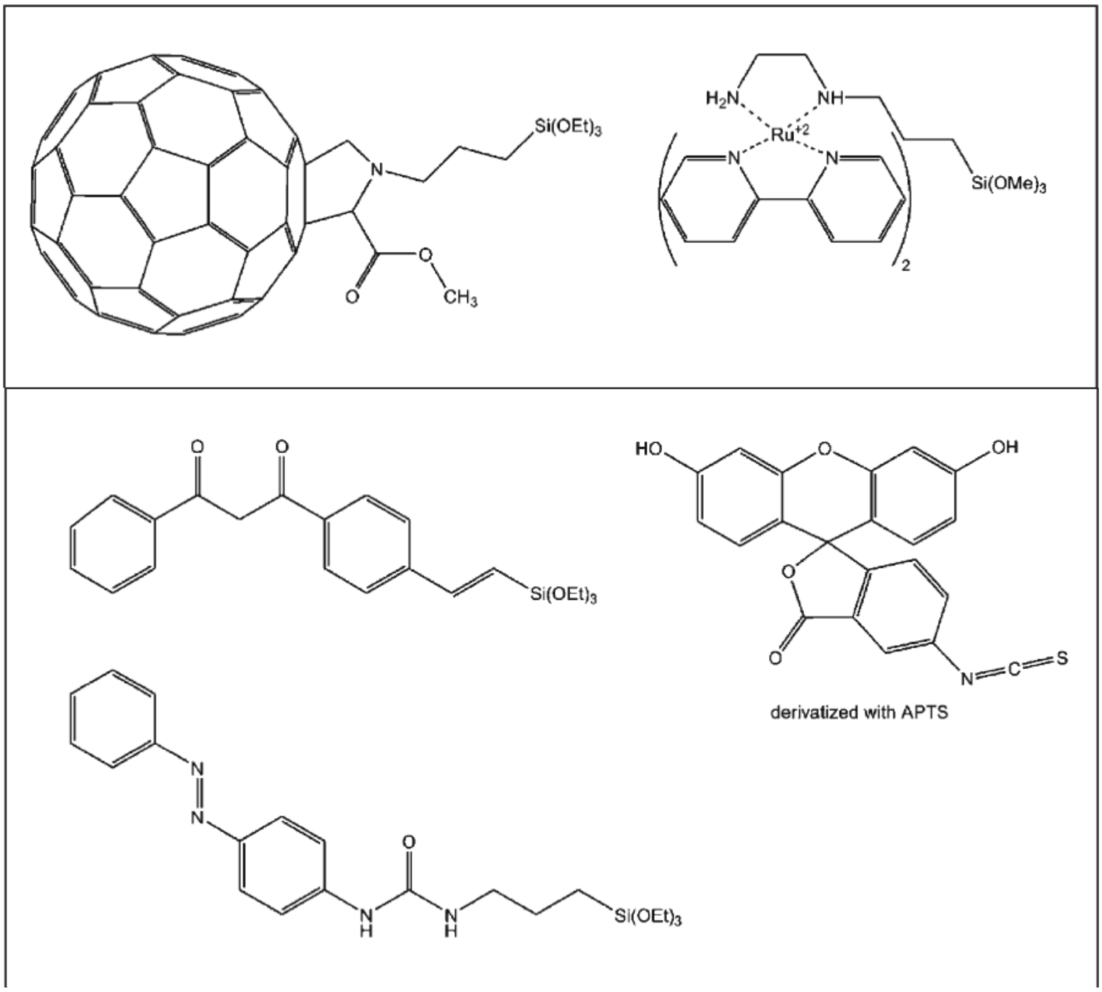


Figure 2.20 (Continued): Selection of representative organofunctional silanes available for the preparation of inorganic–organic hybrid materials (APTS= aminopropyl-trialkoxysilane).

The selection of porous matrices that are discussed in the following sections of this chapter is somewhat arbitrary, but represents the general reaction schemes and the problems associated with the different pathways in the synthesis of hybrid porous materials.

2.3 Urethane Acrylates

The reaction of isocyanate group with the hydroxyl group of an acrylic or methacrylic monomer (Figure 2.21) will give the corresponding urethane acrylate or methacrylate. If diisocyantes are utilised, then acrylate di-functionality may be obtained. In contrast with epoxy acrylates, where onle a few similar starting materials are available, urethane acrylates can be prepared from a large, diverse range of raw materials. This results in many possible variations in preparation and a very large range of properties of finished products. The diisocyanates which may be acrylated include toluene diisocyanate (TDI), tetramethylxylene diisocyanate (TMXDI), hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI, and its chain isomer, trimethylhexamethylene diisocyanate (TMDI), dicyclohexylmethane diisocyanate (H_{12}MDI), xylene diisocyanate (XDI) and diphenylmethane diisocyanate (MDI). HMDI and TDI are extremely hazardous, being relatively volatile. To minimize this problem, oligomers of HMDI are used. TDI is reacted with a triol to give a relatively safe product. H_{12}MDI consists of three stereoisomers because of the reduction of the aromatic MDI. Hydroxy functional monomers include hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA) and hydroxyethyl methacrylate (HEMA). If other hydroxy containing compounds are also present, like polyethers, polyesters or polyols that contain more than one hydroxyl group per molecule, then chain extension is possible. This results in a wide range of prepolymers that vary in functionality and molecular weight with corresponding variations in final film properties [52]. Urethane acrylates probably offer a far wide range of final film properties than any other class of radiation curable oligomers.

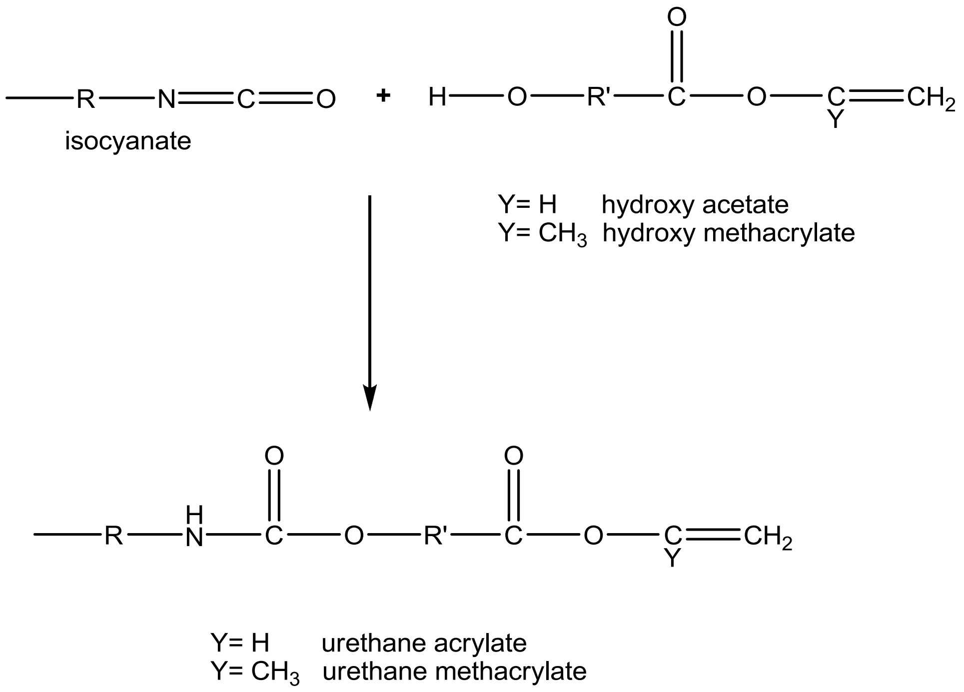


Figure 2.21: Isocyanate-Hyrdoxyl Acrylate Reaction

2.3.1 Types of Urethane Acrylates

2.3.1.1 Polyether Urethane Acrylates

Polyether urethane acrylates or methacrylates can be considered to consist of three components. Polyether polyol, multifunctional isocyanate and hydroxy acrylate or methacrylate. An isocyanate functional adduct is produced by capping a polyether with a diisocyanate, which is then reacted with an unsaturated hydroxy compound, such as 2-hydroxyethyl acrylate. Substituting 2-hydroxyethyl methacrylate (for 2-hydroxyethyl acrylate), results in the corresponding polyether urethane methacrylate.

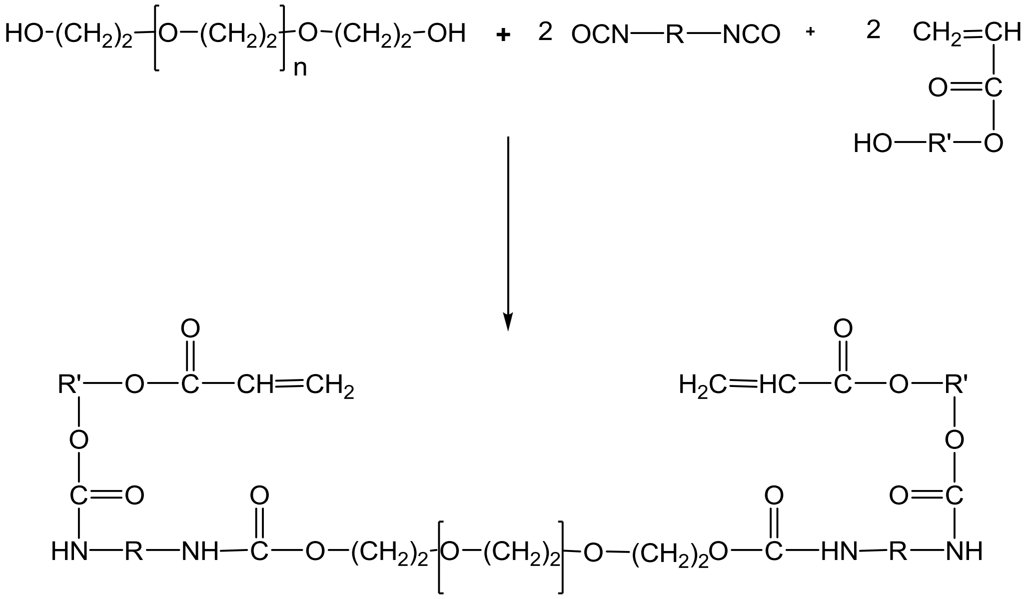


Figure 2.22: Formation of a Polyether Urethane Acrylate

2.3.1.2 Multicomponent Urethane Acrylates

If instead of totally reacting a diisocyanate with a hydroxy acrylate, a portion of the acrylate is replaced by one or more hydroxy functional materials, then an immense range of structures is possible. This possibility is enhanced if the alternative hydroxy materials have multi-hydroxy functionality. Therefore, the range of properties is too large for typical urethane acrylate properties to be given. Owing to the complexity of these materials, even identical stoichiometric mixtures may yield products with significantly different properties under different reaction conditions. Viscosity is one example of a property that can vary dramatically. Flexible urethane acrylates can be made by the reaction of a diisocyanate with a long chain glycol. The half adduct of a diisocyanate acrylate may also be used. Aliphatic diol polyethers, such as polyethylene glycol, polypropylene glycol and caprolactone polyols, are widely used for this purpose, as are polyesters with an excess of hydroxy groups. As the flexibility increases, the hardness, speed of cure, and solvent resistance of the films decrease. A hard urethane acrylate could be formed from a highly branched multifunctional polyol like pentaerythritol, and a diisocyanate and hydroxy acrylate, or a diisocyanate and hydroxy acrylate half adduct. It may be necessary to select reactants to ensure that steric hindrance does not cause incomplete reaction. There are two possible methods of preparing the same urethane acrylate when a modifying hydroxyl component is used. In the first method, the diisocyanate and the hydroxy acrylate (or methacrylate) are reacted and the half (or partial) adduct is then reacted with the modifying hydroxy compound. In the second method, the modifying hydroxy compound is reacted with the diisocyanate and the resulting product is then reacted with the hydroxy acrylate.

2.3.1.3 Polyester Urethane Acrylates

Polyester urethane acrylates or methacrylates can be considered to consist of three major components. Polyester polyol, multifunctional isocyanate and hydroxy compound containing reactive unsaturation which would typically be an acrylate or methacrylate. The reaction is taken to an initial molecular weight of around 1000. A typical polyester structure is given in Figure 2.23.

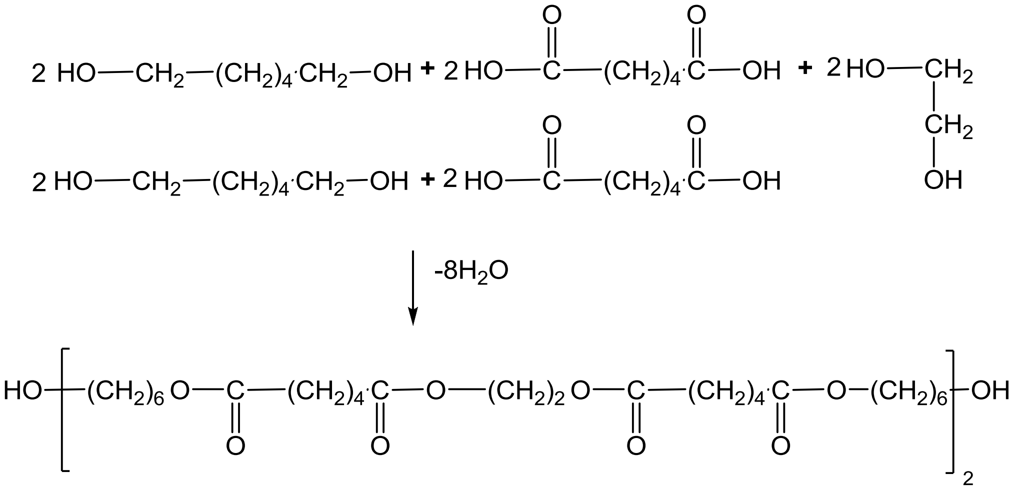


Figure 2.23: Polyester Structure for Acrylation

2.3.1.4 Polyol Urethane Acrylates

Hydroxyl groups are also present in molecules other than polyesters or polyethers. If there is more than one hydroxyl group per molecule, then the molecule can be described as a polyol. Most polyols that are not polyethers or polyesters, which might be used to form urethane acrylates, are relatively simple molecules (di-, tri-, or tetra-polyols) that are often used in polyester formulation. Examples of some of these polyols include ethylene glycol, propylene glycol, 1,6 hexanediol, glycerol, trimethylolpropane (TMP), and pentaerythritol. Structures of these molecules are shown in Figure 2.24.

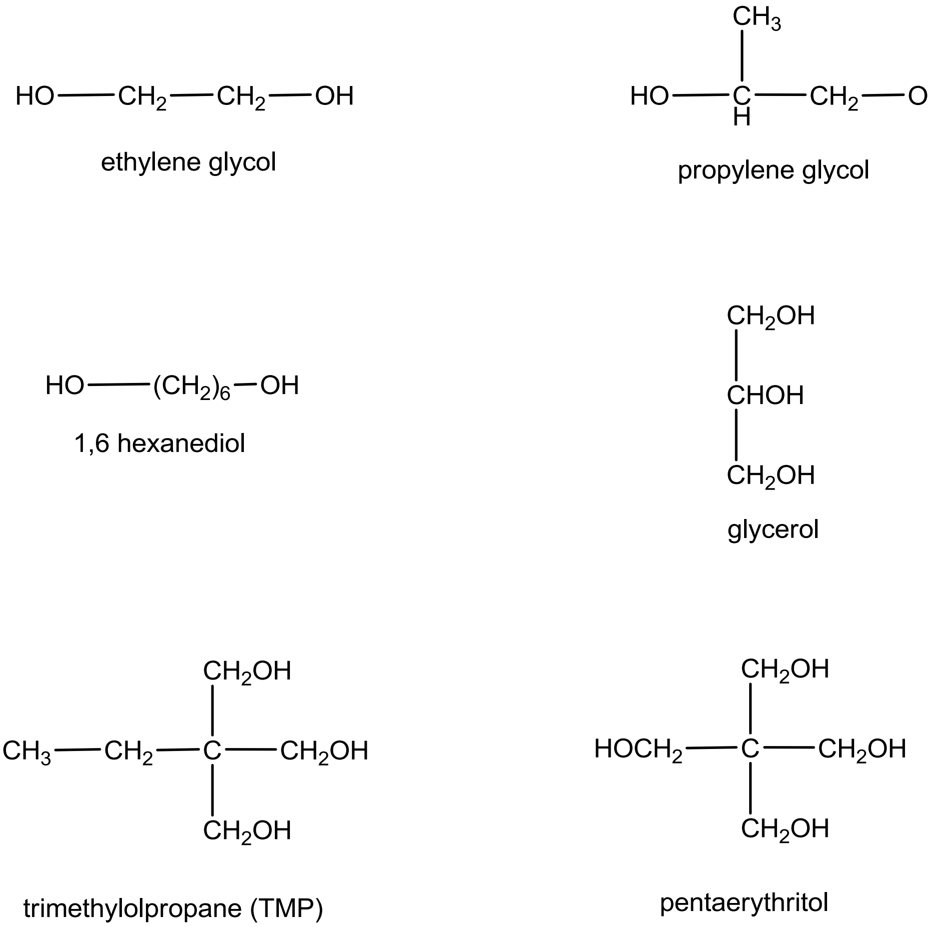


Figure 2.24: Structures of some non-polyether, non-polyester polyols

2.4 UV Coatings

2.4.1 Inroduction to Coatings Technology

Coatings are found almost anywhere in daily life, the most prominent examples are architectural wall coatings and automotive paints. They are applied in order to provide:

a) decorative appearance, and/or

b) protective barrier.

The main functions of a coating are thus on the one hand to ensure the desired appearance (colour, gloss) and on the other hand the necessary protection, against corrosion, Stone chipping, scratches, abrasion or chemical attack, like red wine, coffee or mustard on furniture coatings or acid rain, tree resins or bird excrements on automotive coatings. Whereas the do-it-yourself architectural coatings are almost all water-based, the vast majority of industrially used coatings, applied in factories on various substrates, like vehicles, furniture, metal cans, paperboards, etc., still contain solvents. The coatings and application spectrum discussed in this book are predominantly based on the industrial coatings sector, which had a share of about 40% of the whole worldwide coatings market (60% architectural).

2.4.2 UV Technology and Applications

UV curing has now been established as an alternative curing mechanism to thermal hardening, contrary to the past, where it was only considered for the curing on temperature sensitive substrates, like wood, paper and plastics. This alternative curing technology uses the energy of photons of radiation sources in the short wavelength region of the electromagnetic spectrum in order to form reactive species, which trigger a fast chain growth curing reaction.

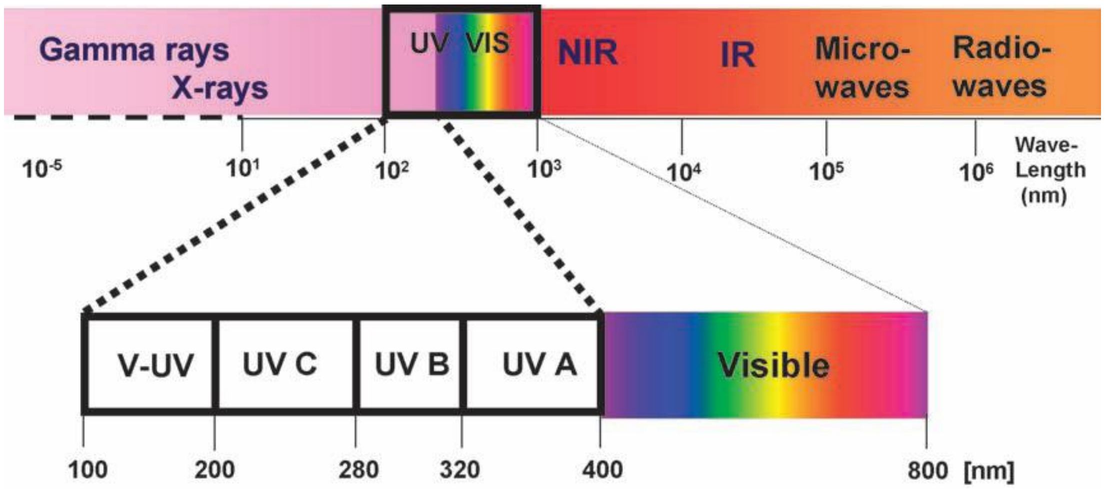


Figure 2.25: Electromagnetic energy spectrum

Out of the electromagnetic spectrum (shown in Figure 1.5 is the range from the nearinfrared (NIR), over visible and ultraviolet (UV) to electron beams and X-ray) the UV region, further classified into UV-A, UV-B, and UV-C radiation, is mainly used for this technology. The energy content of a photon is defined by the equation;

$$E = h\nu = hc/\lambda, \qquad \textbf{(2.1)}$$

where ν is the frequency and λ is the wavelength (nm). This equation tells us, that the shorter the wavelength, the higher the energy of a photon. UV light in the wavelength region of 300–400 nm should already be able to cleave C–C bonds. The high energy photons of e-beam and X-ray are sufficient to cleave C–C or C–H bonds, thus, they do not need a special photoinitiator for forming the desired radical species as initiators for polymerization. In the case of UV exposure, however, photoinitiators are commonly used, since the direct cleavage processes are not efficient enough. The photoinitiators are excited and after a cascade of reactions form the desired reactive species. In the case of using longer wavelength exposures, more complicated energy transfer reactions are needed. From the spectrum of usable radiation energy sources, UV technology is by far the most common one. From the higher energy radiation sources, e-beam technology has been widely explored for coatings technologies. It is still the most economical technology for industrial applications with very high volumes. However, the high safety requirements related to the use of e-beam technology and the high investment costs hamper the widespread use of this technology.

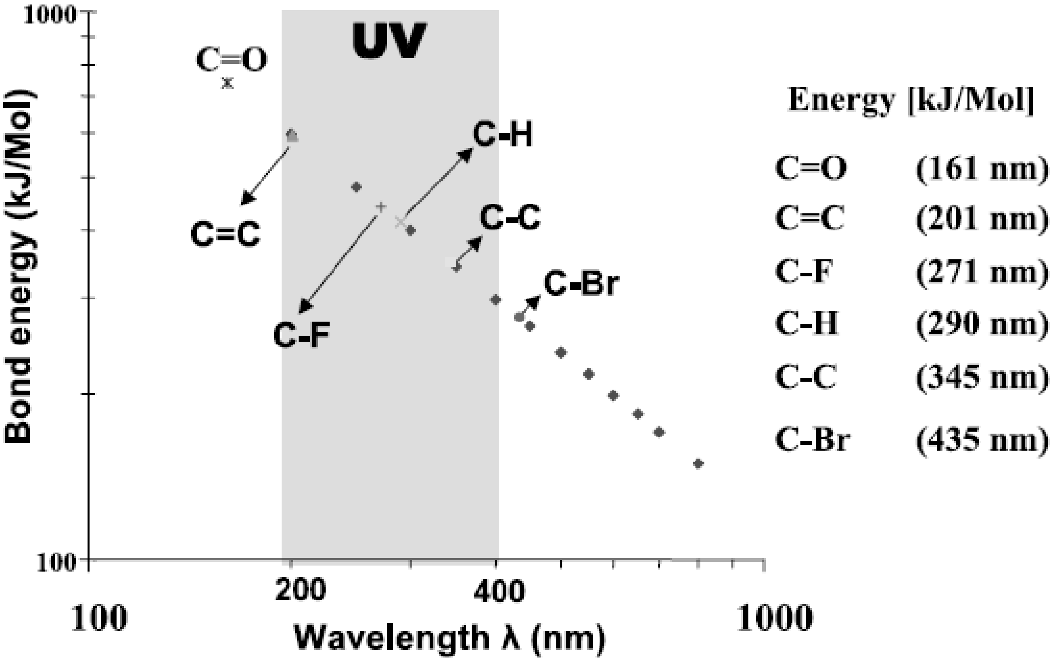


Figure 1.26: Energies as a function of wavelenght in comparison to bond energies

At the RadTech Conference 2005 in Barcelona, considerable interest has been expressed in the session dealing with e-beam technology for "printing, varnishing and laminating for the packaging industry".10 The reasons for this alertness are new developments of compact and less expensive EB equipment and new formulation advances in flexographic printing inks, coatings and adhesives. Especially in the packaging printing for food contact applications the use of EB technology has advantages over UV coatings since no photoinitiator is needed, which can migrate, if the coating is inadequately cured. UV curable coatings are traditionally used on temperature sensitive substrates, like wood, paper and plastics, for example, clear coats for parquet, furniture, vinyl flooring, on plastic substrates (crash helmet, boards), compact discs, headlight lenses or overprint varnishes (posters, high gloss packaging). However, since coatings are used almost everywhere, the UV coatings market is expanding to new applications, where traditionally thermal curing systems have been the workhorses. Applications like UV curable coatings on metals (automotive, coil coating) and exterior uses on windows, on glass, bikes, on appliances, like refrigerators, washing machines, and most prominently on cars are good examples. A multiplicity of coating applications is often less noticed, such as adhesives and protective coatings for DVD and CD's, protective coating on glass fiber wires, inside and outside of beverage cans, on automotive parts, like headlight mirrors and in multiple functions on electronic parts. This list can easily be extended even further. Up to now, UV curable systems are mainly used in clear coat applications, thus posing high demands on the performance of this layer; at the surface of the coating it is exposed to attack by mechanical or chemical stresses, like scratches, household chemicals (detergents, red wine, coffee, mustard), by air polluents (acids, water, bird excrements) as well as Stone chipping or many other impacts. The formulations used for radiation curable coatings depend therefore on the specific performance requirements and on the application technique. The traditional formulations of UV curable coatings are still 100% liquids (or also commonly referred to 100% solids, despite used in liquid form, in order to point out that they contain no solvents or other volatiles). However, in the meantime, due to the consideration of UV curing as an alternative to thermal hardening, the use of small amounts of solvents in order to reduce the viscosity, the formulation of UV curable water-based systems and the development of UV powder have been pursued. The market penetration of UV coatings is up to now still regarded as a niche technology. This is due to several factors, one decisive reason is based on the curing technology itself, which is still stamped as a two-dimensional curing process, in which only planar substrates are feasible. Up to now there are only few applications involving three-dimensional objects. As shown schematically in the diagram of Figure 2.27, the application processing is mainly based on industrial applications on two-dimensional substrates. The substrate is first coated, exemplarily shown is a casting line, and then passed under lamp units, where it is exposed to intense radiation.Within a fraction of a second, the liquid low molecular mass is thereby transferred via a photo-induced radical polymerization to a solid crosslinked network. After the end of the line, the fully cured and dry substrate can be stacked and further processed immediately. Typical compositions of UV curable coatings (Table 2.1) contain in the range of 25% to 90% oligomeric resins, which are responsible for the film formation and the basic coating properties. Reactive diluents are low molecular weight compounds, which are incorporated into the polymer network, and used instead of solvents (in conventional lacquers) in order to adjust the viscosity to the requirements of the application process. Typical application viscosities range from 3000–5000 MPa s (Pascal × second) for roller application to 100–200 mPa s for spray applications.

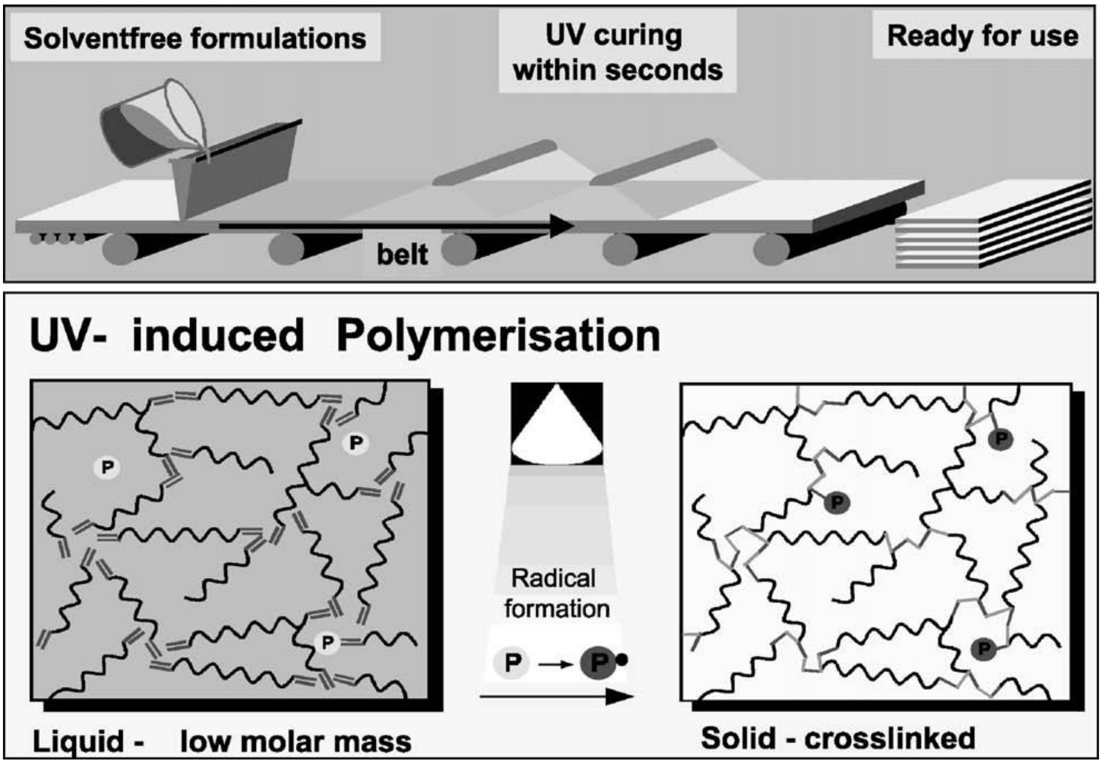
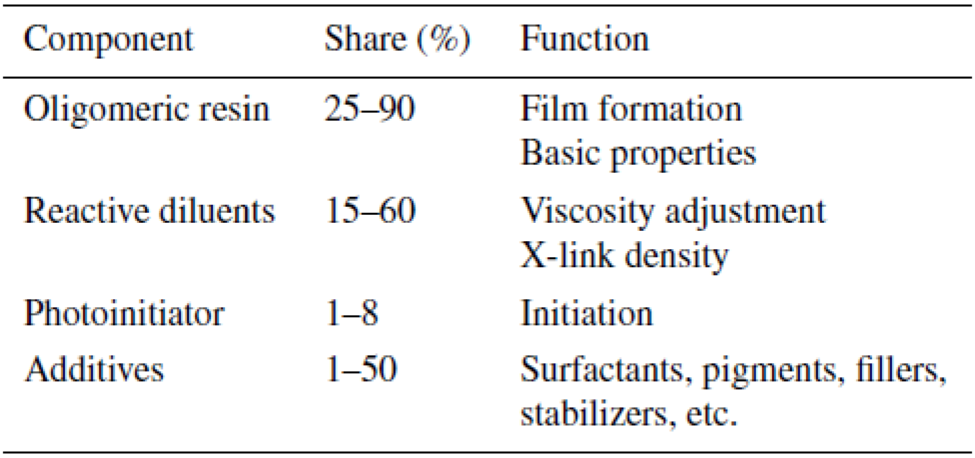


Figure 2.27: Scheme of the UV curing process and UV induced cross-linking

Table 2.1: General composition and function of an UV lacquer



Component	Share (%)	Function
Oligomeric resin	25–90	Film formation Basic properties
Reactive diluents	15–60	Viscosity adjustment X-link density
Photoinitiator	1–8	Initiation
Additives	1–50	Surfactants, pigments, fillers, stabilizers, etc.

In UV curable lacquers, about 1–8% photoinitiators, as well as several other additives (from 1% up to 50%), like leveling agents, stabilizers, UV absorbers, radical scavengers, pigments and so on, are used to tailor the formulation to the application process and coating property requirements. This general composition of UV curable coatings applies to radically polymerizable coatings as well as to cationically curable systems and EB curable coating, which, however, do not need photoinitiators.

2.4.3 Advantages and Drawbacks of UV Coatings

Economical advantages are energy saving (commonly rapid cure at room temperature), high production speed, small space requirements and immediate post cure processing possible. Ecological advantages are in general solvent free formulations (VOC reduction), possibility of easy recycling (waste reduction) and energy saving. Performance advantages are low substrate heating, high product durability, application versatility, high scratch resistance and chemical resistance, exceptional abrasion, stain and solvent resistance and superior toughness.

Drawbacks are material costs are higher than, e.g., alkyds, polyesters or epoxies, 3D curing equipment development is in its infancy, UV curing in the presence of UV stabilizers decelerated, oxygen inhibition at the surface (in many radical curing systems), sensitivity to moisture (cationic curing system), difficult through-cure of pigmented coatings (at thicknesses >5 μm), topics to eliminate weaknesses, improving adhesion to metal, plastics, minimizing skin irritation caused by some reactive diluents, reducing odor (of the formulations), reducing extractables of cured coatings, improving photoinitiators (cost, migration, volatility) and direct food contact packaging approval.

2.4.4 The UV Curing Process

The UV curing process is predominantly determined by the desired application of the coating. The intended end-product governs the substrate to be coated. This may be an abrasion resistant clear coat for ready-to-install parquet or an overprint varnish for paper cards, a coloured base coat and a clear coat for plastic automotive parts or metal coils, as well as a flexible protective coat for window frames. The function of the coating, for instance the colouration of the part, the protection against corrosion, scratching, chemical attack or against weathering deterioration, determines the type and property requirements of the coating as well as the thickness required. The targeted properties, like high gloss appearance, abrasion resistance, colour effects, hardness, flexibility, resistance against chemicals or scratches, have to be provided by the chemical formulation, consisting of base resins, diluents, photoinitiators and various additives. Furthermore, an appropriate selection of the components has to be done in order to enable an effective curing process; for instance, in coatings containing pigments or UV light stabilizers, the spectral absorbance of the photoinitiator has to be adjusted to a spectral region where the pigments or UV absorbers are fairly transparent. This fine tuning is necessary to match the characteristics of the lamp system with the chemistry of the coating to provide an economic curing process. Besides the physical properties of the cured material to be obtained, the economics of the coating process is the most important variable which decides over the type of coating used. Thus, in order to calculate the total costs of a coating process, not only materials costs but the whole process design and the equipment set-up have to be considered in order to compare different coating processes with each other. UV curable coatings are always in competition with thermally curable systems of the classical solvent-type, water-based or powder coatings. Some economic factors of UV curing have been discussed by Stowe,1 with cost examples for ink, coating and adhesive applications in comparison with thermal hardening, if applicable. UV curing in general offers a number of advantages over competitive coatings, while some can be related to costs, others relate to performance, environmentally compliance or processes not achievable with other methods.

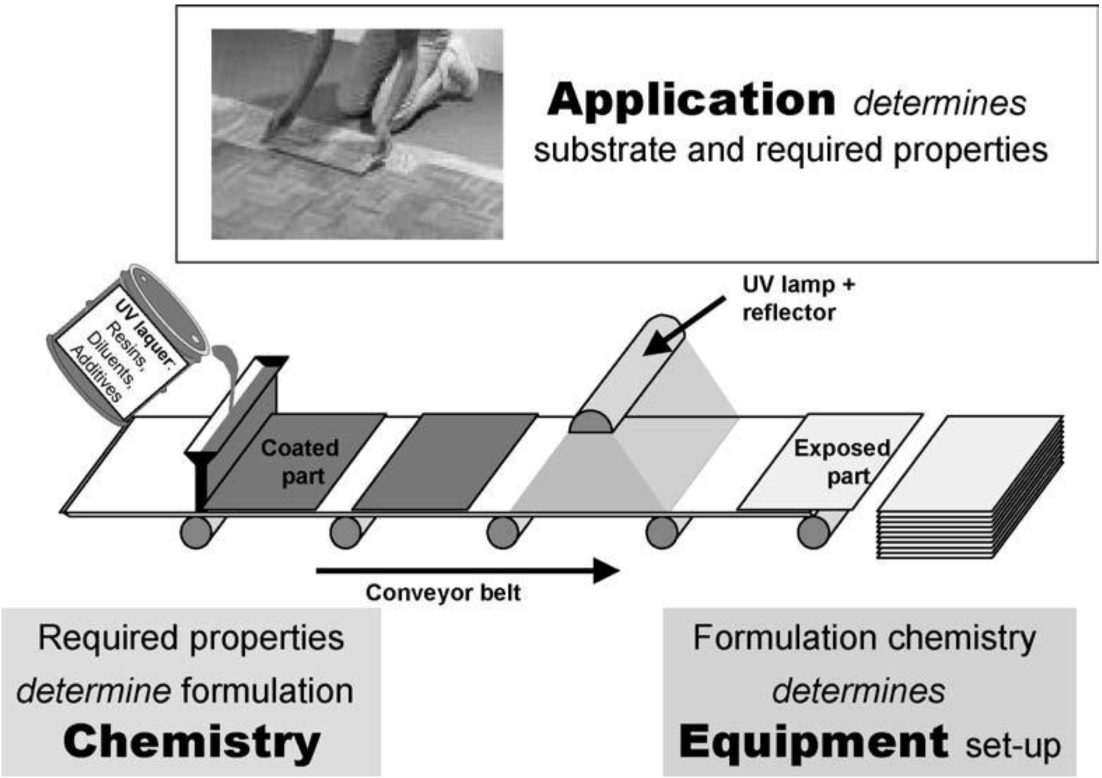


Figure 2.28: Interaction of UV process design parameters.

Thus, the UV curing process relies crucially on an efficient cogging of the required application properties with the chemistry chosen to fulfill the performance requirements as well as the UV curing equipment applied to provide a fast and complete cure in order to meet the economical and ecological aspects of coating technology (Figure 2.28). UV curing in its basics is a fast, room temperature curing process indicating low energy consumption and requiring little space for the equipment [53].

2.4.5 The Photochemical Process

2.4.5.1 Photoinduced Curing Chemistry

Photoinduced curing can be realized as in the preparation of conventional linear polymers by a step like process, as used in polyaddition and polycondensation reactions or by a chain process occurring in polymerization reactions (Figure 2.29).

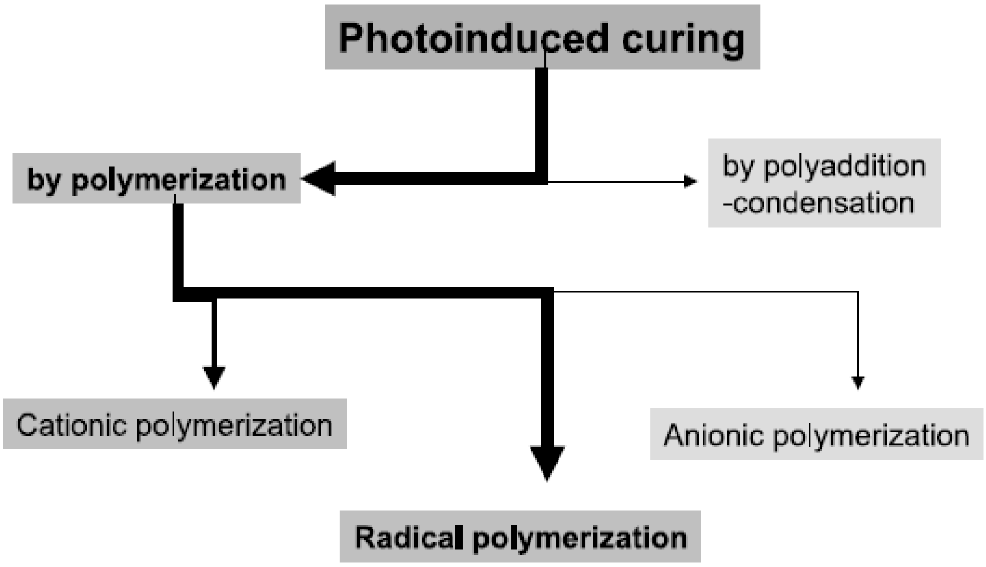


Figure 2.29: Possibilities of photoinduced curing

The photoinduced polyaddition technology has been for a long time the workhorse of photoresist technology, for example, the crosslinking of resins was achieved by photoinduced dimerization of cinnamates. This photodimerization is an example of a direct photoreaction where every step of polymer built-up is initiated by an absorbed photon, thus every single reaction step is dependent on the quantum yield of the photoreaction (generally very much smaller than 1) [54]. On the contrary, in polymerization reactions induced by light only the initiating step is dependent on the photoreaction ($\Phi < 1$). The photopolymerization reaction then is a chain reaction, where one produced initiator radical can add up to several thousand monomer units, thus the overall quantum yield of the total reaction is much bigger than 1. Whereas the photoinduced radical polymerization is now the mainstream technology, the photoinduced ionic curing reactions are not so well explored and developed, mainly due to the lack of easily available photoinitiators [55-57]. The basic principles of curing and network formation are similar in radical and cationic induced curing. The cationic curing has its main advantages in the oxygen insensitive curing and in the good adhesion mainly to metals achieved with the cationic curable epoxy systems. The UV curing technology is based on the photoinitiated rapid transformation of a reactive liquid formulation into a solid coating film. The initiating species may be a cation, an anion or a radical. The vast majority of UV curable coatings are based on radical producing photoinitiators. The main components of such formulations based on radical polymerizations are reactive resins containing a plurality of polymerizable double bonds, which govern mainly the desired properties of the final coating; copolymerizable, monomeric diluents, which are responsible for the reduction or adjustment of the viscosity of the formulation, a function taken by the solvent in conventional formulations; photoinitiators or a photoinitiating system containing photoinitiator and photosensibilizer or coinitiators; and, if necessary, other coating additives, like surface active additives, slip additives, fillers, pigments, light stabilizers, etc. The chemistry involved in the radical initiated UV induced crosslinking can be divided into the three steps, initiation, propagation and termination. Although the UV energy applied in photocuring may cleave C–C and C–H bonds, the commonly used monomers do not produce sufficient amounts of initiating species, which is due to low absorbance and poor cleavage efficiency. Thus, a special photoinitiator is usually applied, which is excited and ultimately yields via intersystem crossing, accompanied by various deactivation reactions, the formation of a radical species, which can initiate radical polymerization. The following polymerization reaction follows almost exactly the rules of conventional radical polymerization. Thus, only the initiation step is different to thermal initiated radical polymerization. The light absorption and the following processes are outlined in a Jablonski diagram (Figure 2.30). The process starts with the absorption of a photon by the photoinitiator molecule, which results in excitation of an electron into higher singlet states.

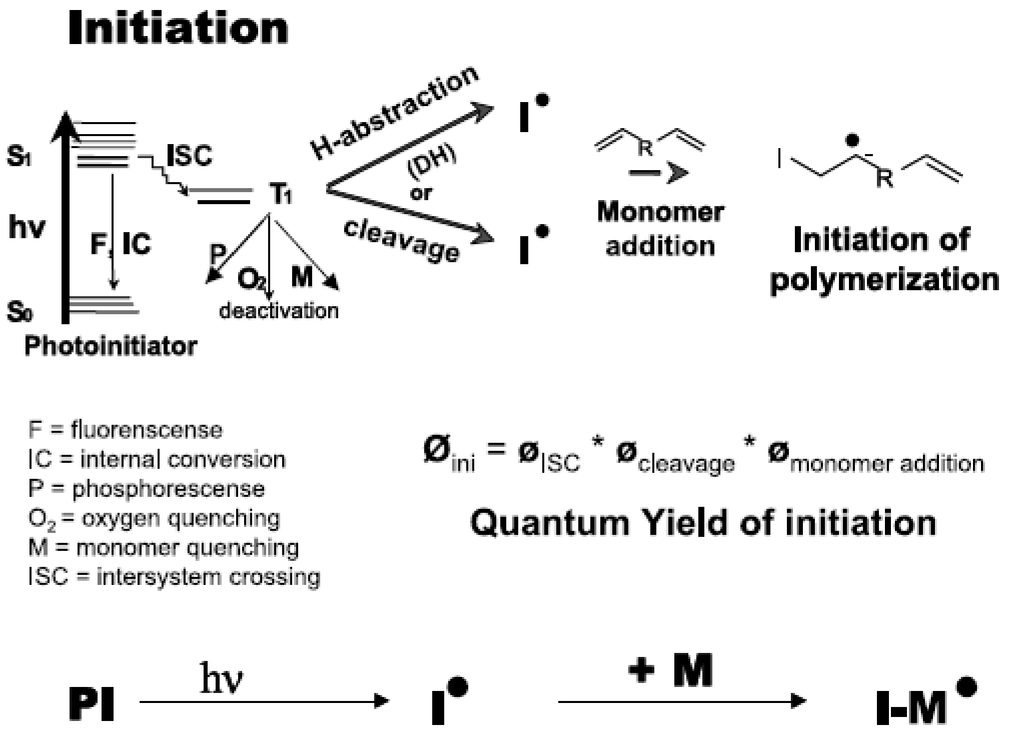


Figure 2.30: Jablonsky-type diagram for photoinduced radical photoinitiation

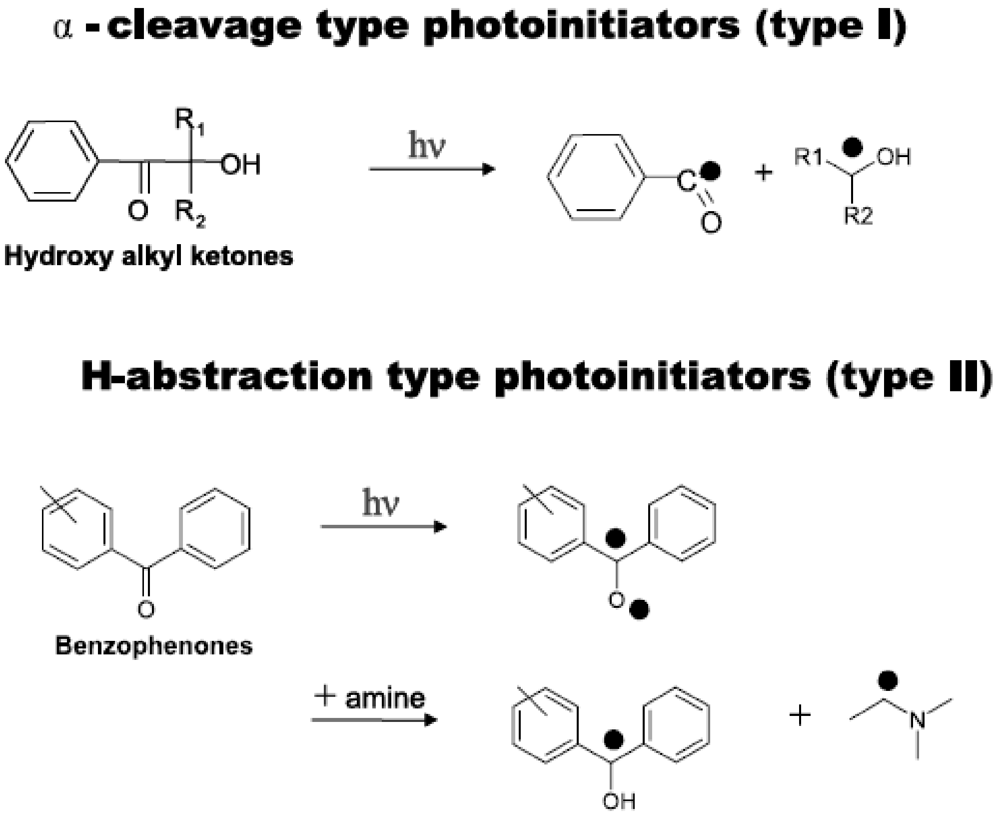


Figure 2.31: Photoinitiator types

From these excited states, various processes can follow. First, deactivation can proceed by radiationless internal conversion and evolution of heat back to the ground state or by emission of fluorescence. Second, by intersystem crossing (ISC) an electron spin inversion leads to the excited triplet state. The photochemical processes which lead to the desired active species (e.g., free radicals) often take place from the excited triplet state, where the molecule posses two unpaired electrons, rather than from the singlet state. The formation of the reactive species, namely free radicals, competes with further deactivation processes, like monomer quenching, oxygen quenching and phosphorescence. The direct oxygen quenching of the photoinitiator excited states is not very likely in the case of the extremely shortlived triplet states of α-cleavable type photoinitiators, but much more pronounced in the hydrogen abstraction type owing to the relatively long-lived triplet states [58]. From the triplet state two main reactions can lead to initiating species, the intramolecular scission of an α-bond, or the intermolecular abstraction of a hydrogen atom. The intramolecular scission is the most effective process in the formation of radicals, since the hydrogen abstraction is a bimolecular type reaction, which is diffusion controlled and may be accompanied by several deactivation reactions. The quantum yield of initiation, representing the number of growing chains per photon absorbed reflects the importance of the processes leading to initiation over all the indicated processes of deactivation. The efficiency of the photoinitiation is a function of different quantum yields, since several side reactions can occur in every step. Thus, the overall yield of initiation is a complex function of different quantum yields, represented exemplarily in Figure 2.30. Two examples of photoinitators, an alpha type scission initiator and a hydrogen abstraction type photoinitiator are shown in Figure 2.31. Propagation (Figure 2.32) is the key step to very efficient curing, since it is a chain reaction where for instance one produced radical can add more than 1000 monomer units within a fraction of a second. The steps after the initiation are very similar to the normal radical polymerization of monofunctional monomers, which are widely used to synthesize thermoplastic polymers, like polyethylenes, polypropylene or polystyrenes. The main difference in coating systems is the use of multifunctional monomers or oligomers, which leads to the formation of networks. In the propagation reaction transfer reactions also often play a significant role, where the growing radical chain does not add to another monomer unit, but abstracts hydrogen radical from a neighbouring R–H group. The remaining radical can then start another growing chain, thus leading to the termination of the growing polymer chain, but not to the termination of the chain reaction. The reaction of the radicals with oxygen does not play a significant role in the polymerizations of linear polymers, since they are normally conducted under inert conditions. However, the curing of coatings is normally performed under atmospheric conditions, thus, the oxygen interference plays a major role. The termination reactions are also manifold (Figure 2.33). Besides the termination with an initiator radical, several other termination reactions play a role, especially the recombination of growing radical species or elimination reaction of the chain end.

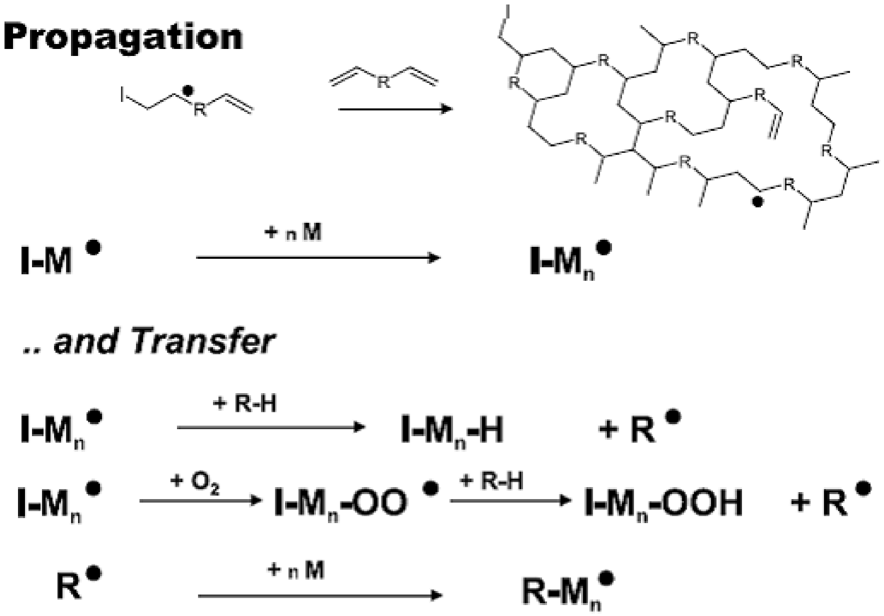


Figure 2.32: Propagation and transfer

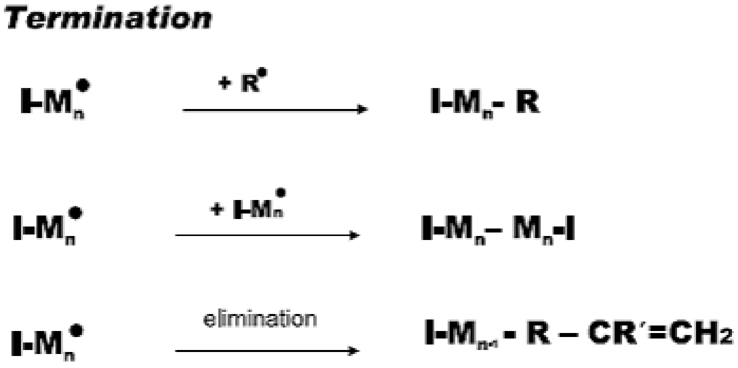


Figure 2.33: Termination reaction

3.EXPERIMENTAL PART

3.1 Materials

For the synthesis of terephthalic acid modified epoxy acrylate resin , Bisphenol A type epoxy resin (from Elkay Chemicals), Hydroquinone, Triethylamine (TEA, from Acros Chemicals), Acrylic acid and Terepthalic acid (from Merck Chemicals), Vinyltrimethoxysilane (from Aldrcih Chemicals), Dipropyleneglycoldiacrylate (DPGDA, Cytec Chemicals), 1,6-hexanedioldiacrylate (HDDA, from Sartomer Chemicals) and a Irgacure 184 (from Ciba Chemicals) were used.

Epoxy Resin is bisphenol A diglycidyl ether resin, was used as epoxy resin. Epoxy equivalent weight is 190 g/Eq. Density of epoxy resin is 1,12-1,15 g/ml. Viscosity, according to Brookfield, 600-800 cps at 25^0C.

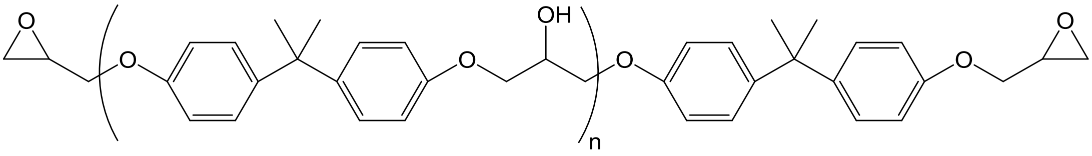


Figure 3.1: Bisphenol A diglycidyl ether resin

Hydroquinone (benzene-1,4-diol) was used as inhibitor. It is white solid and its density is $1,3g/cm^3$.

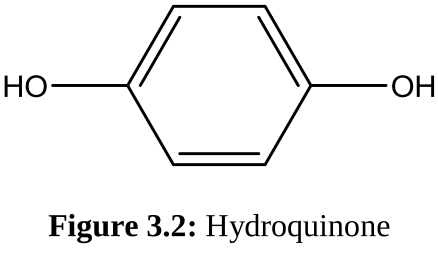


Figure 3.2: Hydroquinone

Acrylic Acid is the simplest unsaturated carboxylic acid, consisting of a vinyl group connected directly to a carboxylic acid terminus. It was used to allow epoxy resin curing by UV light. Its density is 1,051 g/ml. They have excellent color, UV, and thermal stability.

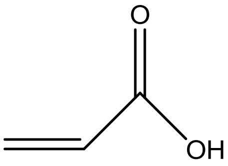


Figure 3.3: Acrylic acid

Terephthalic Acid is a unsaturated organic compound. It is used as a reactant in the synthesis of modified epoxy acrylate resin. M_w is 166.13 g/mol.

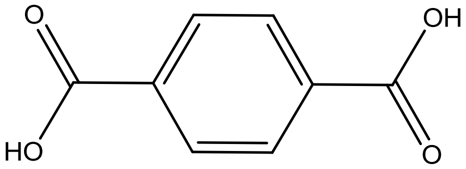


Figure 3.4: Terephthalic acid

Vinyltrimethoxysilane (VTS) was used in the formation of film. Its density is 0,9817 g/ml.

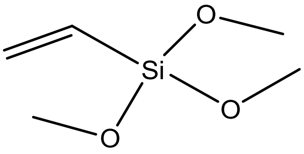


Figure 3.5: Vinyltrimethoxysilane

Urethnane Acrylate (UA) was used in the formation of film.

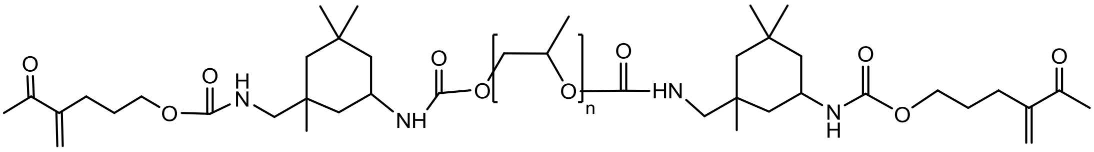


Figure 3.6: Urethane Acrylate

Dipropylene glycol diacrylate (DPGDA) is a difunctional monomer used to increase the gelation stability of UV film formulations at elevated temperatures. It has low viscosity, high T_g, and fast cure speed. It was used as a crosslinking agent in photopolymerization system.

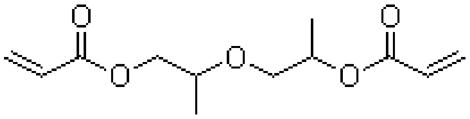


Figure 3.7: Dipropylene glycol diacrylate

HDDA (1,6-hexanedioldiacrylate) is a low viscosity, fast curing monomer with low volatility, a hydrophobic backbone, and good solvency for use in free radical polymerization. It was used for lower viscosity and crosslinking in polymerization.

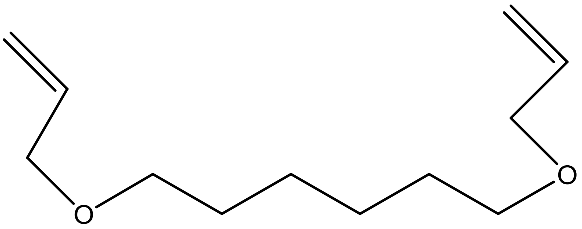


Figure 3.8: HDDA

Irgacure 184 (1-hydroxy-cyclohexyl-phenyl-ketone)

IRGACURE 184 is a highly efficient non-yellowing photoinitiator which is used to initiate the photopolymerisation of chemically unsaturated prepolymers - e.g. acrylates - in combination with mono- or multifunctional vinyl monomers.

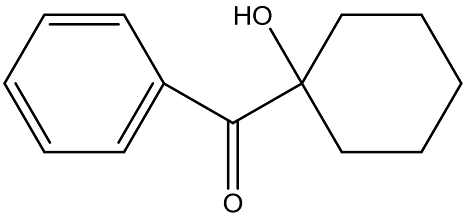


Figure 3.9: Irgacure 184

3.2 Equipments

3.2.1 Infrared Analysis (IR)

Infared analyses were performed with Thermo Scientific Nicolet IS10 FT-IR spectrometer.

3.2.2 Nuclear Magnetic Resonance (NMR)

^{1}H-NMR analyses were performed with a Bruker 250 MHz Spectrometer.

3.2.3 UV Spectroscopy Analysis

UV spectroscopy analyses were performed with Shimadzu PharmaSpec UV-1700 UV-Visible Spectrophotometer.

3.2.4 Thermogravimetrical Analysis (TGA)

Thermogravimetric analyses were performed with a TA TGA Q50 instrument at a heating rate of 20 °C/min.

3.2.5 Contact Angle Meter

The contact angles of cured UA-C films were measured by KSV CAM 100 instrument.

3.2.6 Gloss Meter

The gloss (20°, 60° and 85°) of cured urethane acrylate films were measured by BYK-Gardner (Micro-TRI) gloss meter.

3.2.7 Pendulum Hardness Tester

A König Pendulum Hardness (BYK-Gardner) tester was used to measure the film hardness of the urethane acrylate films.

3.2.8 Tensile Loading Machine

Zwick Z010 Universal Tensile Tester was used to determine properties such as modulus, elongation at break and strength.

3. 3 Synthesis

3.3.1 Synthesis of Terephthalic acid modified Epoxy Acrylate

10 gr epoxy resin (epoxy equivalent value 185-195 g/mol), hydroquinone, triethylamine were charged into 50 mL three-necked round bottom flask, equipped with nitrogen inlet and thermometer, condenser. The mixture was stirred for 30 min at room temperature and heated to 50 ^{0}C and stirred for 30 min at this temperature. So the mixture was heated to 60, 70, 80 ^{0}C as stepwise and finally heated to 90 ^{0}C. The reaction was kept at this temperature for 3 hours. The system was cooled down to 60 ^{0}C and acrylic acid was added to mixture as dropwise at this temperature. After addition was completed, the mixture was heated to 80 ^{0}C and kept at this temperature for 24 hr until acid value of resin was reached between 1 and 2. . It was controlled by titration of 0,1N KOH solution with phenolphthalein indicator. The product was clear, yellow, viscous liquid and checked by infrared spectroscopy.

Table 3.1: The compositions of synthesized resins

sample name	epoxy resin (mmol)	terephthalic acid (mmol)	acrylic acid (mmol)	triethyl amine (ml)
Tamer 0	52,6	0	52,6	0,034
Tamer 5	52,6	1,315	49,97	0,034
Tamer 10	52,6	2,63	47,34	0,034
Tamer 15	52,6	3,945	44,71	0,034

3.3.2 Synthesis of Urethane Acrylate

1 mol of polyol polypropylene glycol and acetone were placed into a three-necked reaction kettle equipped with a magnetic stirrer, heating mantle, reflux condenser, dropping funnel and nitrogen inlet and $CaCl_2$ tube. 2 mole of isophorone diisocyanate (IPDI) dissolved in acetone was dropped into the reactor. The dibutyltinlaurate added as catalys, the temperature was increased to 55 ^{o}C. The reaction was continued till the NCO content reached the theoretical value as determined by dibutylamine titration. Then 2 mol of hydroxyethyl methacrylate (HEMA) dissolved in acetone was added dropwise through the dropping funnel for over a period of 30 min and mixed. The reaction was continued until NCO peak at 2270 cm^{-1} dissappeared totally in the FTIR spectra of samples taken from the

reaction ketle every 0,5 h. The final product was vacuum dried at ambient temperature.

3.4 Preparation of Formulations

Three different formulation were applied for polymerization system. Three of them were also prepared for UV curing. The compositon of formulations is given in table.

Table 3.2: UV curing formulations

sample code	terephthalic acid modification ratio (%)	modified resin (wt.%)	HDDA (wt.%)	DPGDA (wt.%)	photoinitiator (wt.%)
T 0	0	50	10	37	3
T 5	5	50	10	37	3
T 10	10	50	10	37	3
T 15	15	50	10	37	3

Table 3.3: UV curing formulations with VTS

sample code	terephthalic acid modification ratio (%)	modified resin (wt.%)	vinyl trimethoxy silane (wt.%)	HDDA (wt.%)	DPGDA (wt.%)	Photo initiator (wt.%)
Si-T 0	0	47	3	10	37	3
Si-T 5	5	47	3	10	37	3
Si-T 10	10	47	3	10	37	3
Si-T 15	15	47	3	10	37	3

Table 3.4: UV curing formulations with UA

sample code	terephthalic acid modification ratio (%)	modified resin (wt.%)	urethane acrylate (wt.%)	HDDA (wt.%)	DPGDA (wt.%)	photoinitiator (wt.%)
UA-T 0	0	47	20	10	20	3
UA-T 5	5	47	20	10	20	3
UA-T 10	10	47	20	10	20	3
UA-T 15	15	47	20	10	20	3

3.4.1 Preparation of Test Samples

I. Free Films

To prepare free films, teflon mould having 10mm x 50mm x 1mm spaces was used. Free film formulations were prepared according to the table 3.1. Solutions were kept under vacuum approximately 30 minutes to remove bubbles, then poured into the spaces on the teflon mould. The mould was then placed under UV lamp and irradiated for 300 seconds. The films were kept waiting for a couple of days before further tests. After that thermal and characterization analysis, chemical resistance and strain-stress tests were applied on these free films.

II. Coated plexiglass plates

Firstly, temporary polyetylene coating films were pulled away by force from plexiglass plates surface. 1g of film solution for each plates was prepared. The plexiglass plates were put on smooth surface and coated with a film by pulling a glass rod from one side to another. Wet films were cured under EMA UV machine for 10 pass and kept waiting for a couple of days before further tests. Cross-cut, pencil hardness, gloss, contact angle and pendulum hardness tests were applied on these plates.

3.5 Analyses

Following tests; Infrared Analysis (IR), Nuclear Magnetic Resonance Spectroscopy (NMR), Thermogravimetric Analysis (TGA), Pendulum Hardness, Contact Angle Measurement, Gloss and Tensile tests, Pencil Hardness, Solvent Resistance and Gel Content were performed to monitor thermal, morphological and film properties of films.

3.5.1 Infrared Analysis

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification. Infrared radiation spans a section of the electromagnetic spectrum having wavenumbers from roughly 13,000 to 10 cm^{-1}, or wavelengths from 0.78 to 1000 μm. It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies. IR absorption positions are generally presented as either wavenumbers ($\tilde{\nu}$) or wavelengths (λ). Wavenumber defines the number of waves per unit length. Thus, wavenumbers are directly proportional to frequency, as well as the energy of the IR absorption. The wavenumber unit (cm^{-1}, reciprocal centimeter) is more commonly used in modern IR instruments that are linear in the cm^{-1} scale. In the contrast, wavelengths are inversely proportional to frequencies and their associated energy. At present, the recommended unit of wavelength is μm (micrometers), but μ (micron) is used in some older literature [59].

3.5.2 Nuclear Magnetic Resonance Analysis

Nuclear magnetic resonance (NMR) is a property that magnetic nuclei have in a magnetic field and applied electromagnetic (EM) pulse or pulses, which cause the nuclei to absorb energy from the EM pulse and radiate this energy back out. The energy radiated back out is at a specific resonance frequency which depends on the strength of the magnetic field and other factors. This allows the observation of specific quantum mechanical magnetic properties of an atomic nucleus. Many types of information can be obtained from an NMR spectrum. Much like using IR to identify functional groups, analysis of a NMR spectrum provides information on the number and type of chemical entities in a molecule. However, NMR provides much more information than IR. All stable nuclides that contain an odd number of protons and/or of neutrons have an intrinsic magnetic moment and angular momentum, in other words a nonzero spin, while all nuclides with even numbers of both have spin 0. The most commonly studied nuclei are ^{1}H (the most NMR-sensitive isotope after the radioactive ^{3}H) and ^{13}C, although nuclei from isotopes of many other elements (e.g. ^{2}H, ^{10}B, ^{11}B, ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{23}Na, ^{29}Si, ^{31}P, ^{35}Cl, ^{113}Cd, ^{129}Xe, ^{195}Pt) are studied by high-field NMR spectroscopy as well. When an atom is placed in a magnetic field, its electrons circulate about the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus which opposes the externally applied field. The magnetic field at the nucleus (the effective field) is therefore generally less than the applied field by a fraction σ.

The electron density around each nucleus in a molecule varies according to the types of nuclei and bonds in the molecule. The opposing field and therefore the effective field at each nucleus will vary. This is called the chemical shift phenomenon. The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and a standard, relative to the standard. This quantity is reported in ppm and given the symbol delta, δ. In NMR spectroscopy, this standard is often tetramethylsilane, $Si(CH_3)_4$, abbreviated TMS. The chemical shift is a very precise metric of the chemical environment around a nucleus.

In this study, NMR analysis were used to support characterization of materials beside IR analysis.

3.5.3 Thermogravimetric Analysis

Thermogravimetry has become a general method for comparing the thermal stability of polymers. TGA measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere [60]. Measurements are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can characterize materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration. In comparing thermal stability, it should be remembered that TGA measurements only record the loss of volatile fragments of polymers, caused by decomposition. TGA cannot detect any chemical changes or degradation of properties caused by cross-linking [61].

In this study, thermal stability was evaluated using a Q50 TGA from TA Instruments. Film samples of 5–10 mg were placed in the sample pan and heated from 25 °C to 700°C under N_2 (flow rate: 90 mL/min) at an applied heating rate of 20°C /min. During the heating period, the weight loss and temperature difference were recorded as a function of temperature. The results are given in Table 4.1, Table 4.2 and Table 4.3.

3.5.4 Gel Content Measurement

A cured film sample (m_1) was accurately weighted, and then added to the Soxhlet extractor with acetone as extraction agent for 6 hrs. The cured film was dried until its weight was constant (m_2). Gel content of the cured film was calculated by equation,

Gel content (%) = $(m_2/m_1) \times 100\%$

Where m_1 is the weight of the cured film sample; m_2 is the residual weight of the cured film sample. The results are shown on the Table 4.4.

3.5.5 Solvent Resistance

The solvent resistance of the cured films was determined by immersing in various solvents (m_1, 0.005-0.03g g/10 ml) for one day. After than cured films were dried until its weight were constant. After drying, the films were reweighted (m_2) and weight loss was calculated.

Weight loss (%) = $(m_1-m_2) / m_1 \times 100$

Solvents used in this test and results are shown in the Table 4.5-4.16.

3.5.6 Contact Angle Measurement

The determination of solid-vapor γ_{SV} and solid-liquid γ_{SL} interfacial tensions is of importance in a wide range of problems in pure and applied science. Because of the difficulties involved in measuring directly the surface tension involving a solid phase, indirect approaches are called for: Several independent approaches have been used to estimate solid surface tensions, including direct force measurements; contact angles; capillary penetration into columns of particle powder; sedimentation of particles; solidification front interaction with particles; film flotation; gradient theory; Lifshitz theory of van der Waals forces; and theory of molecular interactions. Among these methods, contact angle measurements are believed to be the simplest [62]. Contact angle measurement is easily performed by establishing the tangent (angle) of a liquid drop with a solid surface at the base. The attractiveness of using contact angles θ to estimate the solid-vapor and solid-liquid interfacial tensions is due to the relative ease with which contact angles can be measured on suitably prepared solid surfaces. It will become apparent later that this seeming simplicity is, however, very misleading. The possibility of estimating solid surface tensions from contact angles relies on a relation which has been recognized by Young in 1805 [63]. The contact angle of a liquid drop on a solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions: solid-vapor, γ_{SV}, solid-liquid, γ_{SL}, and liquid-vapor, γ_{LV} (Fig.3.26). This equilibrium relation is known as Young's equation where θ is the Young contact angle, i.e. a contact angle which can be inserted into Young's equation. It will become apparent later that the experimentally accessible contact angles may or may not be equal to $\theta_{Y.}$

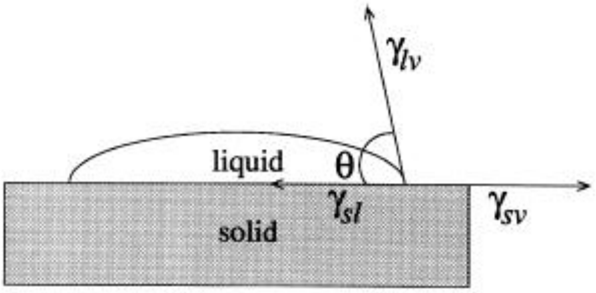


Figure 3.10: Scheme of a sessile-drop contact angle system

Contact angle is a well-known technique for investigating and controlling adhesion, surface treatments and cleaning, and polymer film modification. The wetting of solid substrates is a basic feature of many natural and industrial processes and contact angle is a simple, rapid, and sensitive method of characterizing the wettability of a solid surface [62]. The wettability of the film surfaces was measured using a contact angle KSV CAM100 system at ambient temperature. The equilibrium contact angles of 5µL water droplets were measured by the sessile drop method. The contact angles were measured as follows: a 5μL water droplet was placed on the sample using a syringe, and contact angle was recorded.

The water contact angle of films prepared in our experiments are listed in Table 4.17.

3.5.7 Gloss Test

The traditional definition of gloss considers the light reflected at the surface of coatings. The reflection of light varies depending on the smoothness of the surface so the illuminated environment is reproduced more or less efficiently. The sensory impression perceived by the eye is recognized as gloss.

To increase the measuring accuracy and improve the reproducibility of the measurements it has become reliable procedure with samples manifesting different gloss to also set various angles of incidence and reflection for the measuring beam. Owing to the higher proportion of reflection light with larger angles of incidence matt surfaces are measured with a large angle of incoming light (85^0C), semi-gloss ones are measured with a medium angle (60^0C) and high-gloss ones with only a very small angle (20^0C). Modern devices contain all 3 measuring geometries and can be used universally by switching to the various ranges.

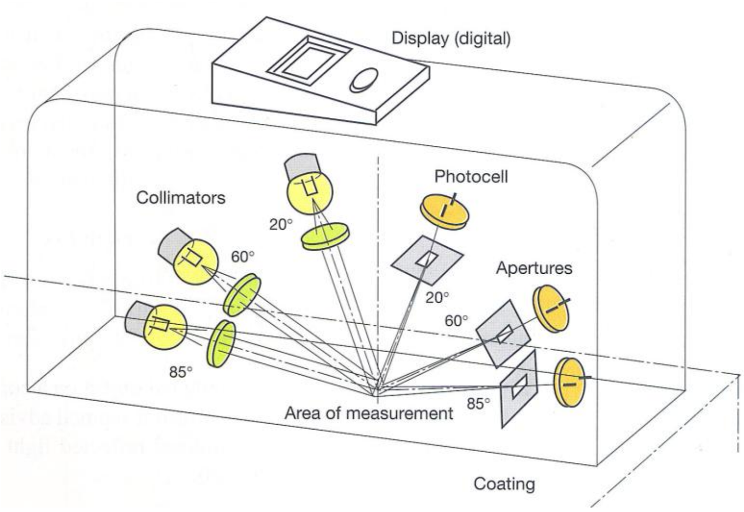


Figure 3.11: Scheme of a measurement device for gloss at different angles

The test was applied to the cured films coated on plexiglass plates to measure their gloss properties. The test results are shown at Table 4.18.

3.5.8 Pendulum Hardness Test

König pendulum hardness method which is frequently encountered in practice is used for measuring the hardness of the samples. The device itself consist of a pendulum, to the support of which two agate balls are attached. The pendulum is placed on the coating with the two balls 5 mm in diameter and moved 6° away from the position of rest. After releasing the 200 g pendulum the oscillations are recorded by a counter. The measure of damping is the number of oscillations or the time in seconds which elapses until the amplitude of the pendulum has dropped from 6° to 3°.

Pendulum hardness of the cured film was measured to determine the film hardness. The test results are shown at Table 4.19.

3.5.9 Pencil Hardness Test

Non-standard but well-accepted measure of the hardness of pencil leads (made of different proportions of graphite and clay), commonly ranging from 6B (maximum graphite, hence softest) to 6H (least amount of graphite, hence the hardest) with HB (roughly equal amounts of graphite and clay, hence medium soft/hard) in the middle. Pencil hardness is used in indicating the toughness of surface coatings by testing which number pencil-lead can scratch it.

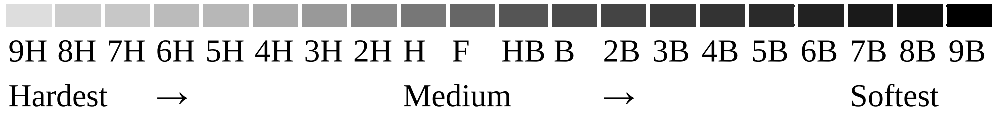


Figure 3.12: Pencil hardness and properties

Pencil Hardness (ASTM D-3363) was performed to check the through cure of coatings. Pencil hardness property of coating was determined using pencils ranging from H to 8H and the pencil that will not stratch the coating reported as pencil scratch hardness. The results are given in Table 4.20.

3.5.10 Tensile Test

Tensile properties indicate how the material will react to forces being applied in tension. A tensile test is a fundamental mechanical test where a carefully prepared specimen is loaded in a very controlled manner while measuring the applied load and the elongation of the specimen over some distance. Tensile tests are used to determine the modulus of elasticity, elastic limit, elongation, proportional limit, reduction in area, tensile strength, yield point, yield strength and other tensile properties. The main product of a tensile test is a load versus elongation curve which is then converted into a stress versus strain curve. Since both the engineering stress and the engineering strain are obtained by dividing the load and elongation by constant values (specimen geometry information), the load-elongation curve will have the same shape as the engineering stress-strain curve. The stress-strain curve relates the applied stress to the resulting strain and each material has its own unique stress-strain curve. If the true stress, based on the actual cross-sectional area of the specimen, is used, it is found that the stress-strain curve increases continuously up to fracture. The linear-elastic region of the curve indicates that no plastic deformation has occurred. In this region, when the stress is reduced, the material will return to its original shape. In this linear region, the line obeys the relationship defined as Hooke's Law where the ratio of stress to strain is a constant. The slope of the line in this region where stress is proportional to strain and is called the modulus of elasticity or Young's modulus. The modulus of elasticity (E) defines the properties of a material as it undergoes stress, deforms, and then returns to its original shape after the stress is removed. It is a measure of the stiffness of a given material. To compute the modulus of elastic, simply divide the stress by the strain in the material. Since strain is unitless, the modulus will have the same units as the stress, such as kpi or MPa. The modulus of elasticity applies specifically to the situation of a component being stretched with a tensile force. This modulus is of interest when it is necessary to compute how much a rod or wire stretches under a tensile load. Axial strain is always accompanied by lateral strains of opposite sign in the two directions mutually perpendicular to the axial strain. Strains that result from an increase in length are designated as positive (+) and those that result in a decrease in length are designated as negative (-). Poisson's ratio is defined as the negative of the ratio of the lateral strain to the axial strain for a uniaxial stress state. Poisson's ratio is sometimes also defined as the ratio of the absolute values of lateral and axial strain. This ratio, like strain, is unitless since both strains are unitless. For stresses within the elastic range, this ratio is approximately constant. For a perfectly isotropic elastic material, Poisson's Ratio is 0.25, but for most materials the value lies in the range of 0.28 to 0.33. Generally for steels, Poisson’s ratio will have a value of approximately

0.3. This means that if there is one inch per inch of deformation in the direction that stress is applied, there will be 0.3 inches per inch of deformation perpendicular to the direction that force is applied.

In this study, tensile tests were applied to 10mm x 50mm x 1mm epoxyacrylate free films. The results are shown on Table 4.21-4.23.

4. RESULTS AND DISCUSSION

In this thesis, terephthalic acid modified epoxy acrylate resins at different modification ratios were synthesized and employed in various formulations for preparation of UV-cured coatings.

Terephthalic acid modified epoxy acrylates were incorporated into the formulations containing mono- and diacrylates, photoinitiator and coated on plexiglass plates and cured by UV light. Also, free films of all formulations are prepared and cured by the same way. Cured films were analysed for chemical, thermal and mechanical properties.

4.1 Synthesis of Terephthalic acid Modified Epoxy Acrylate

Terephthalic acid modified epoxy acrylate was synthesized according to the procedure (Figure 4.1) mentioned in section 3.3.1. Firstly, terephthalic acid reacted with about 5% mol ratio of epoxy groups in epoxy resin and secondly, acrylic acid reacted with remaining epoxy groups to yield epoxy acrylate. The resulting product was checked by FT-IR spectroscopy technique.

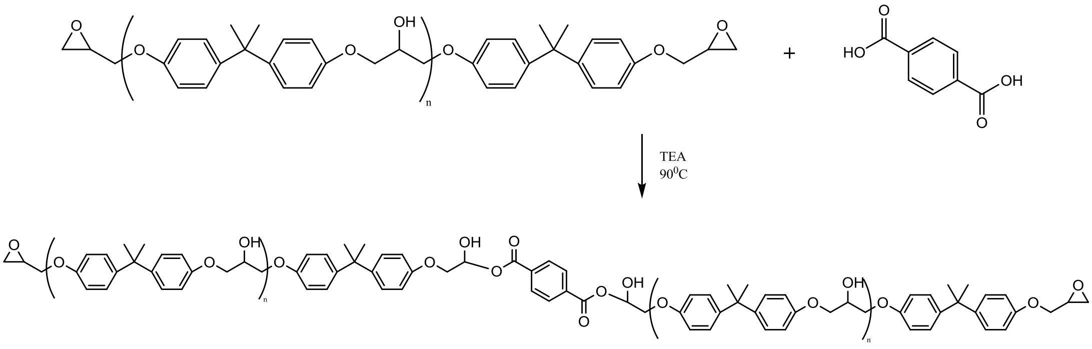


Figure 4.1. Synthesis of terephthalic acid modified epoxy

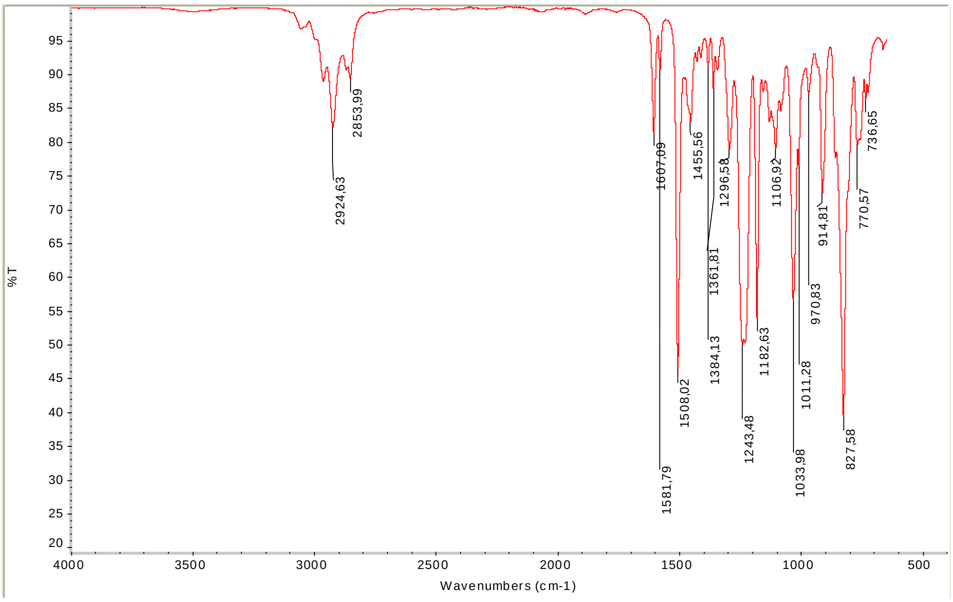


Figure 4.2: IR spectrum of pure epoxy resin

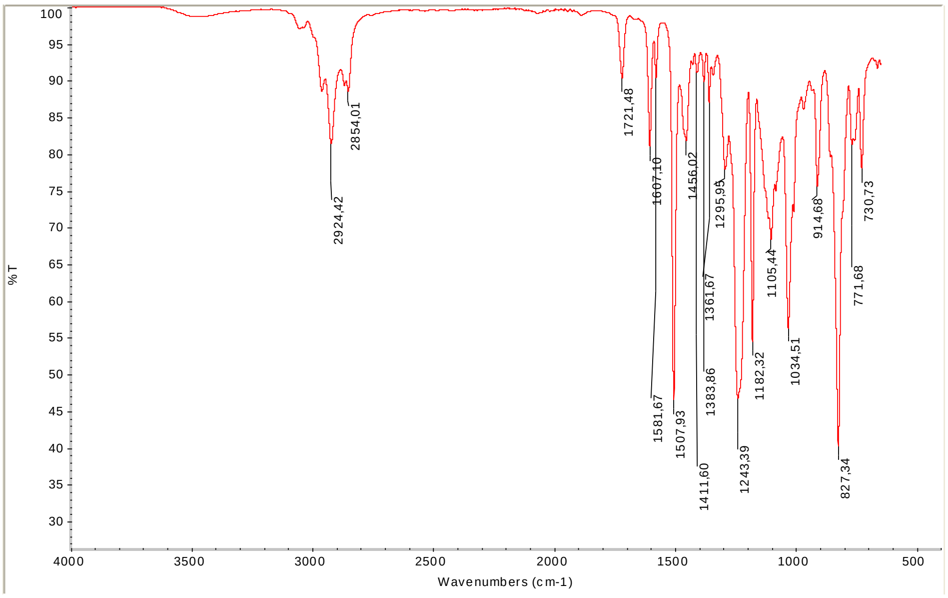


Figure 4.3: IR spectrum of terephthalic acid modified epoxy

As can be seen from Figure 4.3 the broad band at about 3400 cm^{-1} corresponds to formation of hydroxyl groups via reaction of epoxy group. The band at 1721 cm^{-1} indicates the formation of ester carbonyl. The bands at 2800 to 3000 cm^{-1} belong to methyl and methylene groups and epoxy ring at 914 cm^{-1}. The Figure 4.2 shows pure epoxy resin. So it is proved that terephthalic acid reacts with epoxy groups in epoxy resin

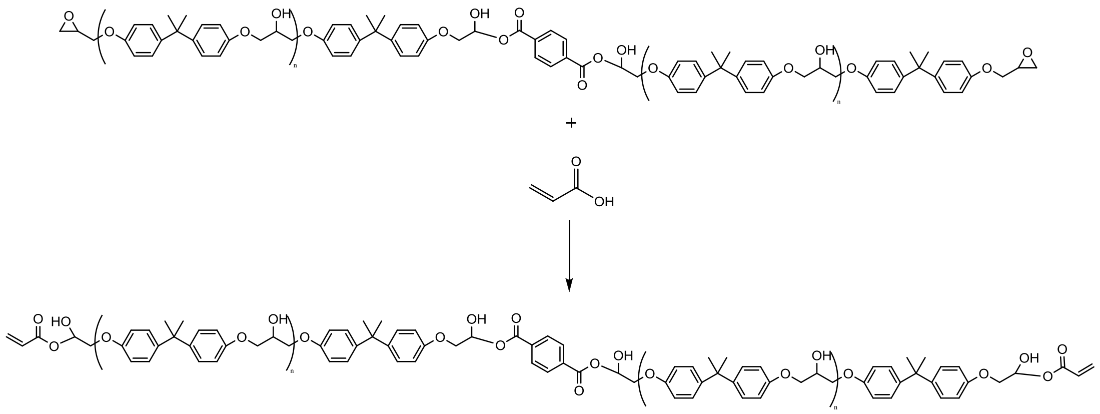


Figure 4.4: Synthesis of terephthalic acid modified epoxy acrylate

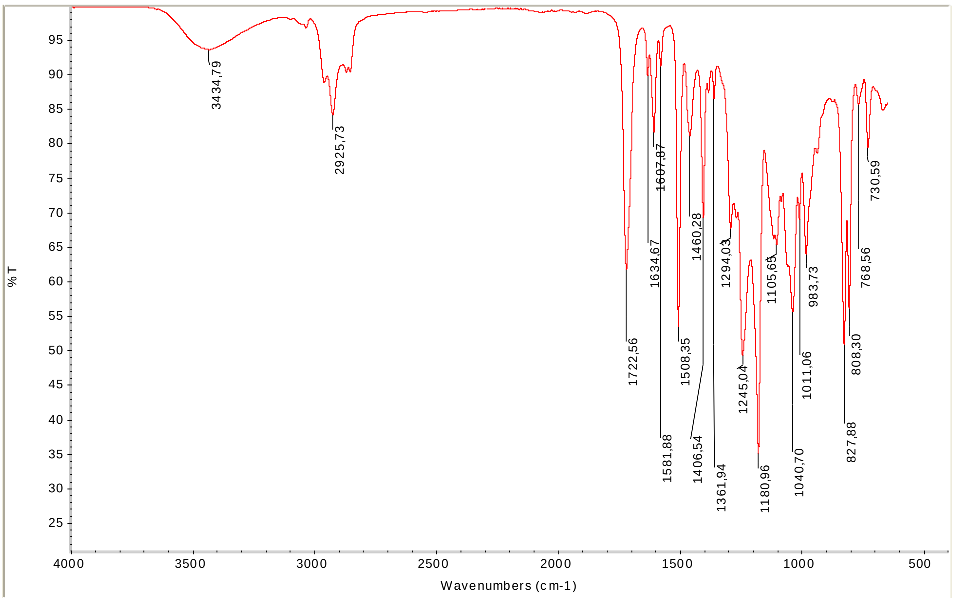


Figure 4.5: The IR spectrum of terephthalic acid modified epoxy acrylate

According to Figure 4.5 the sharpness of band at about 3400 cm^{-1} increases due to the reaction of acrylic acid with epoxy groups by indicating the formation of the hydroxyl groups. Formation of ester carbonyl group was also detected by the increase in the intensity of band at 1720 cm $^{-1}$. The reaction of acrylic acid with epoxy groups was also followed by the disappearance of band at 914 cm $^{-1}$ which belongs to epoxy ring. The band at 1634 cm^{-1} reveals C=C double bond due to acrylic acid. As a result, these confirm that the reaction completely occurs.

4.2 Synthesis of Urethane Acrylate

Urethane acrylate was synthesized according to the procedure mentioned in section 3.3.2. Isophorone diisocyanate was reacted with polypropyleneglycol and 2-hydroxyethylmethacrylate to yield urethane acrylate. Completion of reaction was checked by FT-IR.

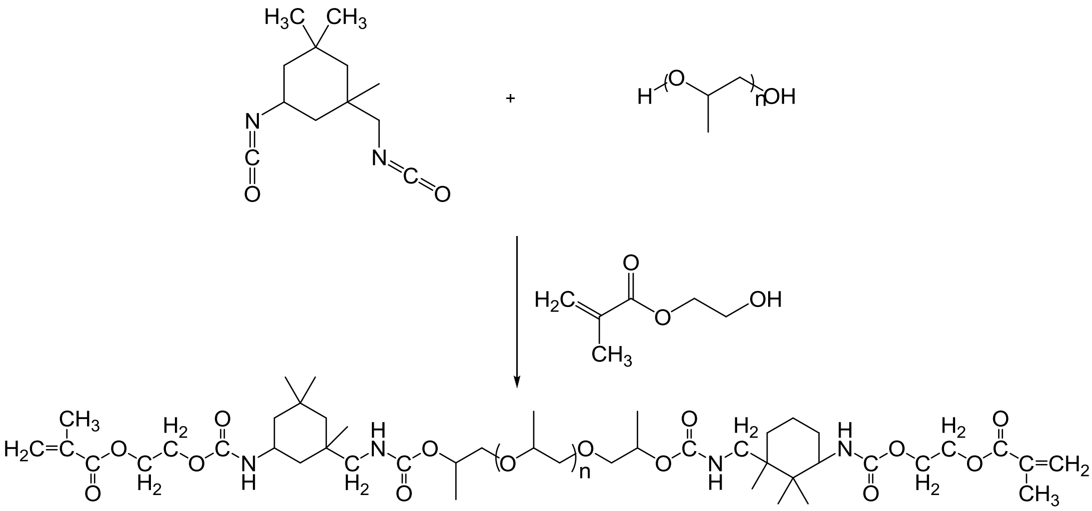


Figure 4.6: Synthesis of Urethane Acrylate

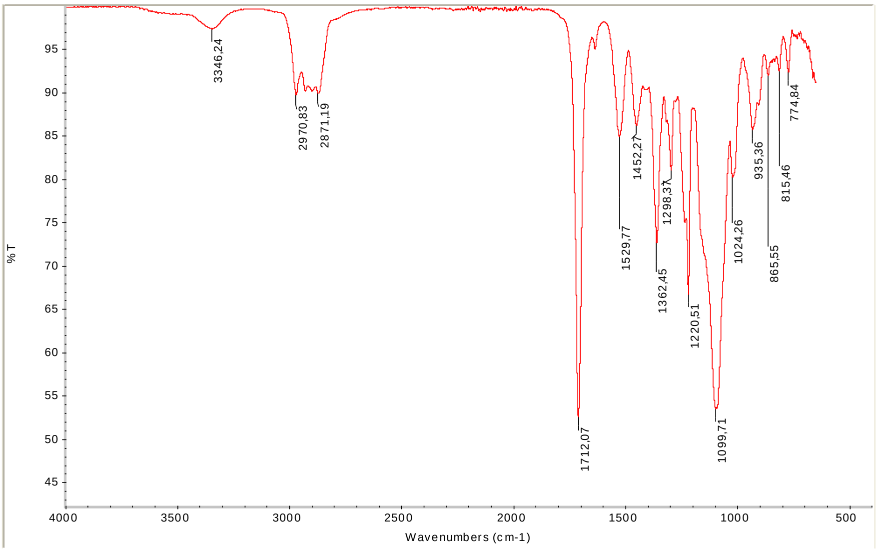


Figure 4.7: The IR spectrum of urethane acrylate

The IR spectrum in Figure 4.7 contains characteristic peaks of N-H (3346 cm^{-1}), and C=O (1712cm^{-1}), -C-N- stretching bands 1544 cm^{-1}, C-H aliphatic stretching band

(2859 cm^{-1}) are also observed. The dissappearence of the absorption bands of the NCO group (2270 cm-1) of IPDI also proves the synthesis of the urethane acrylate. The absorption band at 1093 cm^{-1} originates from C-O-C group. There are phenyl absorption bands at 1537 cm^{-1}.

4.3 Film Formation

Films were prepared according to procedure mentioned in section 3.4. After curing obtained samples are subjected to further tests.

4.3.1 Thermogravimetric Analysis

TGA analysis were carried out in a nitrogen atmosphere at a heating rate of 20°C/min between 30°C and 700°C for analysing thermal stabilities of the epoxy acrylate films**.** Figure 4.8, 4.9 and 4.10 shows TGA curves for free films of three different formulations. Table 4.1., 4.2. and 4.3 also indicate TGA values of TGA thermograms.

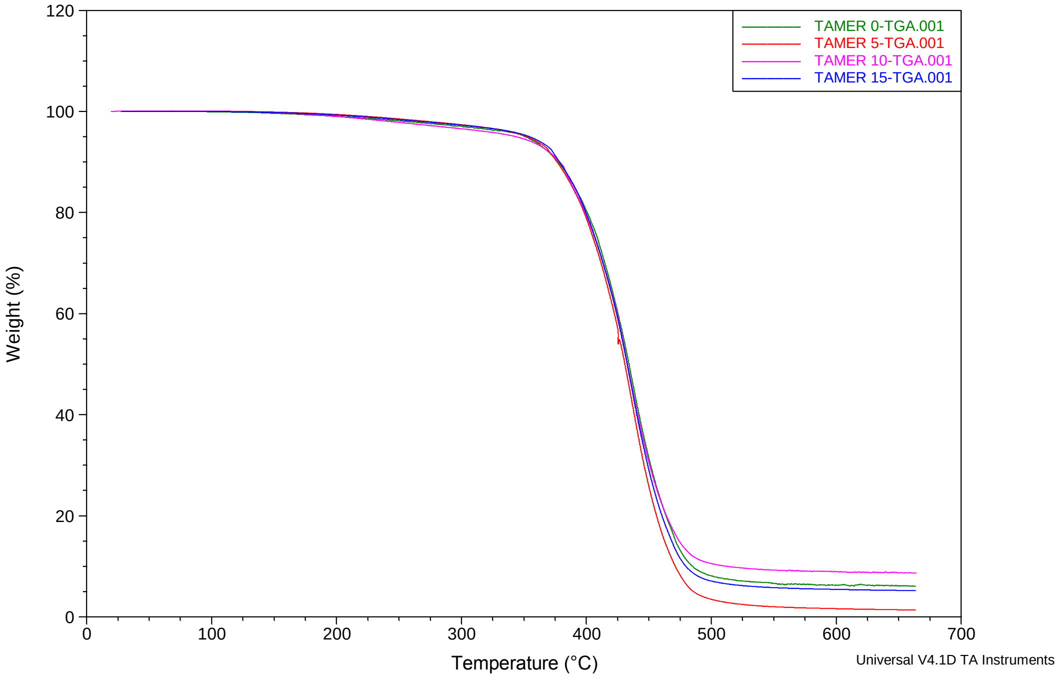


Figure 4.8: TGA thermogram of epoxy acrylate films

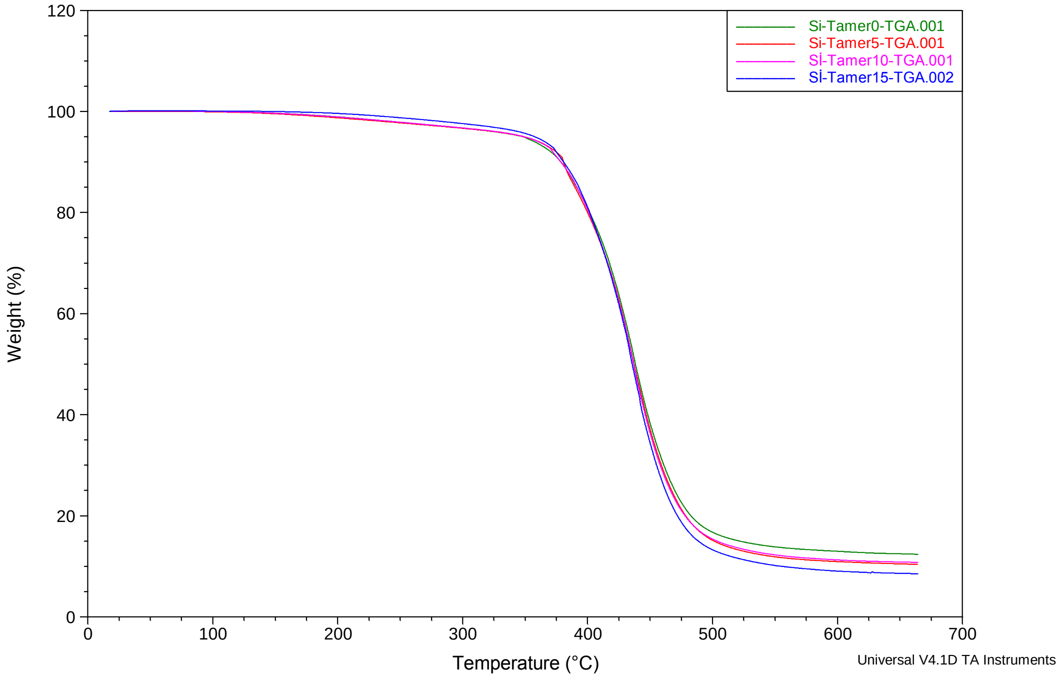


Figure 4.9: TGA thermogram of epoxy acrylate films with VTS

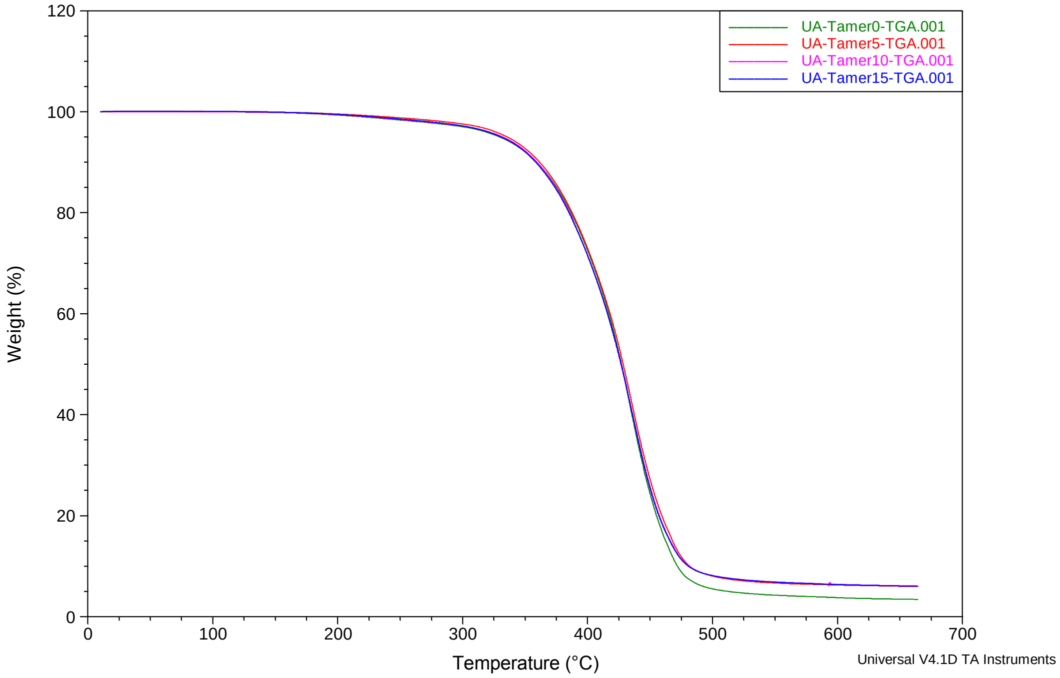


Figure 4.10: TGA thermogram of epoxy acrylate films with UA

All samples except that those with UA exhibited 5% weight loss at around 350^0C and the sample with UA showed 5% loss at around 330^0C, followed 50% weight loss at around 430 for all epoxy acrylate films. The increasing in terephthalic ratio caused a little increase while char yield decreases for modifed sample. It can be assumed that terephthalic acid reduces flame resistant of coating. To use VTS in film formulation results in increasing thermal stability according to 50% weight loss and gains char yield which increases. By adding urethane acrylate to film forumaltion thermal stability decreases but char yield shifted higher value due to methyl groups on PPG and HEMA used to syntesize urethane acrylate.

Table 4.1: TGA analysis values of epoxy acrylate films

Sample	5% weight loss temperature (^{0}C)	50% weight loss temperature (^{0}C)	Char yield (%)
T 0	351	434	6.1
T 5	352	431	1.4
T 10	344	433	8.7
T 15	354	433	5.2

Table 4.2: TGA analysis values of epoxy acrylate films with VTS

Sample	5% weight loss temperature (^{0}C)	50% weight loss temperature (^{0}C)	Char yield (%)
Si-T 0	349	438	12.4
Si-T 5	349	437	10.4
Si-T 10	349	437	10.8
Si-T 15	358	436	8.5

Table 4.3: TGA analysis values of epoxy acrylate films with UA

Sample	5% weight loss temperature (^{0}C)	50% weight loss temperature (^{0}C)	Char yield (%)
UA-T 0	330	427	3.4
UA-T 5	337	428	6.0
UA-T 10	332	427	6.1
UA-T 15	331	427	6.1

4.3.2 Gel Content

This test was applied to measure the polymerization degree of the system. This procedure was proceeded as mentioned in section 3.5.4 and gel content values are listed in Table 4.4.

Table 4.4: Gel content of cured films

Sample	Gel Content (wt %)
T 0	99
T 5	99
T 10	98
T 15	98
Sample	Gel Content (wt %)
Si-T 0	98
Si-T 5	99
Si-T 10	97
Si-T 15	99
Sample	Gel Content (wt %)
UA-T 0	98
UA-T 5	98
UA-T 10	99
UA-T 15	99

This results show us that unreacted part of cured materials are mostly under wt. 3%. It may be attributed that gel content values of the films increase because of high polymerization degree**.**

4.4.3 Solvent Resistance

This test was applied according to section 3.5.5. The solvents and the results were listed in tables.

Table 4.5: Solvent resistance of T 0

Solvents	Weight loss (%)	Appearance
Xylene	–	Good
Methanol	–	Good
Chloroform	< 1	Good
10% CH_3COOH	–	Good
10% HCl	–	Good
10% NaOH	< 1	Good

Table 4.6: Solvent resistance of T 5

Solvents	Weight loss (%)	Appearance
Xylene	–	Good
Methanol	–	Good
Chloroform	< 1	Broken
10% CH_3COOH	–	Good
10% HCl	–	Good
10% NaOH	< 1	Good

Table 4.7: Solvent resistance of T 10

Solvents	Weight loss (%)	Appearance
Xylene	–	Good
Methanol	–	Good
Chloroform	< 1	Broken
10% CH_3COOH	–	Good
10% HCl	–	Good
10% NaOH	< 1	Good

Table 4.8: Solvent resistance of T 15

Solvents	Weight loss (%)	Appearance
Xylene	–	Good
Methanol	–	Good
Chloroform	< 1	Broken
10% CH_3COOH	–	Good
10% HCl	–	Good
10% NaOH	< 1	Good

Table 4.9: Solvent resistance of Si-T 0

Solvents	Weight loss (%)	Appearance
Xylene	< 1	Good
Methanol	–	Good
Chloroform	< 1	Good
10% CH_3COOH	–	Good
10% HCl	–	Good
10% NaOH	–	Good

Table 4.10: Solvent resistance of Si-T 5

Solvents	Weight loss (%)	Appearance
Xylene	< 1	Good
Methanol	−	Good
Chloroform	< 1	Broken
10% CH_3COOH	−	Good
10% HCl	−	Good
10% NaOH	−	Good

Table 4.11: Solvent resistance of Si-T 10

Solvents	Weight loss (%)	Appearance
Xylene	< 1	Good
Methanol	−	Good
Chloroform	< 1	Broken
10% CH_3COOH	−	Good
10% HCl	−	Good
10% NaOH	−	Good

Table 4.12: Solvent resistance of Si-T 15

Solvents	Weight loss (%)	Appearance
Xylene	< 1	Good
Methanol	−	Good
Chloroform	< 1	Broken
10% CH_3COOH	−	Good
10% HCl	−	Good
10% NaOH	−	Good

According to results, modified samples immersed in chloroform have broken appearance, other samples have good appearance for all films of code T and all of code Si-T. For films of code UA-T, samples inluding unmodified epoxy acrylate film in chloroform have broken appearance, others have good appearance due to urethane acrylate in film formulation. It can be said that there is no weight loss for all cured films.

Table 4.13: Solvent resistance of UA-T 0

Solvents	Weight loss (%)	Appearance
Xylene	-	Good
Methanol	-	Good
Chloroform	<1	Broken
10% CH_3COOH	-	Good
10% HCl	-	Good
10% NaOH	-	Good

Table 4.14: Solvent resistance of UA-T 5

Solvents	Weight loss (%)	Appearance
Xylene	-	Good
Methanol	-	Good
Chloroform	<1	Broken
10% CH_3COOH	-	Good
10% HCl	-	Good
10% NaOH	-	Good

Table 4.15: Solvent resistance of UA-T 10

Solvents	Weight loss (%)	Appearance
Xylene	-	Good
Methanol	-	Good
Chloroform	<1	Broken
10% CH_3COOH	-	Good
10% HCl	-	Good
10% NaOH	-	Good

Table 4.16: Solvent resistance of UA-T 15

Solvents	Weight loss (%)	Appearance
Xylene	-	Good
Methanol	-	Good
Chloroform	<1	Broken
10% CH_3COOH	-	Good
10% HCl	-	Good
10% NaOH	-	Good

4.3.4 Contact Angle Measurement

The contact angle value of a liquid on a film is a direct reflection of the surface wettability. Contact angles of water were measured on plexiglass plates coated with four different urethane acrylate films. For each measurement one drop of water was tested on the surfaces and results are shown in Table 4.17

Table 4.17: Contact angle results

Sample	Water Contact Angle (°)
T 0	76
T 5	76
T 10	80
T 15	78
Sample	Water Contact Angle (°)
Si-T 0	70
Si-T 5	78
Si-T 10	82
Si-T 15	81
Sample	Water Contact Angle (°)
UA-T 0	75
UA-T 5	78
UA-T 10	80
UA-T 15	76

According to Table 4.17, epoxy acrylate coating with no modification for all formulation has a hydrophobic, apolar surface. Upon 15% modification with terephthalic acid, the contact angle value shifts to higher value. This is an expected behaviour assuming that aromatic moiety comes from terephthalic acid makes the surface more hydrophobic.

4.3.5 Gloss Tests

Gloss of the coated plates were measured at the angles of 20^0 and 60^0. For gloss test, plexiglass plates were coated as mentioned in section 3.5.7. and results are given in table 4.18.

Table 4.18: Gloss test values of coated films

Sample	Gloss	
	20°	60°
T 0	155	151
T 5	157	152
T 10	159	153
T 15	161	153
Sample	Gloss	
	20°	60°
Si-T 0	157	151
Si-T 5	158	151
Si-T 10	159	151
Si-T 15	159	152
Sample	Gloss	
	20°	60°
UA-T 0	160	154
UA-T 5	161	156
UA-T 10	161	156
UA-T 15	162	156

It is actually the ability of a surface to reflect light into the specular direction. The factors that affect gloss are the refractive index of the material, the angle of incident light and the surface topography. Materials with smooth surfaces appear glossy, while very rough surfaces reflect no specular light and therefore appear matt. In table 4.18 we can see the increase in gloss with increasing content of terepthalic acid. Further using urethane acrylate in formulation causes a smoother surface than compared to others.

4.3.6 Pendulum Hardness Test

König pendulum hardness test is applied after all formulations coated plexiglass plates.

Table 4.19: Pendulum hardness results (oscillation)

Sample	Pendulum Hardness
T 0	79
T 5	80
T 10	80
T 15	81
Sample	Pendulum Hardness
Si-T 0	82
Si-T 5	82
Si-T 10	82
Si-T 15	85
Sample	Pendulum Hardness
UA-T 0	83
UA-T 5	84
UA-T 10	85
UA-T 15	85

The hardness of the coating is the most important factor affecting the abrasion and scratch resistance. Hard coatings give better scratch resistance, whereas abrasion resistance is also affected by surface friction. Chain flexibility and crosslinking degree of the network play a major role in the value of hardness. As the terephthalic acid content increases, pendulum hardness values of the films increase. The hybrid resin has an increased hardness of about 2–5%, depending onto coating formulation. Moreover urethane acrylate gains a high value compared to others due to bulky methyl groups on backbone of urethane acrylate.

4.3.7 Pencil Hardness

Pencil hardness test was applied on plexiglass plates mentioned in section 3.5.9. This test is applied to understand hardness of the surface in addition to pendulum hardness. In table 4.20 results are listed.

Table 4.20: Pencil hardness results

Sample	Pencil Hardness
T 0	>7H
T 5	>7H
T 10	>7H
T 15	>7H
Sample	Pencil Hardness
Si-T 0	>7H
Si-T 5	>7H
Si-T 10	>7H
Si-T 15	>7H
Sample	Pencil Hardness
UA-T 0	>7H
UA-T 5	>7H
UA-T 10	>7H
UA-T 15	>7H

Pencil hardness depends on photocrosslinking degree as well as chemical structure of coatings. As can be seen in table, pencile hardness of formulations has the same high value as modification ratio of terephthalic acid increases. Therefore the resistance of coating is completely well because of photopolymerization degree.

4.3.8 Tensile Test

The mechanical specification of free films, prepared at 50x10x1mm dimensions, made clearly with measurement of stress-strain values. Stress-strain values for urethane acrylate system are given in Table 4.21-4.23

Table 4.21 : Stress-Strain Analysis of Epoxy Acrylates

Sample	E-Modulus (N/mm^2)	Tensile Strength (MPa)	Elongation at Break (%)
T 0	489,2	34,6	9,1
T 5	456,5	33,8	11,4
T 10	363,7	25,4	11,4
T 15	400,4	30,6	9,00

Table 4.22: Stress-Strain Analysis of Epoxy Acrylates with VTS

Sample	E-Modulus (N/mm^2)	Tensile Strength (MPa)	Elongation at Break (%)
Si-T 0	400,4	30.1	9,6
Si-T 5	387,4	24,5	8,9
Si-T 10	370,8	17,9	5,5
Si-T 15	406,4	32,7	11,3

Table 4.23: Stress-Strain Analysis of Epoxy Acrylates with UA

Sample	E-Modulus (N/mm^2)	Tensile Strength (MPa)	Elongation at Break (%)
UA-T 0	251,8	18,3	40,4
UA-T 5	223,9	15,0	36,7
UA-T 10	211,5	13,5	49,3
UA-T 15	187,3	11,9	58,9

The application of polymeric coating is very much dependent on tensile properties, particularly modulus, tensile strength and elongation up to tearing point. These properties are also related to the crosslinking density in polymeric film as well as to the chemical structure of the formulation. Polymeric film prepared from unmodified epoxy acrylate resin for all formulation exhibited higher modulus and tensile strength. The higher strength and modulus is due to the fact that there is a greater amount of crosslink density and rigidity of the epoxy chain as well. As seen from results the tensile strength and modulus decrease as the modification ratio is increased up to 15. The terephthalic acid segments cause epoxy chain more long so it makes the chain more flexible. In the table, for T 15 and Si-T 15 modulus and tensile strength has increased. It can be considered that a great amount of terephthalic acid causes the crystalline structure. For epoxy acrylate film with UA, modulus and tensile strength has low value while elongation increases. The reason is that PPG used to form urethane acrylate consists of long chains so it makes th structure more flexible.

5. CONCLUSIONS

The aim of this was to improve the physical and mechanical properties of UV curable acrylated epoxy based protective coatings. For this purpose, epoxy resin was modified with different amounts of terephthalic acid and then capped with acrylic acid. The obtained resin was used to prepare three different formulations.

UV curable, hard and clear coatings were applied on plexiglass substrates. At low modification ratios, the coating samples yielded better flexibility, namely it can be seen from stress-strain results. However it is found the most of the basic properties were affected by the modification ratio, since terephthalic acid segments easily form crystalline domains after a critial concentration. At low terephthalic acid ratio, the tensile strength and modulus of the coatings decreases sligthly and then by further increasing the terephthalic acid content better tensile strength and modulus with respect to neat epoxy acrylate coatings were obtained. Using urethane acrylate in formulation reveals the smooth and flexible structure as can be understood from results. Thermal stability of epoxy acrylate films for all formulations has a high and fair value.

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