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SURFACE COATING WITH HYBRID EPOXY RESIN

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Polymer Science and Technology

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ABBREVIATIONS

TTT	: Time-Temperature Transition
UV	: Ultra Violet
NMR	: Nuclear Magnetic Resonance
TGA	: Thermal Gravimetical Analysis
FT-IR	: Fourier Transform Infrared
DPP	: Diphenylpropane
BPA	: Bisphenol A
DGEBPA	: Diglycidyl Ether of Bisphenol A
EPA	: Epoxy Acrylate
IPTEOS	: (3-isocyanatopropyl)triethoxysilane
TEA	: Triethylamine
DBTL	: Dibutyl Tinlaurate
VTs	: Vinyltrimethoxysilane
HDAA	: 1,6-hexanedioldiacrylate

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SURFACE COATING WITH HYBRID EPOXY RESIN

SUMMARY

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. They hold prime position in the coating industry due to their chemical and corrosion resistance, good mechanical properties, excellent adhesion to a variety of substrates, and dielectric properties, high tensile, flexural and compressive strength and thermal stability. Acrylic or methacrylic acids are generally used to open the epoxy groups to obtain acrylated or methacrylated oligomers according to the end-user requirements. Acrylated epoxy resins combine the desirable properties of epoxy resins and acrylates such as good resistance against atmospheric conditions and chemicals, hardness, and gloss. . On the other hand, UVcurable acrylic urethane coatings are also used in a variety of applications due to their versatility, durability, appearance and superior weatherability compared to other resin systems. Because of this strong need for high performance coatings; extensive researches have been made to obtain materials that combine the desirable properties of organic polymers (elasticity, processability) and inorganic solids (hardness, chemical inertness and thermal resistance). Organic–inorganic hybrid materials offer the opportunity to combine both these properties. These materials manifest some advantages such as low optical propagation loss, high chemical and mechanical stabilities as well as good compatibility with different surfaces to be coated . Additionally, hybrid materials have low water absorption and water vapor permeability. The most commonly employed preparation procedures for these materials are the use of sol–gel method. The formation of interpenetrating networks is one of the several approaches, which is used in design of hybrid systems. Recently, combining silica groups into epoxy backbone for the formation of dual hybrid systems became an attractive way to significantly improve the electrical, thermal and flame retardance properties of the epoxy resins. The thermal stability of the organic-inorganic hybrid network material based on a epoxy acrylate resin can be improved with increasing silica content. The excellent thermal stability of silicon-containing epoxy compounds satisfies the requirements for application in advanced electronics.

This work involves the synthesis of novel hybrid oligomers based on a epoxy acrylate resin (EA). The EA resin was modified with various amount of 3-isocyanatopropyl trimethoxysilane (IPTMS) coupling agent. The formulated oligomers was polymerized by photo and thermal polymerization methods.

HİBRİD EPOKSİ REÇİNELERLE YÜZEY KAPLAMA

ÖZET

Ticari reçineler arasında epoksi reçineleri en yaygın türdür ve reçinelerdeki mevcut aktif epoksi gruplarından karakterize edilebilirler. Bu yapıların kimyasal ve korozyan direnci, iyi mekanik özellikleri, çeşitli yüzeylere karşı gösterdiği mükemmel yapışma ve dielektrik özellikleri, yüksek gerilme, bükülme ve sıkışma dayanıklılığı ve ısısal kararlılığı, epoksi reçinelerin kaplama endüstrisinde öncül bir konumda bulunmasını sağlamaktadır. Oligomerlerdeki serbest epoksi grupları akrilik asid ve türevleriyle tepkimeye girerek epoksi akrilat reçineleri oluşturmaktadır. Epoksi akrilat reçineleri, epoksi reçinlere ve akrilatlarla ait istenen spesifik özellikleri birleştirir. Bunun yanı sıra, diğer reçine sistemleriyle karşılaştırıldığında dayanıklılık, görünüş ve yüksek iklimsel uygulamalara karşı dirençlerinden dolayı akrilik üretan kaplamalar çeşitli uygulamalarda kullanılmaktadır. Yüksek performanslı kaplamalara karşı duyulan ihtiyaçtan dolayı, organik polimerlere ve inorganik katılara ait istenen özellikleri içeren maddelerin eldesi için geniş çaplı araştırmalar yapılmaktadır. Organik-inorganik hibrid malzemeler bu iki yapıya ait özelliklerin birleşmesine imkan sağlamaktadır. Bu malzemeler yüksek kimyasal ve mekanik kararlılık ve kaplamalarda çeşitli yüzeylerle kaplamalarda iyi uyumluluk sağlama gibi bazı avantajlar ortaya koymaktadır. Bunlara ek olarak, hibrid malzemeler düşük su ve su buharı geçirgenliğine sahiptirler. Bu malzemelerin eldesinde yaygın olarak kullanılan prosedür sol-jel metodudur. Hibrid sistemlerin eldesinde, iç içe geçmiş ağların oluşumu birkaç yaklaşımdan biridir. Son zamanlarda, hibrid sistemlerin oluşumu için epoksi zincirine silika gruplarının takılması, epoksi reçinelerin elektrisel, ısısal ve yanma geciktirici özelliklerinin geliştirilmesinde önemli bir yol olmuştur. Epoksi akrilat reçinelerdeki silika içeriğinin artırılması hibrid malzemenin ısısal kararlılığının gelişmesini sağlar. Mükemmel ısısal kararlılıklı silikon içerikli epoksi maddeler gelişmiş elektronik uygulamalardaki gereksinimlere yüksek oranda cevap vermektedir.

Bu çalışma epoksi akrilat reçine esaslı hibrid oligomerlerin sentezini içermektedir. Epoksi akrilat reçineleri çeşitli oranlarda 3-isosiyonatopropil trietoksisilan bağlantı ajanıyla modifiye edilmiştir. Elde edilen oligomerler termal ve foto polimerizasyon yöntemleriyle polimerleştirilmiştir.

1. INTRODUCTION

A composite material, by definition, is the result of interatomic or molecular interactions between two or more components, the overall properties of which are superior to those of the individual components alone [1]. Dental composites are composed of a polymer matrix, usually methacrylate-based, and filler particles, commonly glass, quartz, or ceramic oxide, such as alumina or silica. Coupling agents such as silanes are widely used to improve the bonding at the filler/polymer-matrix interface [2,3].

The modern technology focuses on the development of reliable high performance coating materials having superior thermal and mechanical properties ideally suitable for adverse environmental conditions. Organic materials can not be used alone for high performance applications because they have limited properties. Therefore, organic/inorganic composites are frequently employed in order to overcome the limitation. One of the widely used organic/inorganic composites is an epoxy/silica system. Since epoxy resins as organic matrix have excellent heat, moisture, and chemical resistance and good adhesion to many substrates, they are mostly applied in the field of coatings, adhesives, casting, potting, composites, laminates, and encapsulation of semiconductor devices [4,5].

Organic-inorganic hybrid materials are eminently suitable for dental coating, because the organic part enables certain properties, such as hardness, wear resistance biocompatibility to be improved, while the inorganic part improves the process ability of the coating and allows the preparation of coating with, for example, low surface energy, anti-adhesive properties and therefore limited tendency to plaque formation. Furthermore, functional groups may contribute to improve the adhesion of the coating to the dental substrate [6].

The most commonly employed preparation procedure for these materials are the sol-gel method. The formation of interpenetrating Networks is one of the several approaches, which is used in design of hybrid systems. Difficulties of such an approach are potential incompatibilities between the moieties, leading to phase separation. In addition a major problem arises from the different stabilities of the

materials [7]. However, the class of true hybrids in which mutual chemical bonds between organic and inorganic polymeric systems are formed can solve this problem and present uniform mixing at microscopic level with phase continuity [8]. Recently, combining silica groups into epoxy backbone for the formation of dual hybrid systems became an attractive way to significantly improve the electrical, thermal and flame retardance properties of the epoxy resins. The thermal stability of the organic-inorganic hybrid network material based on epoxy acrylate resin can be improved with increasing silica content [9,10].

This thesis will concern the preparation of novel bifunctional resin prepared by the reaction between epoxy acrylate oligomer and 3-isocyanatopropyl triethoxysilane (IPTEOS). The hybrid networks are polymerized by thermal and photo polymerization methods and are characterized by analysis of various properties such as hardness, gloss, tape adhesion, and stress-strain test. The thermal behaviour of coating is also evaluated.

2. THEORETICAL PART

2.1 Overview of Epoxy Resin

2.1.1 Introduction

Epoxy resins are defined as any molecules containing one or more α - or 1,2-epoxide groups, which can be converted to a thermoset form or a three-dimensional network structure [11]. Compared with other thermosetting resins, epoxy resins have special chemical characteristics. For example, no byproducts or volatiles are formed during curing reactions; shrinkage of cured epoxy products is low; they can be cured over a wide range of temperatures; and the degree of crosslinking can be controlled. The properties of cured epoxy resins have various advantages, including excellent chemical and heat resistance, high hardness and adhesive strength, low shrinkage, good impact resistance, and high electrical insulation [12]. When epoxy resins made their commercial debut in the world around 1947, their advantages in formulation resulted in a variety of major industrial applications, including surface coatings, adhesives, painting materials, potting compounds, composites, laminates, semiconductor encapsulates, castings, lightweight foams, and insulating materials for electric devices. New developments continue in the applications of epoxy materials. 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.

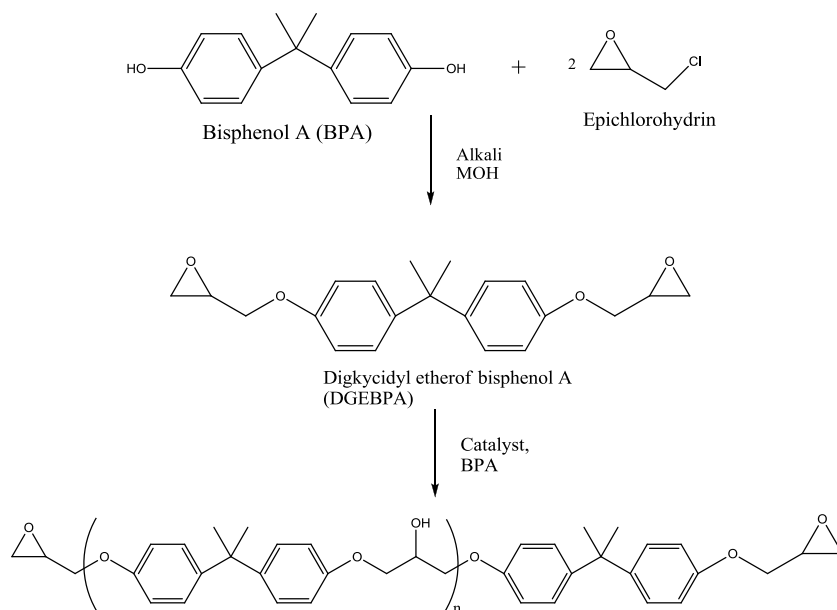


Figure 2.1: Reaction of bisphenol A and epichlorohydrin

Greenlee working for Devoe and Raynolds produced resins which were similar to those of Castan but with a somewhat higher molecular weight with the objective of developing superior surface coatings. The epoxy coatings developed by Greenlee offered improved adhesion, hardness, inertness and thermal resistance compared with alkyd or phenolic resins. Following the first patent application (1948) Greenlee obtained about 40 patents for epoxy resins. The major application of epoxy resins is still for surface coatings which consume about 50% of all epoxy resins produced.

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.

As cure proceeds there are major changes in the properties of the epoxy resins. Initially the resin-hardener mixture is fluid and finally an elastic solid is produced. The glass transition temperature of the curing resin increases as cure proceeds and these changes can be represented in a time-temperature transition (TTT) diagram introduced by Gillham [13].

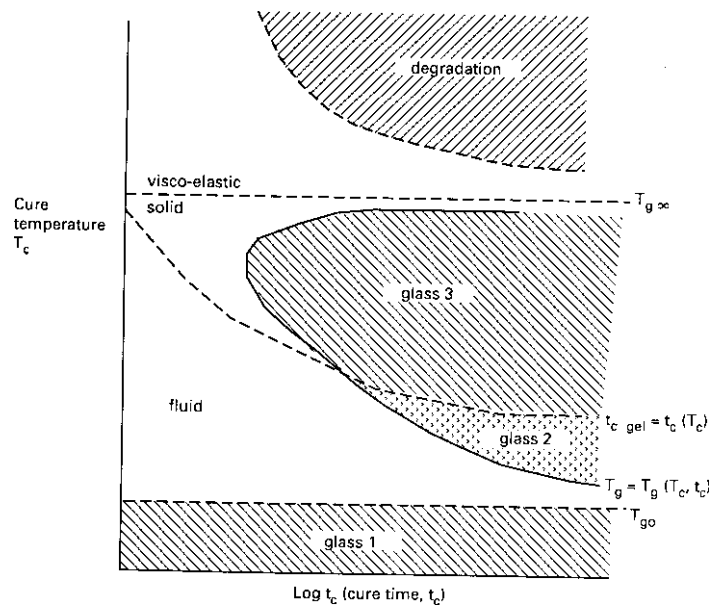


Figure 2.2: Simplified time-temperature-transition diagram [13]

Figure 1.2 is a simplified version which illustrates the dominant effect of the onset of vitrification as T_g increases to the cure temperature T_c . For cure temperatures well above T_g , the rate of reaction between the epoxy and hardener reactive groups is chemically kinetically controlled. When $\Delta T = T_c - T_g$ becomes small the curing reactions become diffusion controlled, and will eventually become very slow and finally stop. For products for which it is necessary to ensure complete reaction of all epoxy groups it is a normal practice to post-cure the resins at an elevated temperature.

For successful application of epoxy resins it is necessary to select a suitable hardener and then cure the resin to attain a controlled network structure.

However, 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·m^{1/2} and have poor resistance to crack propagation [14]. 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 [15], which absorb insignificant amounts of energy during the fracture process [16]. 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 [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 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 2.3.).

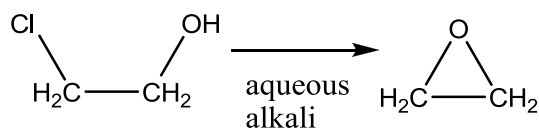


Figure 2.3: Ethylene chlorohydrins reaction

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 [18] 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 [19].

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.

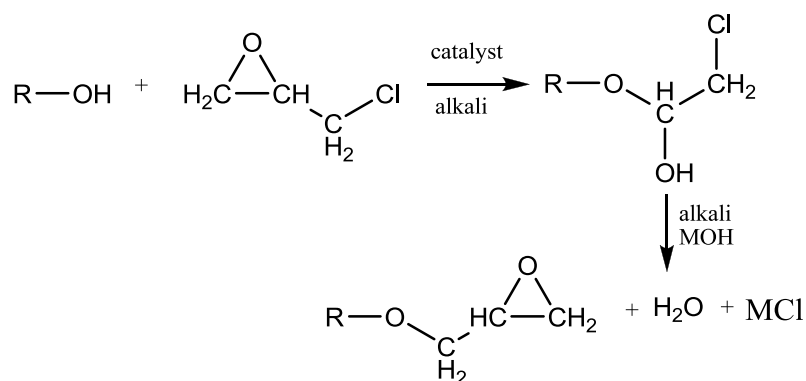


Figure 2.4: Method for synthesis of epoxy rings

MOH could be sodium or potassium hydroxide and has to be used in stoichiometric concentration to neutralize the halogen acid, HCl 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 2.5.).

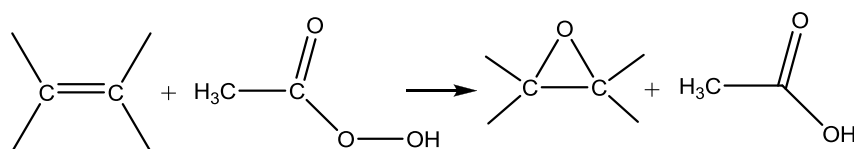


Figure 2.5: Oxidation reaction with peracid

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 [20]. 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 2p 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’ sp³ hybridization with linear bonds between the ring atoms is impossible. The bonding in cyclopropane has been discussed extensively and Halton [21] 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 sp², 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 [22] 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 [20] 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 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:

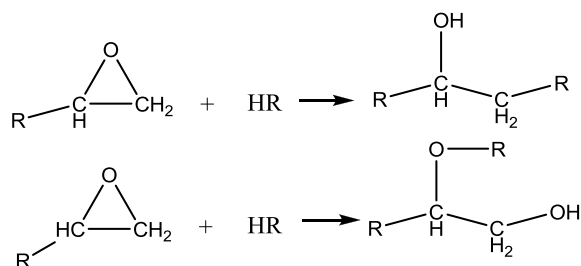


Figure 2.6: Ring opening of epoxy- 1

a secondary alcohol or primary alcohol or a mixture (Figure 2.6.). When HR' is an amine, carboxylic acid or thiol, the 'normal' product, a secondary alcohol, is usually formed (Figure 2.7.).

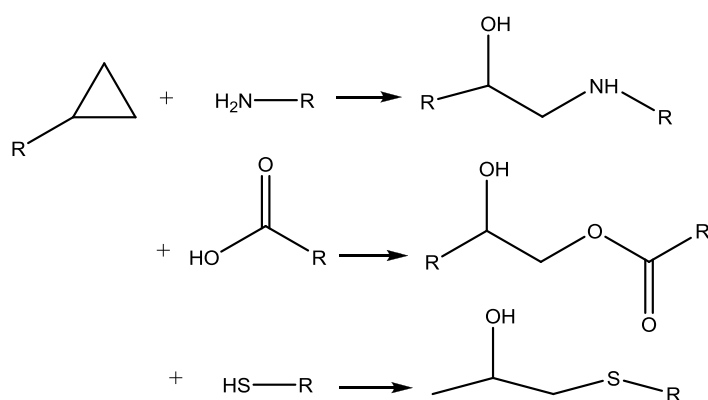


Figure 2.7: Ring opening of epoxy- 2

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.

The kinetics of these reactions is discussed in detail by Frost and Pearson and Parker and Isaacs [23]. The mode of addition may be reversed when R is a strongly electron-attracting group or mixtures may be formed depending on the importance of the various factors involved. Tanaka [19] discusses the configuration of the protonated epoxy group and Lewars [22] their basicity and calculations of proton affinity. The latter also discusses other reactions which involve electrophilic attack on the ring oxygen atom. These include Lewis acids, alkyl halides, halides, peroxy acids, aldehydes and ketones. The reaction of epoxides with epoxides initiated by electrophilic attack can lead to dimerization and also polymerization.

2.1.3 The Synthesis and Manufacture of Epoxy Resin

2.1.3.1 Synthesis of Epoxy Compound

Ethylene oxide can be manufactured by the direct oxidation of ethylene (Figure 2.8.) but unfortunately this process is not so efficient for higher olefines.

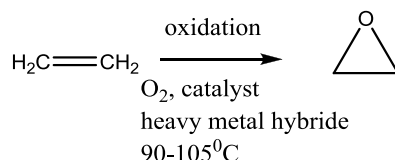


Figure 2.8: Oxidation of ethylene

The methods that have been used for the synthesis of epoxy rings have been discussed by Lwowski and Lewars [22]. A comprehensive review of the synthesis of epoxy compounds is that of Tanaka [19]. The most important for the synthesis of epoxy resins are dehydrohalogenation of halohydrins and the epoxidation of alkenes with peracids or their esters. Details of many actual syntheses of epoxy resins including reaction conditions and yields are given by Sandier and Karo. A very important intermediate for the production of epoxy resins is epichlorohydrin, 2,3 epoxypropylchloride. This is because the epoxy ring reacts readily with hydroxyl compounds such as phenols and alcohols with the formation of a chlorohydrin. The epoxy group is formed by dehydrochlorination with a stoichiometric amount of alkali, such as sodium hydroxide.

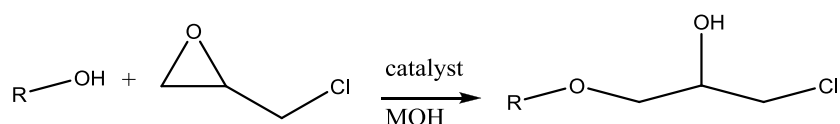
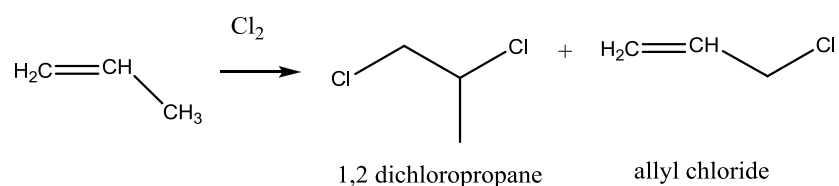


Figure 2.9: Reaction of epoxy ring with hydroxyl compound

The starting compound for the manufacture of epichlorohydrin is propylene which is chlorinated. The allyl chloride is converted to dichlorohydrin by reaction with hypochlorous acid and is then dehydrochlorinated with lime to obtain epichlorohydrin.



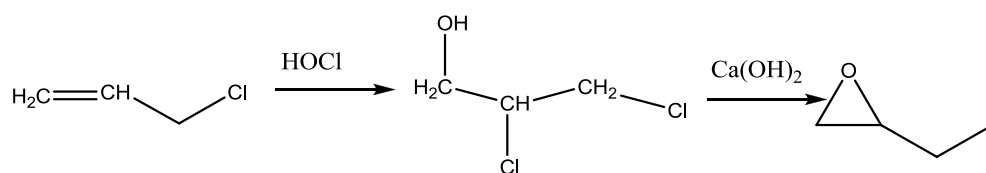


Figure 2.10: Manufacture of epoxy

Industrially epichlorohydrin is either converted to glycerol by reaction with sodium hydroxide or isolated by steam stripping and purified by distillation. An alternative route is from acrolein, produced by oxidation of propylene.

2.1.3.2 Epoxy Resin Manufacture from Epichlorohydrin

Epichlorohydrin is used for the production of a range of epoxy resins because the epoxy group reacts readily with hydroxylic compounds in the presence of an alkali catalyst, MOH, and then a new epoxy ring can be formed by dehydrochlorination.

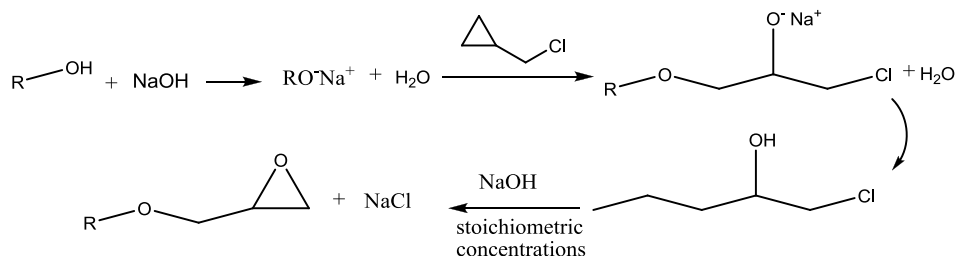


Figure 2.11: Circle of epoxy ring formation

For the production of epoxy resins, the hydroxylic compounds are multifunctional and many such phenols have been studied as possible precursors. Also, some mono-functional phenols have been used for the manufacture of resin 'modifiers'. However, the most important phenol used for the manufacture of epoxy resins is the difunctional bisphenol A which was originally studied by Castan.

2.1.3.2.1 Resin Manufactured from Bisphenol A

Bisphenol A or 2,2-bis(p-hydroxyphenyl)propane is produced from acetone and phenol with an acid catalyst such as 75% sulphuric acid or dry hydrogen chloride acid gas.

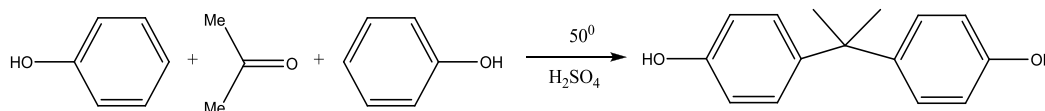


Figure 2.12: Synthesis of bisphenol A

The reaction conditions will depend on the design of the production unit [24]. The purity of the product is high, >95% p,p'-isomer; the other isomers formed are o,p' and o,o'. For resin manufacture the p,p' isomer content should be at least 98%. The light yellow colour of some epoxy resins may be due to trace impurities in the bisphenol A, such as iron, arsenic and highly coloured organic compounds. Other names for bisphenol A are 4,4'-isopropylidene diphenol and diphenylolpropane (DPP).

When a large excess of epichlorohydrin is reacted with bisphenol A with a Stoichiometric amount of sodium hydroxide at about 65°C the resin produced contains about 50% diglycidyl ether of bisphenol A (Figure 2.13.), DGEBA (BADGE) and the reaction may be represented formally as:

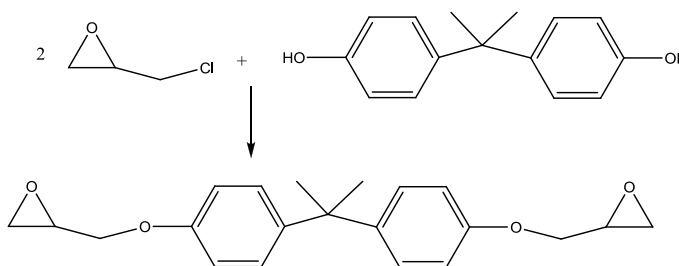


Figure 2.13: Diglycidyl ether of bisphenol A

With pure epichlorohydrin it is necessary to add about 5 w/o water to accelerate the reaction. Recovered and recycled epichlorohydrin usually contains sufficient water. The excess of epichlorohydrin is required to limit the production of higher molecular weight products. It is obvious that DGEBA will react with bisphenol A and so on with the formation of higher molecular weight resins.

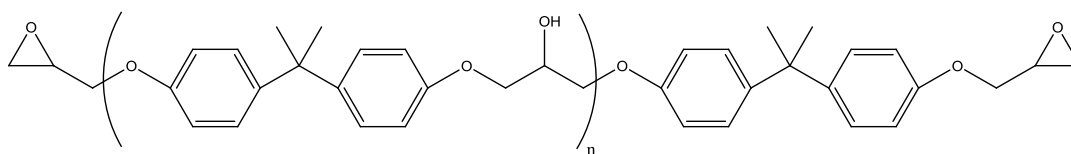


Figure 2.14: Diglycidyl ether of bisphenol A epoxy resin

A range of species is present in any specific reaction product and commercial resins are available with $0 < n < 14$, and may be higher where n is the average number of structure units in the species. A major variable which determines the molecular weight distribution and hence the average molecular weight is the ratio of epichlorohydrin to bisphenol A, but other reaction conditions will affect the product obtained, as will be discussed. For the production of higher molecular weight resins the chain extension process is used. Batzer and Zahir have discussed in detail the molecular weight distributions of epoxy resins prepared by different processes.

Although the commercially produced resins have a distribution of chain lengths it is possible to obtain the DGEBA by molecular distillation and it can also be crystallized. Pure DGEBA is a solid which melts at 43°C . Also in liquid commercial resins that have been stored for prolonged periods some crystallization of DGEBA will occur and the resin appears cloudy. Outlines of the production process for the manufacture of a low molecular weight resin are given by McAdams and Gannon and also Savla and Skeist. Preparative methods are given by Sandier and Karo [25].

Not all of the species present in commercial resins are diepoxides; side reactions can occur when epichlorohydrin is reacted with bisphenol A. These can become more important when higher molecular weight resins are produced. The important side reactions are

i. Hydrolysis of epoxy groups

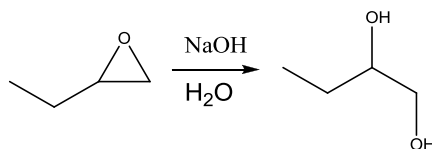


Figure 2.15: Hydrolysis of epoxy group

ii. Formation of bound chlorine

a. Reaction of epichlorohydrin with secondary alcohol

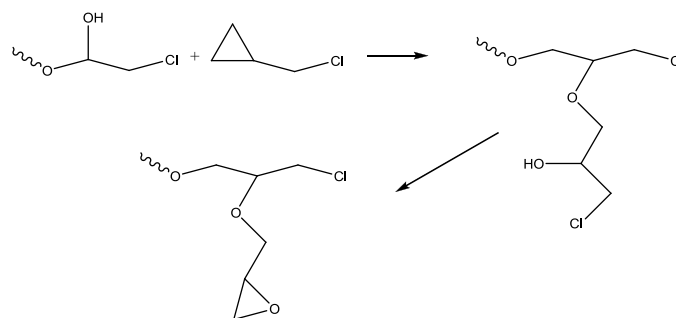


Figure 2.16: Reaction of epichlorohydrin with secondary alcohol

b. Abnormal addition of phenolic hydroxyl

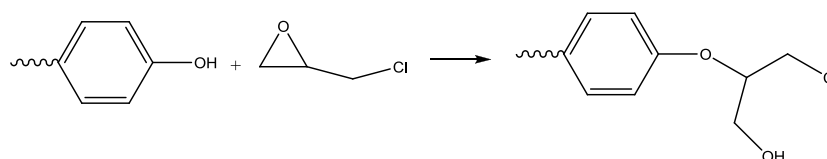


Figure 2.17: Abnormal addition of phenolic hydroxyl

iii. the presence of saponifiable or hydroxy

iv. The formation of branched molecules due to reaction of epichloro-hydrin with secondary hydroxyl groups.

The last traces of inorganic ions in the liquid resins may be difficult to remove but their concentration can be minimized by suitable washing procedures. The actual concentration of trace amounts of residual material may affect the reactivity of the resins. Also, volatile low molecular weight compounds have to be removed since only small amounts, ca. 1 w/o, can significantly reduce the viscosity of the resin. Liquid resins find applications which include coatings, castings, tooling and adhesives, and are also used as starting materials for the manufacture of higher molecular weight and modified resins.

2.1.3.2.2 High Molecular Weight Bisphenol A Resin

It is obvious that the bisphenol A/epichlorohydrin ratio is important for control of the average molecular weight of the resins produced with the repeat unit so that the larger the value of n the smaller the epichlorohydrin/bisphenol A ratio required. The purity of the reactants is important and monofunctional reactants

are chain terminators and hence their concentration has to be controlled. However, it is also necessary to optimize the reaction conditions to achieve the degree of polymerization required. For the production of oligomers with $1 < n < 4$ the so-called Taffy process may be used but for much higher molecular weight polymers $3 < n < 20$ the fusion or chain extension process is used.

2.1.3.2.3 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 130°C 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.

2.1.3.2.4 Fusion Process

This also known as the chain extension process for reasons which will become clear. The starting materials for the fusion process are bisphenol A plus a liquid epoxy resin which is essentially difunctional in epoxy groups, produced by the process used for the manufacture of DGEBA.

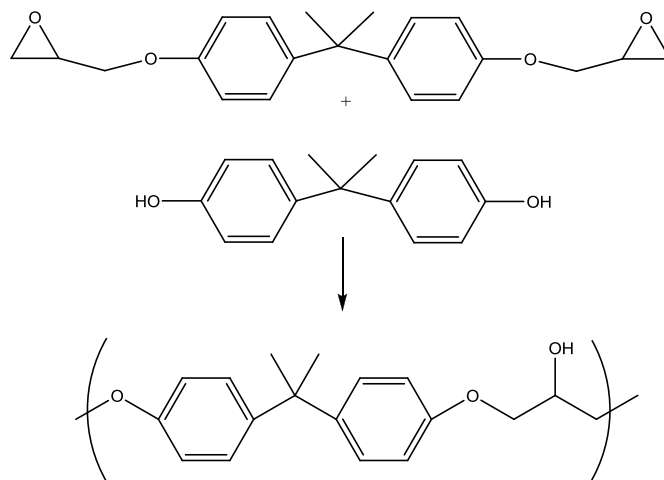


Figure 2.18: Synthesis of resin from DGEBA

The reaction is carried out at temperatures between 180 and 200°C for about 30 minutes with a nitrogen 'blanket' to minimize oxidative degradative reactions. The reaction is very sensitive to type and concentration of catalyst which must be very strictly controlled to ensure production reproducibility. Thus there has been considerable development of specialized catalysts to minimize chain branching and gelation by promoting reaction between phenolic hydroxyl with epoxy groups and limiting the side reactions, especially between epoxy-epoxy and epoxy-alcoholic hydroxyl groups. It can be appreciated that the chain extension process is a step-wise polymerization and the relationship between average molecular weight and extent of reaction will depend on the degree of stoichiometric equivalence in the reacting mixture, i.e. the epoxy/-OH ratio and the extent of side reactions which effectively remove either epoxy or -OH groups and hence alter the effective epoxy/-OH ratio. The important parameters were investigated by Batzer and Zahir [26].

2.1.3.2.5 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 [25].

2.1.3.2.6 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.

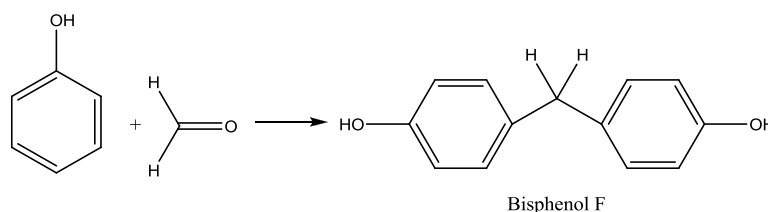


Figure 2.19: Sythesis of bisphenol F

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 [27],

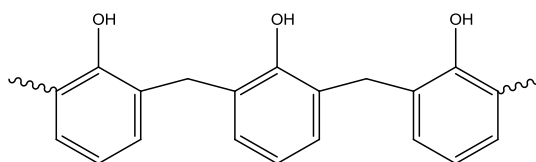


Figure 2.20: Novolac resin

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

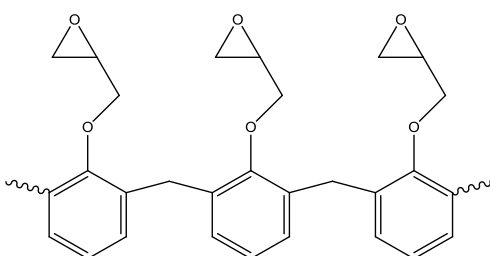


Figure 2.21: Epoxy-novolac

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.

2.1.3.2.7 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 [28].

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 used. 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.

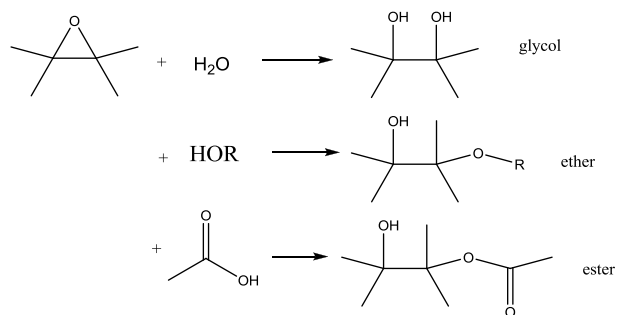


Figure 2.22: Epoxy reactions

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 [29].

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 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.

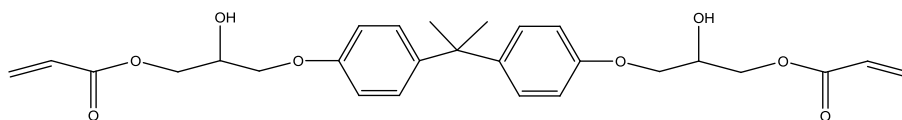


Figure 2.23: Epoxy acrylate

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.

During the curing process, low molecular weight blocking agents can evaporate from the film. Those that can

2.2 Hybrid Materials

2.2.1 Introduction

Recent technological breakthroughs and the desire for new functions generate an enormous demand for novel materials. Many of the well established materials, such as metals, ceramics or plastics cannot fulfill all technological desires for the various new applications. Scientists and engineers realized early on that mixtures of materials can show superior properties compared with their pure counterparts. One of the most successful examples is the group of composites which are formed by the incorporation of a basic structural material into a second substance, the *matrix*. Usually the systems incorporated are in the form of particles, whiskers, fibers, lamellae, or a mesh. Most of the resulting materials show improved mechanical properties and a well-known example is inorganic fiber-reinforced polymers. Nowadays they are regularly used for lightweight materials with advanced mechanical properties, for example in the construction of vehicles of all types or sports equipment. The structural building blocks in these materials which are incorporated into the matrix are predominantly inorganic in nature and show a size range from the lower micrometer to the millimeter range and therefore their heterogeneous composition is quite often visible to the eye. Soon it became evident that decreasing the size of the inorganic units to the same level as the organic building blocks could lead to more homogeneous materials that allow a further fine tuning of materials' properties on the molecular and nanoscale level, generating novel materials that either show characteristics in between the two original phases or even new properties [30].

2.2.1.1 Natural Origins

The Many natural materials consist of inorganic and organic building blocks distributed on the (macro)molecular or nanoscale. In most cases the inorganic part provides mechanical strength and an overall structure to the natural objects while the organic part delivers bonding between the inorganic building blocks and/or the soft tissue. Typical examples of such materials are bone, or nacre. The concepts of bonding and structure in such materials are intensively studied by many scientists to understand the fundamental processes of their formation and to transfer the ideas to artificial materials in a so-called biomimetic approach. The special circumstances under which biological hybrid inorganic organic materials are formed, such as ambient temperatures, an aqueous environment, a neutral pH and the fascinating plethora of complex geometries produced under these conditions make the mimicking of such structures an ultimate goal for scientists. In particular the study of biomineralization and its shape control is an important target of many scientific studies [31]. This primarily interface controlled process still reveals many questions, in particular how such a remarkable level of morphological diversity with a multiplicity of functions can be produced by so few building blocks. In addition to questions concerning the composition of the materials, their unique structures motivate enquiry to get a deeper insight in their formation, often not only because of their beauty but also because of the various functions the structures perform.

A complex hierarchical order of construction from the nanometer to the millimeter level is regularly found in nature, where every size level of the specific material has its function which benefits the whole performance of the material. Furthermore these different levels of complexity are reached by soft chemical self-assembly mechanisms over a large dimension, which is one of the major challenges of modern materials chemistry.

2.2.1.2 Development of Hybrid Materials

Although we do not know the original birth of hybrid materials exactly it is clear that the mixing of organic and inorganic components was carried out in ancient world. At that time the production of bright and colorful paints was the driving force to consistently try novel mixtures of dyes or inorganic pigments and other inorganic and organic components to form paints that were used thousands of years ago. Therefore, hybrid materials or even nanotechnology is not an invention of the last

decade but was developed a long time ago. However, it was only at the end of the 20th and the beginning of the 21st century that it was realized by scientists, in particular because of the availability of novel physico chemical characterization methods, the field of nanoscience opened many perspectives for approaches to new materials.

The combination of different analytical techniques gives rise to novel insights into hybrid materials and makes it clear that bottom up strategies from the molecular level towards materials' design will lead to novel properties in this class of materials. Apart from the use of inorganic materials as fillers for organic polymers, such as rubber, it was a long time before much scientific activity was devoted to mixtures of inorganic and organic materials. One process changed this situation: the sol gel process. This process, which will be discussed in more detail later on, was developed in the 1930s using silicon alkoxides as precursors from which silica was produced [32]. In fact this process is similar to an organic polymerization starting from molecular precursors resulting in a bulk material. Contrary to many other procedures used in the production of inorganic materials this is one of the first processes where ambient conditions were applied to produce ceramics. The control over the preparation of multicomponent systems by a mild reaction method also led to industrial interest in that process. In particular the silicon based sol gel process was one of the major driving forces what has become the broad field of inorganic organic hybrid materials. The reason for the special role of silicon was its good processability and the stability of the SiC bond during the formation of a silica network which allowed the production of organic modified inorganic networks in one step. Inorganic organic hybrids can be applied in many branches of materials chemistry because they are simple to process and are amenable to design on the molecular scale. Currently there are four major topics in the synthesis of inorganic organic materials: (a) their molecular engineering, (b) their nanometer and micrometer-sized organization, (c) the transition from functional to multifunctional hybrids, and (d) their combination with bioactive components.

Some similarities to sol gel chemistry are shown by the stable metal sols and colloids, such as gold colloids, developed hundreds of years ago. In fact sols prepared by the sol gel process, i.e. the state of matter before gelation, and the gold colloids have in common that their building blocks are nanosized particles surrounded by a (solvent) matrix. Such metal colloids have been used for optical

applications in nanocomposites for centuries. Glass, for example, was already colored with such colloids centuries ago. In particular many reports of the scientific examination of gold colloids, often prepared by reduction of gold salts, are known from the end of the 18th century. Probably the first nanocomposites were produced in the middle of the 19th century when gold salts were reduced in the presence of gum arabic. Currently many of the colloidal systems already known are being reinvestigated by modern instrumental techniques to get new insights into the origin of the specific chemistry and physics behind these materials.

2.2.1.3 Definition: Hybrid Materials and Nanocomposites

The term hybrid material is used for many different systems spanning a wide area of different materials, such as crystalline highly ordered coordination polymers, amorphous sol gel compounds, materials with and without interactions between the inorganic and organic units. Before the discussion of synthesis and properties of such materials we try to delimit this broadly-used term by taking into account various concepts of composition and structure (Table 2.1.).

Table 2.1: Different possibilities of composition and structure of hybride materials

Matrix:	crystalline ↔ amorphous
	organic ↔ inorganic
Building blocks:	molecules ↔ macromolecules ↔ particles ↔ fibers
Interactions between components:	strong ↔ weak

The most wide-ranging definition is the following: a hybrid material is a material that includes two moieties blended on the molecular scale. Commonly one of these compounds is inorganic and the other one organic in nature. A more detailed definition distinguishes between the possible interactions connecting the inorganic and organic species. *Class I* hybrid materials are those that show weak interactions between the two phases, such as van der Waals, hydrogen bonding or weak electrostatic interactions. *Class II* hybrid materials are those that show strong chemical interactions between the components. Because of the gradual change in the strength of chemical interactions it becomes clear that there is a steady transition between weak and strong interactions (Fig. 2.23.). For example there are hydrogen

bonds that are definitely stronger than for example weak coordinative bonds. Table 2.2 presents the energetic categorization of different chemical interactions depending on their binding energies.

Table 2.2: Different chemical interactions and their respective strength

<i>Type of interaction</i>	<i>Strength [kJ mol⁻¹]</i>	<i>Range</i>	<i>Character</i>
van der Waals	ca. 50	Short	nonselective, nondirectional
H-bonding	5–65	Short	selective, directional
Coordination bonding	50–200	Short	directional
Ionic	50–250 ^{a]}	Long	nonselective
Covalent	350	Short	predominantly irreversible

^a Depending on solvent and ion solution; data are for organic media.

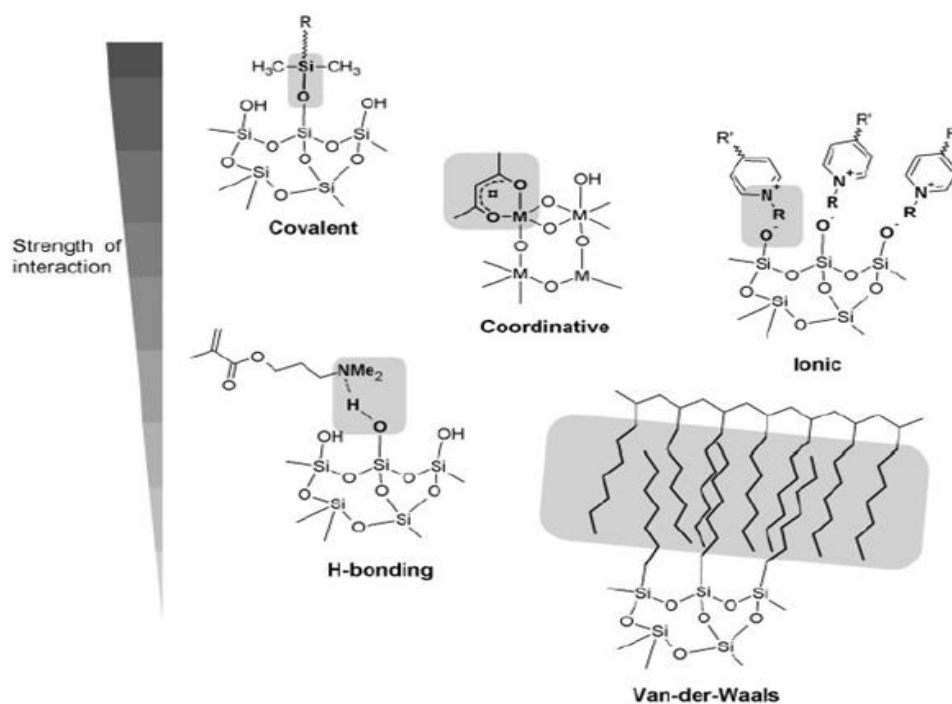


Figure 2.24: Selected interactions typically applied in hybrid materials and their relative strength

In addition to the bonding characteristics structural properties can also be used to distinguish between various hybrid materials. An organic moiety containing a functional group that allows the attachment to an inorganic network, e.g. a trialkoxysilane group, can act as a network modifying compound because in the final structure the inorganic network is only modified by the organic group.

Phenyltrialkoxysilanes are an example for such compounds; they modify the silica network in the sol–gel process via the reaction of the trialkoxysilane group (Figure 2.25a) without supplying additional functional groups intended to undergo further chemical reactions to the material formed. If a reactive functional group is incorporated the system is called a network functionalizer (Figure 2.25c).

The situation is different if two or three of such anchor groups modify an organic segment; this leads to materials in which the inorganic group is afterwards an integral part of the hybrid network (Figure 2.25b). Blends are formed if no strong chemical interactions exist between the inorganic and organic building blocks. One example for such a material is the combination of inorganic clusters or particles with organic polymers lacking a strong (e.g. covalent) interaction between the components (Figure 2.26a). In this case a material is formed that consists for example of an organic polymer with entrapped discrete inorganic moieties in which, depending on the functionalities of the components, for example weak crosslinking occurs by the entrapped inorganic units through physical interactions or the inorganic components are entrapped in a crosslinked polymer matrix [33].

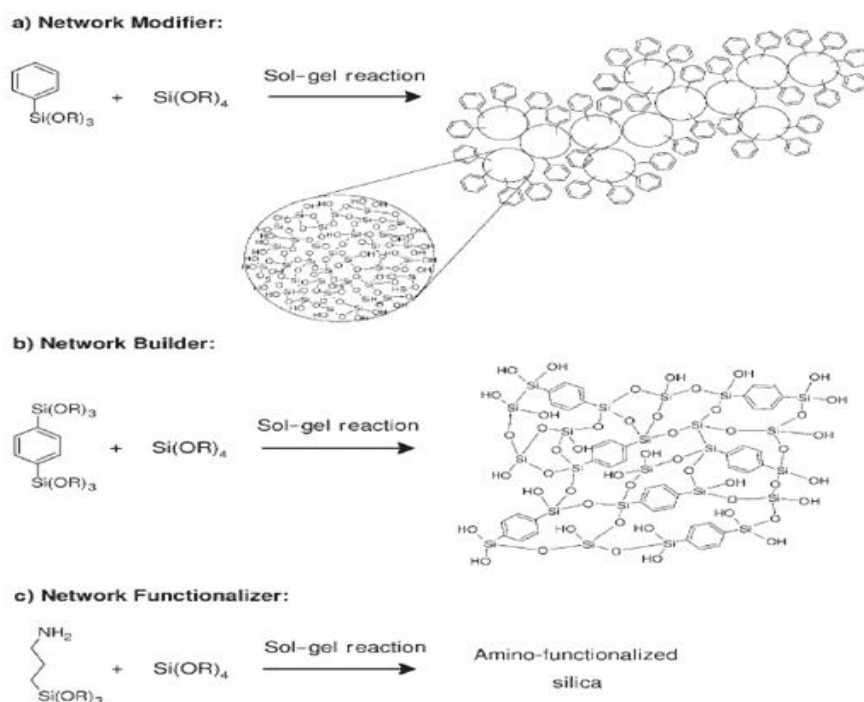


Figure 2.25: Role of organically functionalized trialkoxysilanes in the silicon based sol gel process

If an inorganic and an organic network interpenetrate each other without strong chemical interactions, so called interpenetrating networks (IPNs) are formed (Scheme 2.25b), which is for example the case if a sol gel material is formed in presence of an organic polymer or vice versa. Both materials described belong to class I hybrids. Class II hybrids are formed when the discrete inorganic building blocks, e.g. clusters, are covalently bonded to the organic polymers (Figure 2.26c) or inorganic and organic polymers are covalently connected with each other (Figure 2.26d).

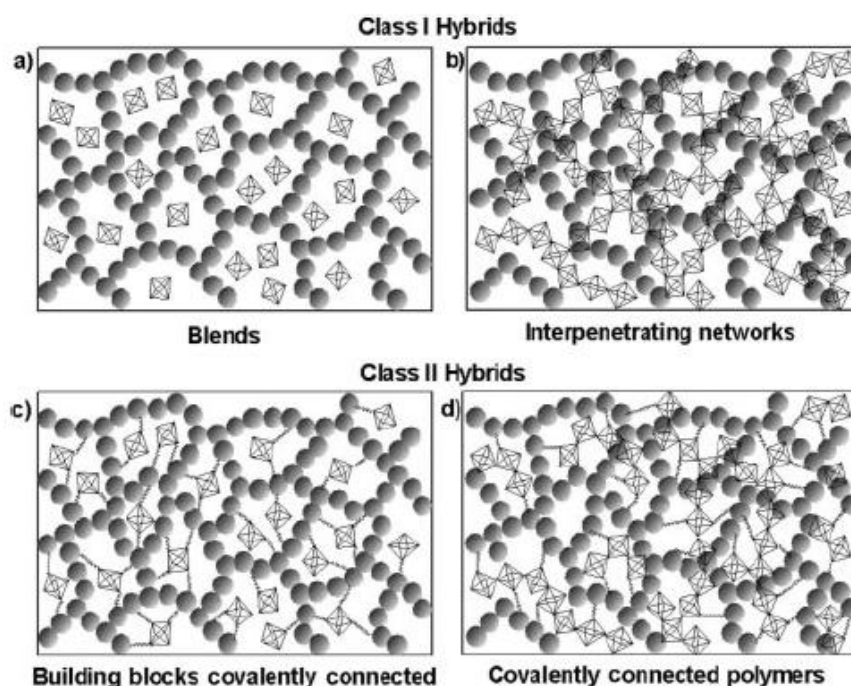


Figure 2.26: The different type of hybrid materials

2.2.1.4 Advantages of Combining Inorganic and Organic Species in One Material

The most obvious advantage of inorganic organic hybrids is that they can favorably combine the often dissimilar properties of organic and inorganic components in one material (Table 2.3). Because of the many possible combinations of components this field is very creative, since it provides the opportunity to invent an almost unlimited set of new materials with a large spectrum of known and as yet unknown properties. Another driving force in the area of hybrid materials is the possibility to create multifunctional materials. Examples are the incorporation of inorganic clusters or

nanoparticles with specific optical, electronic or magnetic properties in organic polymer matrices.

Table 2.3: Comparison of general properties of typical inorganic and organic materials

<i>Properties</i>	<i>Organics (polymers)</i>	<i>Inorganics (SiO₂, transition metal oxides (TMO))</i>
Nature of bonds	covalent [C—C], van der Waals, H-bonding	ionic or ionic-covalent [M—O]
T_g	low (–120°C to 200°C)	high (>>200°C)
Thermal stability	low (<350°C–450°C)	high (>>100°C)
Density	0.9–1.2	2.0–4.0
Refractive index	1.2–1.6	1.15–2.7
Mechanical properties	elasticity plasticity rubbery (depending on T_g)	hardness strength fragility
Hydrophobicity	hydrophilic	hydrophilic
Permeability	hydrophobic ±permeable to gases	low permeability to gases
Electronic properties	insulating to conductive redox properties	insulating to semiconductors (SiO ₂ , TMO) redox properties (TMO) magnetic properties
Processability	high (molding, casting, film formation, control of viscosity)	low for powders high for sol-gel coatings

Probably the most intriguing property of hybrid materials that makes this material class interesting for many applications is their processing. Contrary to pure solid state inorganic materials that often require a high temperature treatment for their processing, hybrid materials show a more polymer-like handling, either because of their large organic content or because of the formation of crosslinked inorganic networks from small molecular precursors just like in polymerization reactions. Hence, these materials can be shaped in any form in bulk and in films. Although from an economical point of view bulk hybrid materials can currently only compete

in very special areas with classical inorganic or organic materials, e.g. in the biomaterials sector, the possibility of their processing as thin films can lead to property improvements of cheaper materials by a simple surface treatment, e.g. scratch resistant coatings.

Based on the molecular or nanoscale dimensions of the building blocks, light scattering in homogeneous hybrid material can be avoided and therefore the optical transparency of the resulting hybrid materials and nanocomposites is, dependent on the composition used, relatively high. This makes these materials ideal candidates for many optical applications. Furthermore, the materials' building blocks can also deliver an internal structure to the material which can be regularly ordered. While in most cases phase separation is avoided, phase separation of organic and inorganic components is used for the formation of porous materials.

Material properties of hybrid materials are usually changed by modifications of the composition on the molecular scale. If, for example, more hydrophobicity of a material is desired, the amount of hydrophobic molecular components is increased. In sol gel materials this is usually achieved if alkyl- or aryl-substituted trialkoxysilanes are introduced in the formulation. Hydrophobic and lipophobic materials are composed if partially or fully fluorinated molecules are included. Mechanical properties, such as toughness or scratch resistance, are tailored if hard inorganic nanoparticles are included into the polymer matrix. Because the compositional variations are carried out on the molecular scale a gradual fine tuning of the material properties is possible. One important subject in materials chemistry is the formation of smart materials, such as materials that react to environmental changes or switchable systems, because they open routes to novel technologies, for example electroactive materials, electrochromic materials, sensors and membranes, biohybrid materials, etc. The desired function can be delivered from the organic or inorganic or from both components. One of the advantages of hybrid materials is that functional organic molecules as well as biomolecules often show better stability and performance if introduced in an inorganic matrix.

2.2.2 Synthetic Strategies Toward Hybrid Materials

In principle two different approaches can be used for the formation of hybrid materials: Either well defined preformed building blocks are applied that react with

each other to form the final hybrid material in which the precursors still at least partially keep their original integrity or one or both structural units are formed from the precursors that are transformed into a novel (network) structure.

Building block approach, as mentioned above building blocks at least partially keep their molecular integrity throughout the material formation, which means that structural units that are present in these sources for materials formation can also be found in the final material. At the same time typical properties of these building blocks usually survive the matrix formation, which is not the case if material precursors are transferred into novel materials. Representative examples of such well defined building blocks are modified inorganic clusters or nanoparticles with attached reactive organic groups (Figure 2.27.). Cluster compounds often consist of at least one functional group that allows an interaction with an organic matrix, for example by copolymerization. Depending on the number of groups that can interact, these building blocks are able to modify an organic matrix (one functional group) or form partially or fully crosslinked materials (more than one group). For instance, two reactive groups can lead to the formation of chain structures. If the building blocks contain at least three reactive groups they can be used without additional molecules for the formation of a crosslinked material [34].

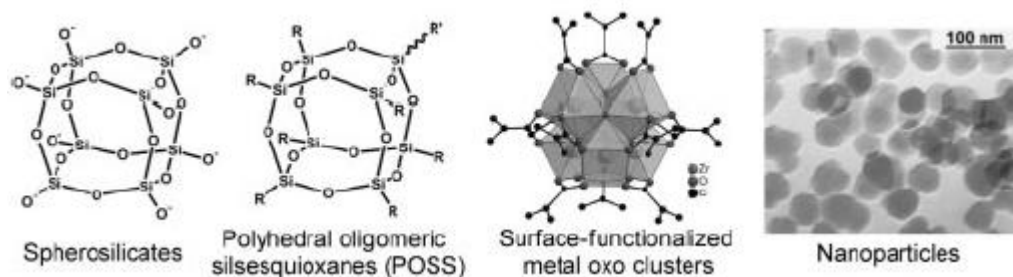


Figure 2.27: Typical well defined molecular building blocks used in the formation of hybrid materials

In situ formation of the components, contrary to the building block approach the in situ formation of the hybrid materials is based on the chemical transformation of the precursors used throughout materials' preparation. Typically this is the case if organic polymers are formed but also if the sol gel process is applied to produce the inorganic component. In these cases well defined discrete molecules are transformed to multidimensional structures, which often show totally different properties from the original precursors. Generally simple, commercially available molecules are applied

and the internal structure of the final material is determined by the composition of these precursors but also by the reaction conditions. Therefore control over the latter is a crucial step in this process. Changing one parameter can often lead to two very different materials. If, for example, the inorganic species is a silica derivative formed by the sol gel process, the change from base to acid catalysis makes a large difference because base catalysis leads to a more particle-like microstructure while acid catalysis leads to a polymer-like microstructure. Hence, the final performance of the derived materials is strongly dependent on their processing and its optimization.

2.2.2.1 In Situ Formation of Inorganic Material

Many of the classical inorganic solid state materials are formed using solid precursors and high temperature processes, which are often not compatible with the presence of organic groups because they are decomposed at elevated temperatures. Hence, these high temperature processes are not suitable for the *in situ* formation of hybrid materials. Reactions that are employed should have more the character of classical covalent bond formation in solutions. One of the most prominent processes which fulfill these demands is the sol gel process. However, such rather low temperature processes often do not lead to the thermodynamically most stable structure but to kinetic products, which has some implications for the structures obtained. For example low temperature derived inorganic materials are often amorphous or crystallinity is only observed on a very small length scale, i.e. the nanometer range. An example of the latter is the formation of metal nanoparticles in organic or inorganic matrices by reduction of metal salts or organometallic precursors.

2.2.2.1.1 Sol Gel Process

This process is chemically related to an organic polycondensation reaction in which small molecules form polymeric structures by the loss of substituents. Usually the reaction results in a three dimensional (3-D) crosslinked network. The fact that small molecules are used as precursors for the formation of the crosslinked materials implies several advantages, for example a high control of the purity and composition of the final materials and the use of a solvent based chemistry which offers many advantages for the processing of the materials formed.

The silicon based sol gel process is probably the one that has been most investigated; therefore the fundamental reaction principles are discussed using this process as a model system. One important fact also makes the silicon based sol gel processes a predominant process in the formation of hybrid materials, which is the simple incorporation of organic groups using organically modified silanes. SiC bonds have enhanced stability against hydrolysis in the aqueous media usually used, which is not the case for many metal carbon bonds, so it is possible to easily incorporate a large variety of organic groups in the network formed. Principally $R_{4-n}SiX_n$ compounds ($n = 1-4$, $X = OR'$, halogen) are used as molecular precursors, in which the SiX bond is labile towards hydrolysis reactions forming unstable silanols (SiOH) that condensate leading to SiOSi bonds. In the first steps of this reaction oligo and polymers as well as cyclics are formed subsequently resulting in colloids that define the sol. Solid particles in the sol afterwards undergo crosslinking reactions and form the gel (Figure 2.28).

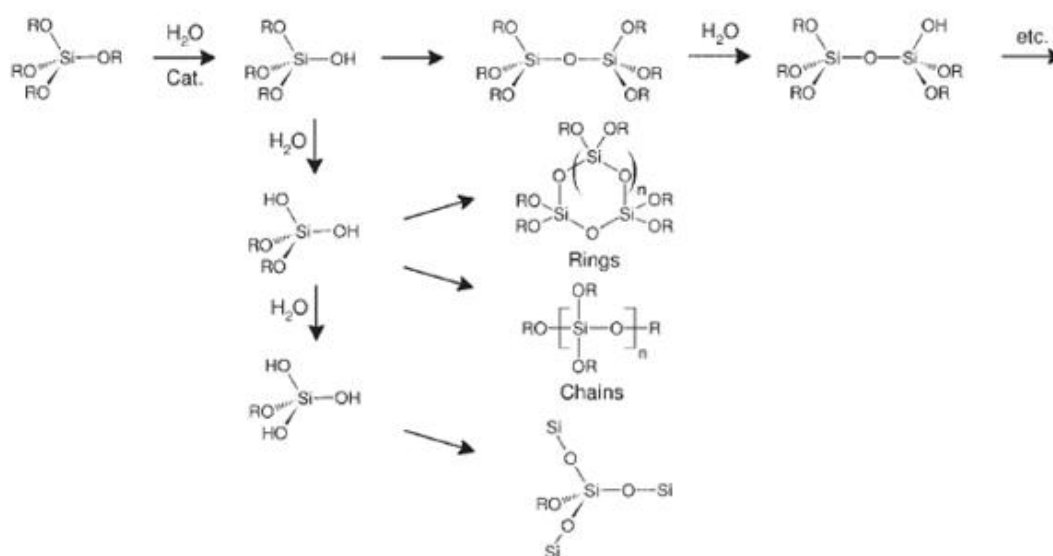


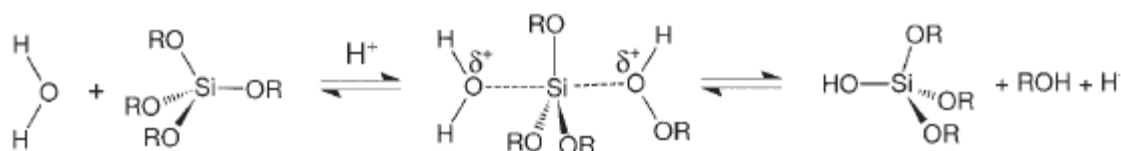
Figure 2.28: Fundamental reaction steps in the sol gel process based on tetraalkoxysilanes

The process is catalyzed by acids or bases resulting in different reaction mechanisms by the velocity of the condensation reaction (Figure 2.29). The pH used therefore has an effect on the kinetics which is usually expressed by the gel point of the sol gel reaction. The reaction is slowest at the isoelectric point of silica (between 2.5 and 4.5 depending on different parameters) and the speed increases rapidly on changing the

pH. Not only do the reaction conditions have a strong influence on the kinetics of the reaction but also the structure of the precursors.

Generally, larger substituents decrease the reaction time due to steric hindrance. In addition, the substituents play a mature role in the solubility of the precursor in the solvent. Water is required for the reaction and if the organic substituents are quite large usually the precursor becomes immiscible in the solvent. By changing the solvent one has to take into account that it can interfere in the hydrolysis reaction, for example alcohols can undergo *trans*-esterification reactions leading to quite complicated equilibria in the mixture. Hence, for a well-defined material the reaction conditions have to be fine-tuned.

Acid Catalysis:



Base Catalysis:

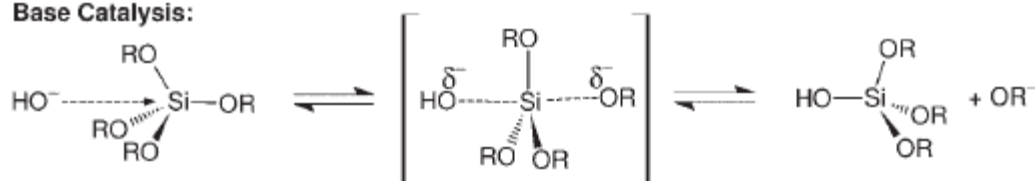


Figure 2.29: Differences mechanism depending on the type of catalyst used in the silicon based sol gel process

The pH not only plays a major role in the mechanism but also for the microstructure of the final material. Applying acid-catalyzed reactions an open network structure is formed in the first steps of the reaction leading to condensation of small clusters afterwards. Contrarily, the base-catalyzed reaction leads to highly crosslinked sol particles already in the first steps. This can lead to variations in the homogeneity of the final hybrid materials as will be shown later. Commonly used catalysts are HCl, NaOH or NH₄OH, but fluorides can be also used as catalysts leading to fast reaction times. The transition from a sol to a gel is defined as the gelation point, which is the point when links between the sol particles are formed to such an extent that a solid material is obtained containing internal pores that incorporate the released alcohol. However at this point the reaction has not finished, but condensation reactions can go on for a long time until a final stage is reached. This process is called ageing. During

this reaction the material shrinks and stiffens. This process is carried on in the drying process, where the material acquires a more compact structure and the associated crosslinking leads to an increased stiffness. During the drying process the large capillary forces of the evaporating liquids in the porous structure take place which can lead to cracking of the materials. Reaction parameters such as drying rate, gelation time, pH, etc. can have a major influence on the cracking of the gels and have therefore to be optimized. Under some circumstances the destruction of the gel network can lead to the formation of powders instead of monoliths during materials formation.

Stress during the drying process can be avoided if the liquid in the pores is exchanged under supercritical conditions where the distinction between liquid and vapor no longer exists. This process leads to so called highly porous aerogels compared with the conventionally dried xerogels. As already mentioned above many parameters influence the speed of the sol gel reaction; if a homogeneous material is required all parameters must be optimized. This is particularly true if hybrid materials are the target, because undesired phase separations of organic and inorganic species in the materials or between the network and unreacted precursors weaken the materials' properties. This can often even be observed by the naked eye if the material turns opaque. The water to precursor ratio is also a major parameter in the sol–gel process. If tetraalkoxysilanes are used as precursors, two water molecules per starting compound are necessary to form completely condensed SiO_2 . Applying a lower $\text{H}_2\text{O}/\text{Si}$ ratio, would lead to an alkoxide containing final material [35].

2.2.2.1.2 Nonhydrolytic Sol Gel Process

In this process the reaction between metal halides and alkoxides is used for the formation of the products (Figure 2.30.). The alkoxides can be formed during the process by various reactions. Usually this process is carried out in sealed tubes at elevated temperature but it can also be employed in unsealed systems under an inert gas atmosphere.

Non-hydrolytic sol-gel process:



In situ formation of alkoxides:



Figure 2.30: Mechanisms involved in the nonhydrolytic sol gel process

2.2.2.1.3 Sol Gel Reactions of Non-Silicates

Metal and transition metal alkoxides are generally more reactive towards hydrolysis and condensation reactions compared with silicon. The metals in the alkoxides are usually in their highest oxidation state surrounded by electronegative OR ligands which render them susceptible to nucleophilic attack. Transition metal alkoxides show a lower electronegativity compared with silicon which causes them to be more electrophilic and therefore less stable towards hydrolysis in the sol gel reactions. Furthermore, transition metals often show several stable coordination environments. While the negatively charged alkoxides balance the charge of the metal cation they generally cannot completely saturate the coordination sphere of the metals, which leads to the formation of oligomers via alkoxide or alcohol bridges and/or the saturation of the coordination environment by additional coordination of alcohol molecules, which also has an impact on the reactivity of the metal alkoxides. More sterically demanding alkoxides, such as isopropoxides, lead to a lower degree of aggregation and smaller alkoxides, such as ethoxides or *n*-propoxides, to a larger degree of aggregation. In addition, the length of the alkyl group in the metal alkoxides also influences their solubility in organic solvents, for example ethoxides often show a much lower solubility as their longer alkyl chain containing homologs.

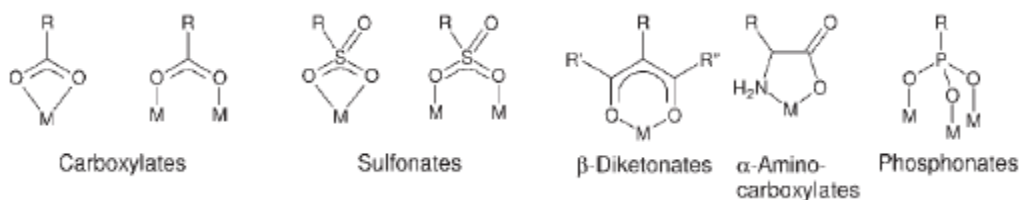


Figure 2.31: Typical coordination pattern between bi- and multidentate ligands and metals that can be applied for the incorporation of organic functionalities in metal oxides

As already mentioned MC bonds in metal alkoxides are in most cases not stable enough to survive the sol gel conditions. Therefore, contrary to the silica route, other mechanisms have to be employed if it is desired that hybrid inorganic organic metal oxide materials be formed in a one step approach. One solution to the latter problem is the use of organically functionalized bi- and multidentate ligands that show a higher bonding stability during the sol gel reaction and, in addition, reduce the speed of the reaction by blocking coordination sites (Figure 2.31.).

2.2.2.1.4 Hybrid Materials by The Sol Gel Process

Organic molecules other than the solvent can be added to the sol and become physically entrapped in the cavities of the formed network upon gelation. For this purpose the molecules have to endure the reaction conditions of the sol gel process, namely the aqueous conditions and the pH of the environment. Hence, functional organic groups that can be hydrolyzed are not tolerated, but a partial tolerance for the pH can be obtained if the sol gel reaction is carried out in a buffer solution. This is particularly necessary if biological molecules, such as enzymes, are to be entrapped in the gel. Physical entrapment has the disadvantage that sometimes the materials obtained are not stable towards phase separation or leaching because of differences in polarity. Chemical modification of organic compounds with trialkoxysilane groups can partially avoid such problems due to co-condensation during the formation of the sol-gel network and thus development of covalent linkages to the network. Trialkoxysilane groups are typically introduced by a platinum catalyzed reaction between an unsaturated bond and a trialkoxysilane (Figure 2.32.).

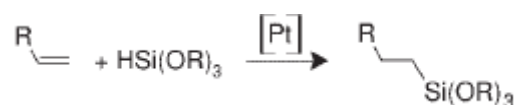


Figure 2.32: Platinum catalyzed hydrosilation for the introduction of trialkoxysilane groups

While the formation of homogeneous materials with a chemical link between the inorganic and organic component is in many cases the preferred route, there are cases where a controlled phase separation between the entrapped organic molecules and the sol gel material is compulsory for the formation of the material, for example in the preparation of mesoporous materials. Besides the entrapment of organic systems,

precursors with hydrolytically stable SiC bonds can also be used for co-condensation reactions with tetraalkoxysilanes. In addition, organically functionalized trialkoxysilanes can also be used for the formation of 3-D networks alone forming so called silsesquioxanes (general formula $R\text{-SiO}_{1.5}$) materials. Generally a 3-D network can only be obtained if three or more hydrolyzable bonds are present in a molecule. Two such bonds generally result in linear products and one bond leads only to dimers or allows a modification of a preformed network by the attachment to reactive groups on the surface of the inorganic network (Figure 2.33.). Depending on the reaction conditions in the sol–gel process smaller species are also formed in the organotrialkoxysilanebased sol gel process, for example cage structures or ladder-like polymers (Figure 2.33.). Because of the stable SiC bond the organic unit can be included within the silica matrix without transformation. There are only a few SiC bonds that are not stable against hydrolysis, for example the $\text{SiC}\equiv\text{C}$ bond where the SiC bond can be cleaved by H_2O if fluoride ions are present. Some typical examples for trialkoxysilane compounds used in the formation of hybrid materials are shown in Scheme 2.34. Usually the organic functionalizations have a large influence on the properties of the final hybrid material. First of all the degree of condensation of a hybrid material prepared by trialkoxysilanes is generally smaller than in the case of tetraalkoxysilanes and thus the network density is also reduced [36].

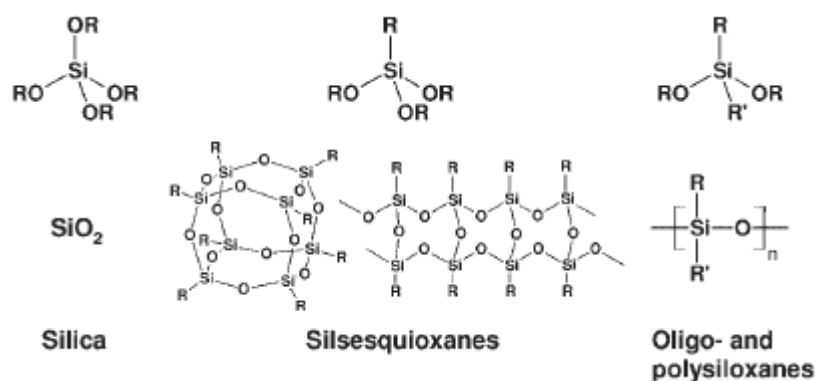


Figure 2.33: Formation of different structure during hydrolysis in dependence of the number of organic substituents compared substituents at the silicon atom

In addition, the functional group incorporated changes the properties of the final material, for example fluoro-substituted compounds can create hydrophobic and

lipophobic materials, additional reactive functional groups can be introduced to allow further reactions such as amino, epoxy or vinyl groups (Scheme 2.34.).

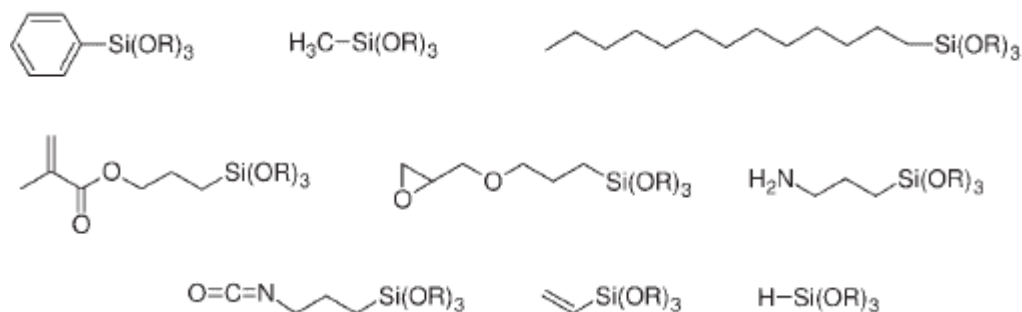


Figure 2.34: Trialkoxysilane precursors often used in the sol gel process

2.2.2.1.5 Hybrid Materials Derived by Combining The Sol Gel Approach and Organic Polymers

Compared with other inorganic network forming reactions, the sol gel processes show mild reaction conditions and a broad solvent compatibility. These two characteristics offer the possibility to carry out the inorganic network forming process in presence of a preformed organic polymer or to carry out the organic polymerization before, during or after the sol gel process. The properties of the final hybrid materials are not only determined by the properties of the inorganic and organic component, but also by the phase morphology and the interfacial region between the two components.

The often dissimilar reaction mechanisms of the sol gel process and typical organic polymerizations, such as free radical polymerizations, allow the temporal separation of the two polymerization reactions which offers many advantages in the material formation. One major parameter in the synthesis of these materials is the identification of a solvent in which the organic macromolecules are soluble and which is compatible with either the monomers or preformed inorganic oligomers derived by the sol gel approach. Many commonly applied organic polymers, such as polystyrene or polymethacrylates, are immiscible with alcohols that are released during the sol gel process and which are also used as solvents, therefore phase separation is enforced in these cases. This can be avoided if the solvent is switched from the typically used alcohols to, for example, THF in which many organic polymers are soluble and which is compatible with many sol gel reactions. Phase separation can also be avoided if the polymers contain functional groups that are

more compatible with the reaction conditions of the sol gel process or even undergo an interaction with the inorganic material formed. This can be achieved, for example by the incorporation of OH groups that interact with, for example, hydroxyl groups formed during the sol gel process or by ionic modifications of the organic polymer. Covalent linkages can be formed if functional groups that undergo hydrolysis and condensation reactions are covalently attached to the organic monomers. Some typically used monomers that are applied in homo- or copolymerizations are shown in Figure 2.35.

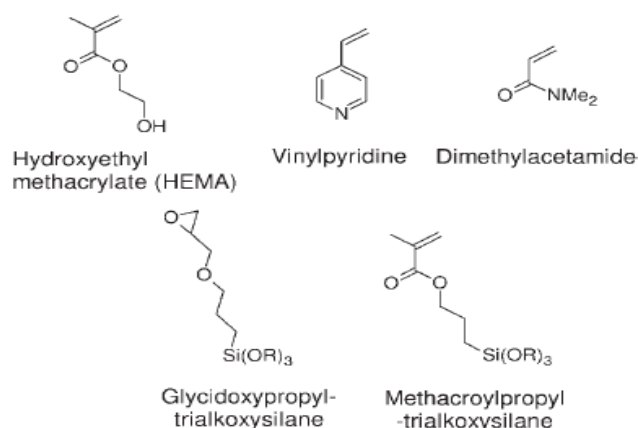


Figure 2.35: Organic monomers typically applied in the formation of sol gel organic polymer hybrid materials

2.2.3 Properties and applications

There is almost no limit to the combinations of inorganic and organic components in the formation of hybrid materials. Therefore materials with novel composition property relationships can be generated that have not yet been possible. Because of the plethora of possible combinations this introductory chapter can only present some selected examples. Many of the properties and applications are dependent on the properties of the precursors and the reader is therefore referred to the following chapters. Based on the increased importance of optical data transmission and storage, optical properties of materials play a major role in many high tech applications. The materials used can reveal passive optical properties, which do not change by environmental excitation, or active optical properties such as photochromic (change of color during light exposure) or electrochromic (change of color if electrical current is applied) materials. Both properties can be incorporated by building blocks

with the specific properties, in many cases organic compounds, which are incorporated in a matrix.

Hybrid materials based on silicates prepared by the sol–gel process and such building blocks reveal many advantages compared with other types of materials because silica is transparent and if the building blocks are small enough, does not scatter light, and on the other hand organic materials are often more stable in an inorganic matrix. One of the most prominent passive features of hybrid materials already used in industry are decorative coatings obtained by the embedment of organic dyes in hybrid coatings. Another advantage of hybrid materials is the increased mechanical strength based on the inorganic structures. Scratch-resistant coatings for plastic glasses are based on this principle. One of the major advantages of hybrid materials is that it is possible to include more than one function into a material by simply incorporating a second component with another property into the material formulation. In the case of scratchresistant coatings, for example, additional hydrophobic or antifogging properties can be introduced. However, in many cases the precursors for hybrid materials and nanocomposites are quite expensive and therefore the preparation of bulk materials is economically not feasible.

One of the advantages of hybrid materials, namely, their quite simple processing into coatings and thin films, can be one solution to this disadvantage. Applying such coatings to cheaper supports can be advantageous. Silica is preferred as the inorganic component in such applications because of its low optical loss. Other inorganic components, for example zirconia, can incorporate high refractive index properties, or titania in its rutile phase can be applied for UV absorbers. Functional organic molecules can add third order nonlinear optical (NLO) properties and conjugated polymers, conductive polymers can add interesting electrical properties. Nanocomposite based devices for electronic and optoelectronic applications include light emitting diodes, photodiodes, solar cells, gas sensors and field effect transistors. While most of these devices can also be produced as fully organic polymer based systems, the composites with inorganic moieties have important advantages such as the improvement of longterm stability, the improvement of electronic properties by doping with functionalized particles and the tailoring of the band gap by changing the size of the particles. The enhancement of mechanical and thermal properties of polymers by the inclusion of inorganic moieties, especially in the form of nanocomposites, offers the possibility for these materials to substitute classical

compounds based on metals or on traditional composites in the transportation industry or as fire retardant materials for construction industry.

Medical materials are also one typical application area of hybrid materials, as their mechanical properties can be tailored in combination with their biocompatibility, for example nanocomposites for dental filling materials. A high content of inorganic particles in these materials provides the necessary toughness and low shrinkage, while the organic components provide the curing properties combined with the paste-like behavior. Additional organic groups can improve the adhesion properties between the nanocomposites and the dentine. Composite electrolyte materials for applications such as solid-state lithium batteries or supercapacitors are produced using organic inorganic polymeric systems formed by the mixture of organic polymers and inorganic moieties prepared by sol gel techniques. In these systems at least one of the network forming species should contain components that allow an interaction with the conducting ions. This is often realized using organic polymers which allow an interaction with the ions, for example via coordinative or by electrostatic interactions. One typical example is proton conducting membranes which are important for the production of fuel cells. The application of hybrid composites is interesting for these systems because this membrane is stable at high temperatures compared with pure organic systems. These are only some applications for hybrid materials and there is a plethora of systems under development for future applications in various fields [38].

3.EXPERIMENTAL PART

3.1 Materials

In silane modified epoxy acrylate (EPA) films synthesis, Bisphenol A type epoxy resin and Aradur 2958 (from Huntsman Chemicals), Hydroquinone, Triethylamine (TEA, from Acros Chemicals), Dibutyltinlaurat (DBTL, from Henkel), Acrylic acid (from Merck Chemicals), (3-isocyanatopropyl)triethoxysilane (IPTEOS, from Fluka Chemicals) , Vinyltrimethoxysilane (from Aldrcih Chemicals), Photomer®4006-F (from Cognis 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 25⁰C.

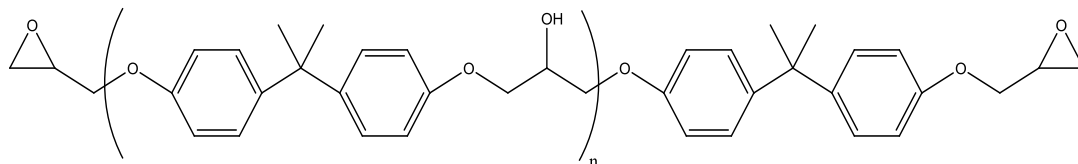


Figure 3.1: Bisphenol A diglycidyl ether resin

Aradur 2958 is aliphatic polyamine. It was used as epoxy curing agent. H⁺ active equivalent weight is 33 g/Eq. Viscosity, according to Brookfield, 190-250 cps at 25⁰C. Amine value is 954-959 mgKOH/g.

Hydroquinone(benzene-1,4-diol) was used as inhibitor. It is white solid and its density is 1,3g/cm³.

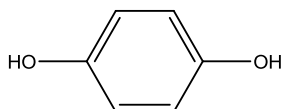


Figure 3.2: Hydroquinone.

Triethylamine (TEA) was used to allow the reaction to take place at a rapid rate and a lower temperatures. Its density is 0,726g/ml

Dibutyl Tinlaurate (DBTL) is a organometallic tin compound that is added to allow the reaction to take place at a rapid rate and a lower temperatures.

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.

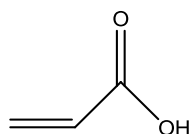


Figure 3.3: Acrylic acid

They have excellent color, UV, and thermal stability. Added to plastics and.

(3-isocyanatopropyl)triethoxysilane (IPTEOS) was used as silane coupling agent. Its density is 0,999 g/ml.

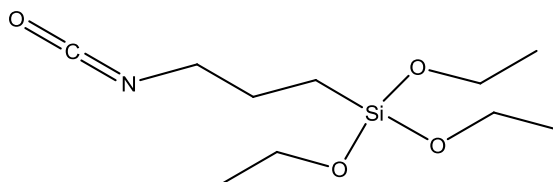


Figure 3.4: IPTEOS

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

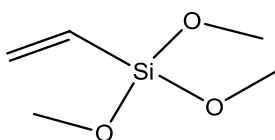


Figure 3.5: Vinyltrimethoxysilane

Photomer®4006-F(Trimethylol propane triacrylate, TMPTA) is an aliphatic trifunctional acrylate of low viscosity, low skin irritancy and excellent reactivity. It was used as crosslinking agent in photopolymerization system.

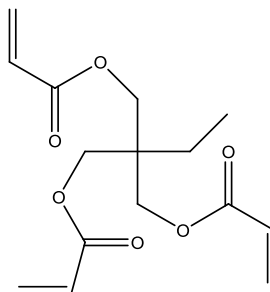


Figure 3.6: Photomer®4006-F

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.

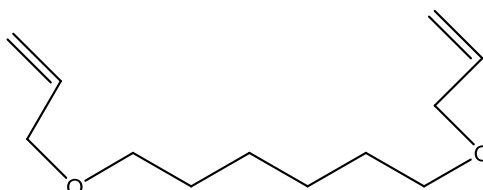


Figure 3.7: HDDA

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.

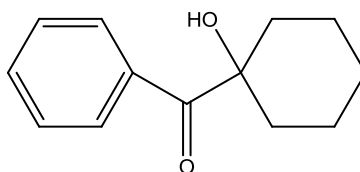


Figure 3.8: Irgacure 184

3.2 Equipments

3.2.1 Infrared Analysis (IR)

Infrared analysis were performed on Thermo Scientific Nicolet IS10 FT-IR spectrometer.

3.2.2 Nuclear Magnetic Resonance (NMR)

H-NMR analysis were recorded on a Bruker 250 MHz Spectrometer.

3.2.3 Thermogravimetical Analysis (TGA)

Thermal gravimetical analysis were performed on a TA TGA Q50 instrument at a heating rate 20 °C/min.

3.2.4 Contact Angle Meter

The contact angle of cured FPU films was measured by KSV CAM 100 instrument.

3.2.5 Gloss Meter

The gloss of cured epoxy acrylate films were measured by BYK-Gardner Micro Gloss instrument.

3.2.6 Pendulum Hardness Tester

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

3.2.7 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 Epoxy Acrylate Synthesis

The reaction was carried out in three-neck 50ml round bottom flask equipped with nitrogen inlet, spiral water condenser, and thermometer. 0,01g hydroquinone and 20g

epoxy resin were added into flask. The flask was placed in oil bath and set at 60⁰C. The reaction mixture was stirred until hydroquinone was dissolved completely. 0,3ml triethylamine was added in the flask and stirred. After the reaction mixture became homogenous, 7,2ml acrylic acid was added dropwise into the system. The heat of oil bath was set at 80⁰C and the mixture was stirred for approximately 10 hour. Acid value of the mixture should be between 1 to 2. It was controlled by titration of 0,1N KOH solution with phenolphthalein indicator. At the end of the reaction, to lower viscosity of the mixture, 20 wt.% HDDA was added and stirred well. The product was clear, yellow, viscous liquid and checked by infrared spectroscopy [44].

3.3.2 Synthesis of Urethane Modified Epoxy Acrylate

The reaction was carried out in a 50ml round-bottom flask, equipped with nitrogen inlet, spiral water condenser, and thermometer. All glassware was kept in the oven overnight and reaction system was cooled under nitrogen to remove humidity. The preparation EPA-Si20 is given as example. 5g epoxy acrylate (80:20, EPA:HDDA, wt%) and two drop pf DBTL were charged into three-necked flask and stirred at 40⁰C until homogenous mixture was obtained. 1,04ml (3-isocyanatipropyl)triethoxysilane was added dropwise to the reaction mixture to modify %20 of hydroxyl groups in epoxy acrylate resin. Disappearance of the characteristic -NCO peak at 2275 cm⁻¹ in the FT-IR spectrum confirmed that the reaction was completed. 20 wt.% HDDA was added to product and stirred well. The product was clear, viscous liquid. It was kept under nitrogen atmosphere in a close tight dark colored tube in the refrigerator and wrapped with aluminium folio for protect light. The same procedure was also used to synthesis urethane modified epoxy acrylate with %30, %40 and %50 modification of hydroxyl content [44].

3.4 Preparation of Formulation

Three different formulation were applied for polymerization system. Two of them were prepared for UV curing, the other one was prepared for thermal curing system. The composition of formulations is given in table.

Table 3.1: UV curing formulation with HDDA

sample code	modification ration(%)	modified resin(g)	HDDA(g)	photomer 4006F(g)	photoinitiator(g)
Si0-HDDA	0	0,48	0,12	0,37	0,03
Si20-HDDA	20	0,48	0,12	0,37	0,03
Si30-HDDA	30	0,48	0,12	0,37	0,03
Si40-HDDA	40	0,48	0,12	0,37	0,03
Si50-HDDA	50	0,48	0,12	0,37	0,03

Table 3.2: UV curing formulation with VTS

sample code	modification ration(%)	modified resin(g)	VTS(g)	photomer 4006F(g)	photoinitiator(g)
Si0-VTS	0	0,48	0,12	0,37	0,03
Si20-VTS	20	0,48	0,12	0,37	0,03
Si30-VTS	30	0,48	0,12	0,37	0,03
Si40-VTS	40	0,48	0,12	0,37	0,03
Si50-VTS	50	0,48	0,12	0,37	0,03

Table 3.3: Thermal curing formulation

sample code	modification ration(%)	modified resin(g)	epoxy resin(g)	aradur 2958(g)
Si0-Amine	0	0,3	0,7	0,2
Si20-Amine	20	0,3	0,7	0,2
Si30-Amine	30	0,3	0,7	0,2
Si40-Amine	40	0,3	0,7	0,2
Si50-Amine	50	0,3	0,7	0,2

3.4.1 Preparation of Hybrid Coating

I. Free Film

To prepare free films, teflon plate, having 10mm x 50mm x 1mm spaces, was used. Hybride free film formulations were prepared according to table. Solutions were kept under vacuum approximately 30 minutes to remove bubbles, then poured in spaces on the teflon. It was placed under UV lamp and irradiated for 500 seconds. For thermal polymerization, all procedures were carried out same and coating formulation were polymerized at 60⁰C for 15 minutes. The films were waited during one day. Thermal and characteristic analysis and strain-stress test were applied on these films.

II. Coated plexiglass plates

Firstly, temporary polyethylene coating films were pulled away by force from plexiglass plates surface. 1g 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 UV lamp for 500 seconds and waited during one day. For thermal polymerization, all procedures were carried out same and plexiglass plates were kept at 60°C for 15 minutes. Gloss, contact angle and pendulum hardness tests were applied on these plates.

3.5 Analysis

Following tests; Infrared Analysis (IR), Nuclear Magnetic Resonance (NMR), Thermal Gravimetric Analysis (TGA), Pendulum Hardness, Contact Angle Measurement, Gloss and Tensile tests, Pencile Hardness, Solvent Resistance and Gel Content were performed to monitor thermal, morphological and film properties of EPA 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[38].

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 ^1H (the most NMR-sensitive isotope after the radioactive ^3H) and ^{13}C , although nuclei from isotopes of many other elements (e.g. ^2H , ^{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 .

$$B = B_0 (1 - \sigma)$$

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 .

$$\delta = (\nu - \nu_{\text{REF}}) \times 10^6 / \nu_{\text{REF}}$$

In NMR spectroscopy, this standard is often tetramethylsilane, $\text{Si}(\text{CH}_3)_4$, abbreviated TMS. The chemical shift is a very precise metric of the chemical environment around a nucleus.

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

3.5.3 Thermal Gravimetric 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 [39]. 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[40].

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 600°C under N_2 (flow rate: 40 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 h. The cured film was dried until its weight was constant (m_2). Gel content of the cured film was calculated by equation,

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

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

3.5.5 Solvent Resistance

The Solvent resistance of the films after curing were immersed in various solvents (m_1 , 0.005-0.03g g/10 ml) for one day. The cured film was dried until its weight was constant. After drying, the films were reweighted (m_2) and calculated weight loss.

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

Solvents used in this test and results are shown in the Table 4.5-9.

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[41].

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 [42] in 1805. 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.3.4.). This equilibrium relation is known as Young's equation:

$$\gamma_{LV} \cos \theta_Y = \gamma_{SV} - \gamma_{SL}$$

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 θ_Y .

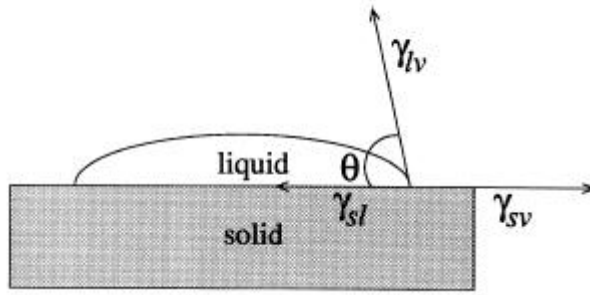


Figure 3.9 : Scheme of a sessile-drop contact angle system

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[41].

The wettability of the film surfaces was measured using a contact angle KSV CAM100 system at ambient temperature. The equilibrium contact angles of 5 μ L water droplets were measured by the sessile drop method. The contact angles were measured as follows: a 5 μ L water droplet was placed on the sample using a syringe, and contact angle was recorded.

The water contact angle of FPU films prepared in our experiments are listed in Table 4.10.

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°), semi-gloss ones are measured with a medium angle (60°) and high-gloss ones with only a very small angle (20°). Modern devices contain all 3 measuring geometries and can be used universally by switching to the various ranges.

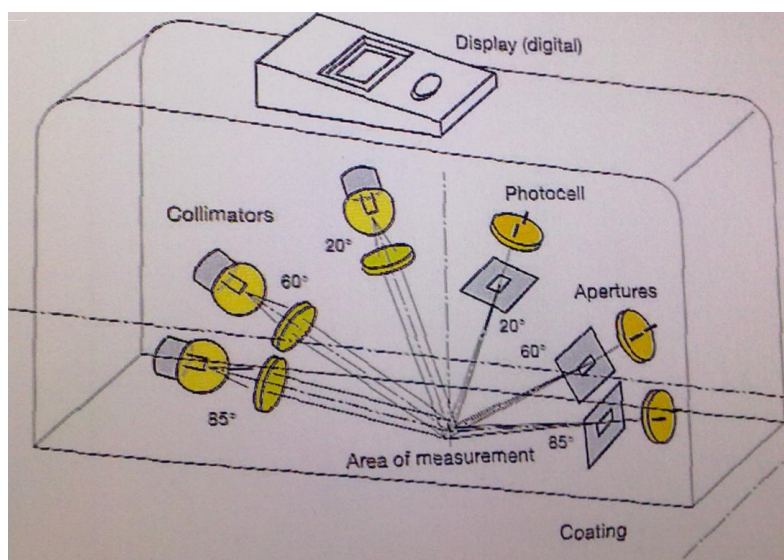


Figure 3.10: Scheme of a measurement device for gloss at different angles [43]

The test were applied the cured EPA film with plexiglass plates to measure their gloss features. . The test results are shown at Table 4.11 for all formulations, respectively.

3.5.8 Pendulum Hardness Tests

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 whic elapses until the amplitude of the pendulum has dropped from 6° to 3° [43].Pendulum hardness of the cured film was measured to determine the film hardness. The test results are shown at Table 4.12. for all formulations, respectively.

3.5.9 Pencile 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.

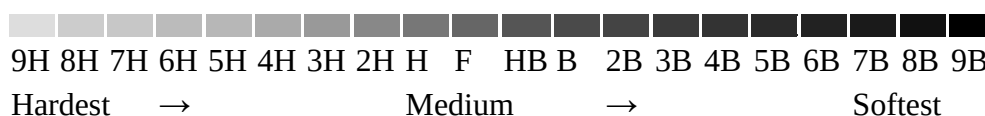


Figure 3.11: Pencile Hardness and Properties

Pencile Hardness (ASTM D-3363) was performed to check the through cure of coatings. Pencile hardness property of coating was determined using pencil ranging from H to 8H and the pencil that will not stretch the coating reported as pencil stretch hardness. The results are given in Table 4.13.

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. A typical engineering stress-strain curve is shown below. 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 elasticity, 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 kpsi 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.

Only two of the elastic constants are independent so if two constants are known, the third can be calculated.

In this study, tensile tests were applied to 10mm x 50mm x 1mm epoxyacrylate free films. The results are shown on Table 4.14, Table 4.15 and Table 4.16.

4.RESULTS AND DISCUSSION

In this thesis, silane modified epoxy acrylate resin and coated materials are prepared. Formulations are consisted of resin, mono-, di-, and triacrylates, photoinitiator and amin hardener. Two different polymerization methods are used, photopolymerization and thermal polymerization. All coating formulations are coated on plexiglass plates and cured by photo and thermal ways. In addition, free films of all materials are prepared and curing same wayds. After curing obtained samples are subjected to further tests.

4.1 Synthesis of Epoxy Acrylate

In this part, epoxy acrylate resin was synthesized according to procedure (Figure 4.1) mentioned in section 3.3.1. Epoxy oligomers were reacted with acrylic acid to yield hydroxyl containing epoxy acrylates via oxyrane ring opening reaction. Completion of reaction was checked by FT-IR spectrum.

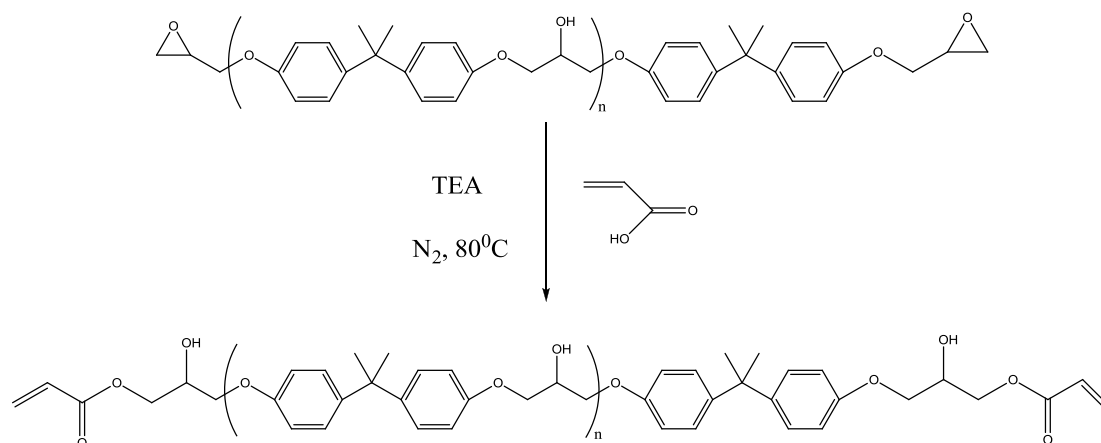


Figure 4.1: Synthesis of epoxy acrylate

The FT-IR spectrum of epoxy acrylate in Figure 4.3. contains characteristic broad band $-\text{OH}$ at 3435 cm^{-1} , $-\text{C}=\text{O}$ at 1722 cm^{-1} , $-\text{C}=\text{C}$ at 1607 cm^{-1} and $-\text{CH}$ at 2925 cm^{-1} . In Figure 4.2, it is showed epoxy resin FT-IR spectrum.

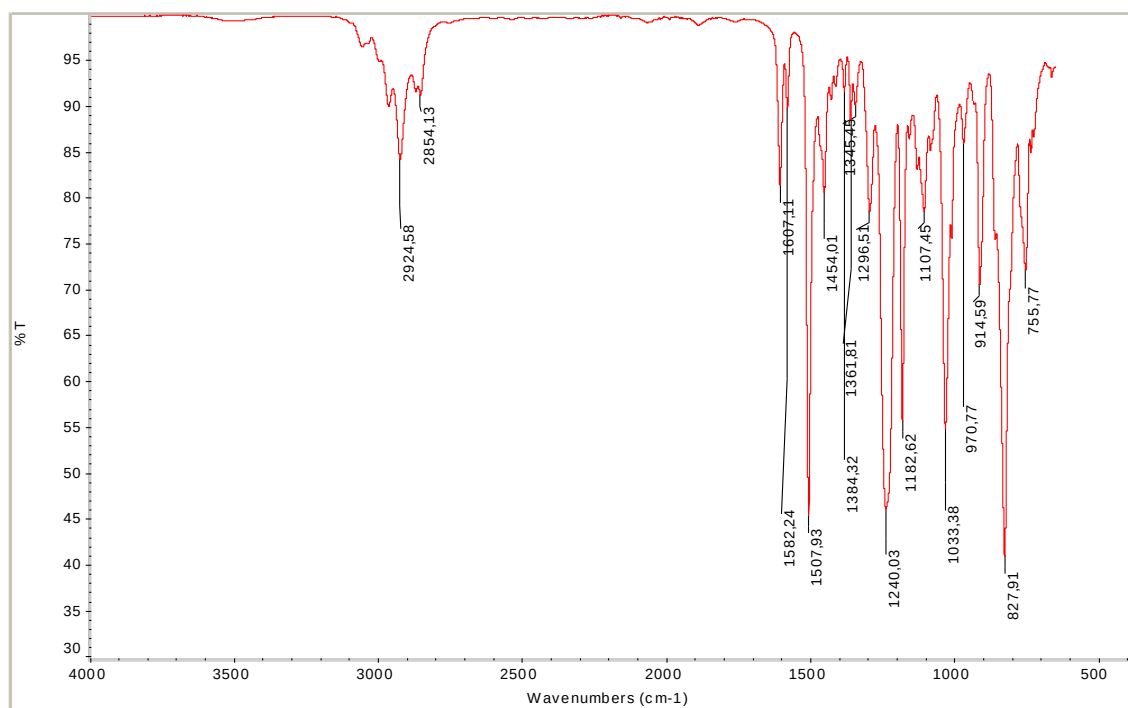


Figure 4.2 IR Spectra of epoxy resin

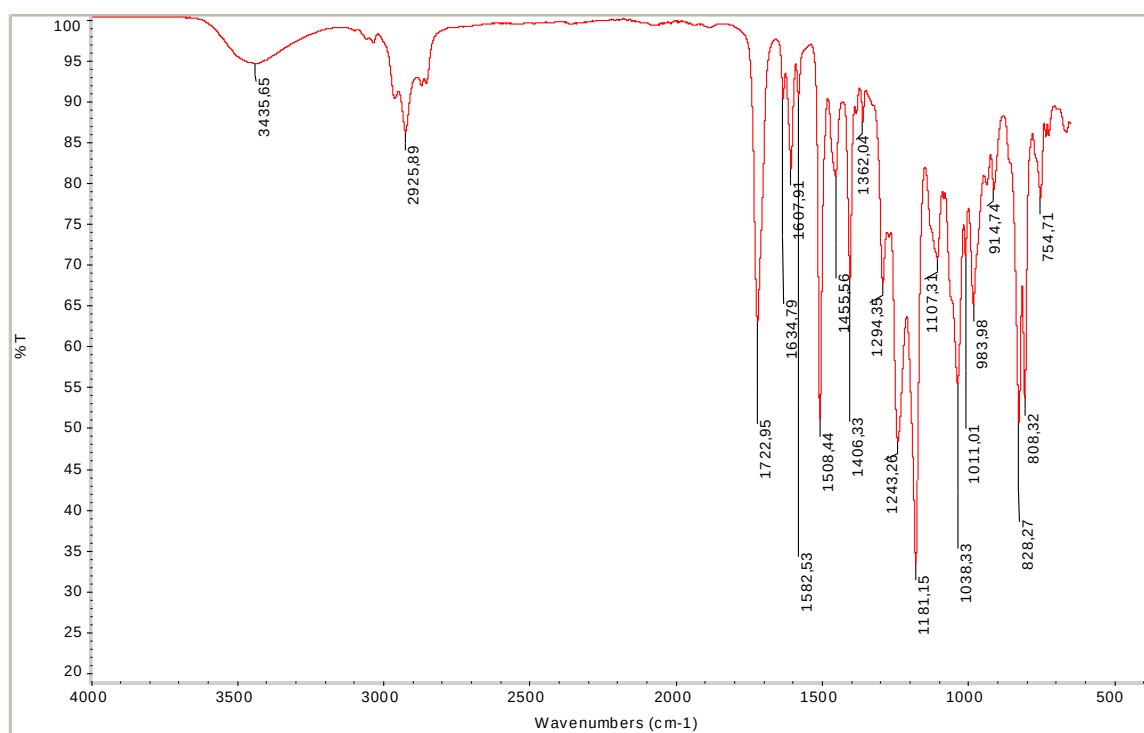


Figure 4.3 IR Spectra of epoxy acrylate

As a result of IR analysis, we can clearly see high decrease of characteristic epoxy group at 914 cm^{-1} . This shows the ring opening of epoxy group was occurred. At the

end of the reaction, $-OH$, $-C=C$ and $-C=O$ groups can be defined as proof of formation of epoxy acrylate.

In characterization of epoxy acrylate, NMR analysis was also applied on epoxy acrylate.

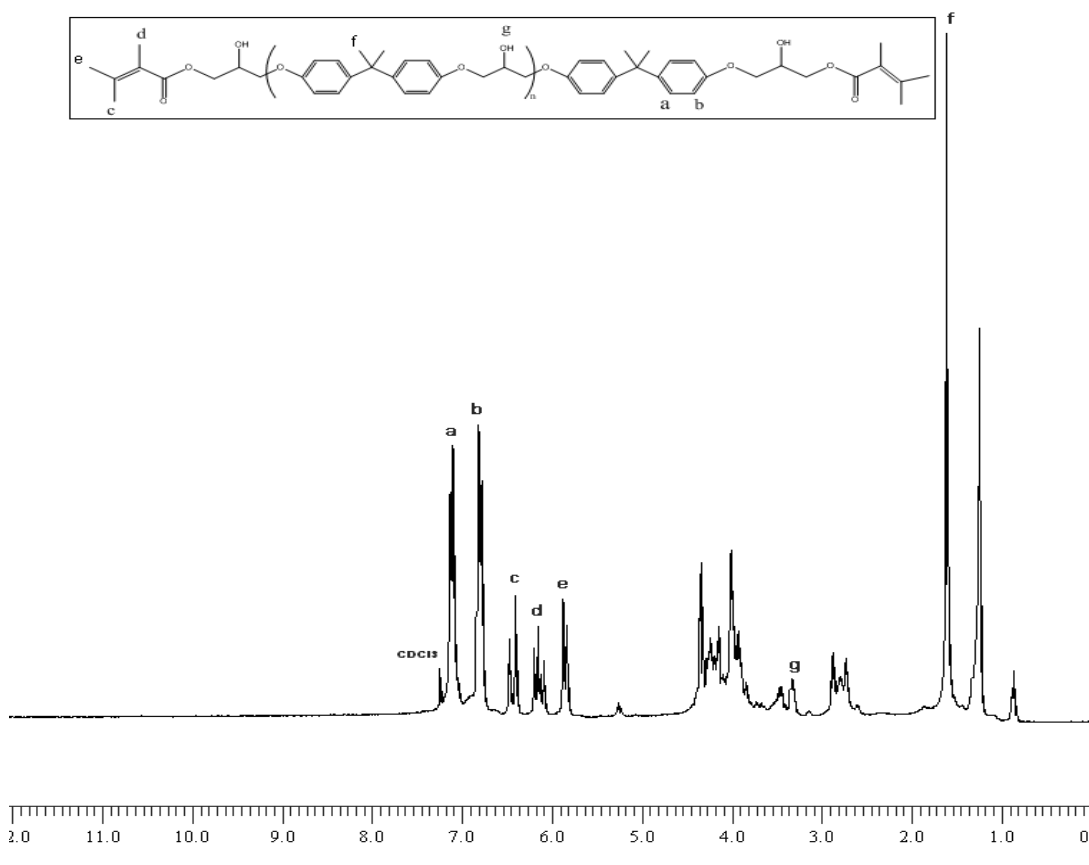


Figure 4.4: ^1H -NMR spectrum of epoxy acrylate

^1H -NMR spectrum of epoxy acrylate was taken in $CDCl_3$ as shown in Figure 4.4.

The spectrum prove the expected structure of epoxy acrylate. According to the spectrum, double bond came from acrylic groups have signals at 5,83-5,87, 6,09-6,2 and 6,40-6,47 ppm. The signal originating from $-OH$ was discerned at 3,45 ppm.

4.2 Synthesis of Urethane Modified Epoxy Acrylate

In this part, urethane modified epoxy acrylate was synthesized according to procedure (Figure 4.5) mentioned in section 3.3.2. Epoxy acrylates were modified by reacting with (3-isocyanatopropyl)triethoxysilane.

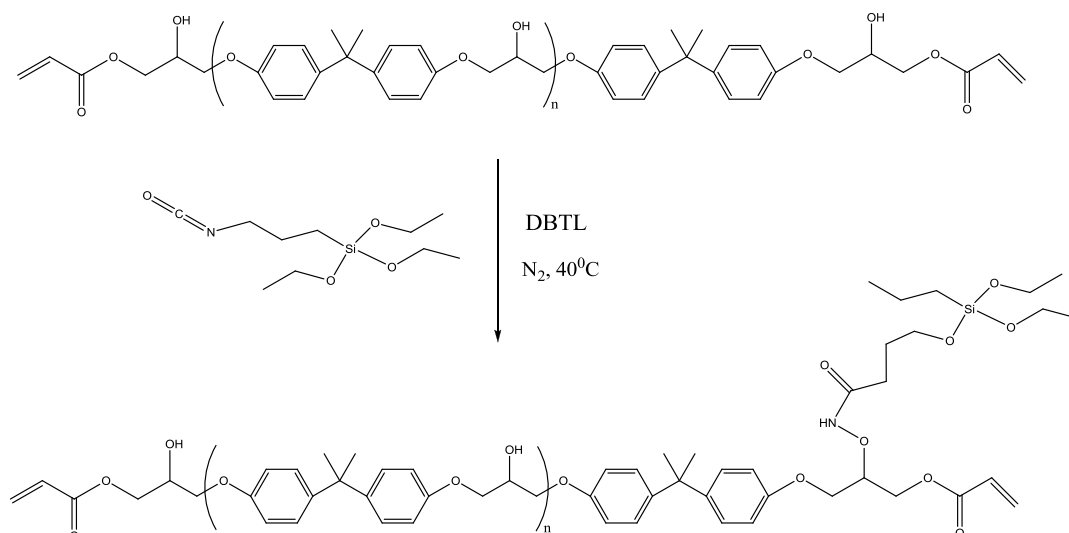


Figure 4.5: Synthesis of urethane modified epoxy acrylate

Formation of the reaction was followed by FT-IR analysis. Disappearance of characteristic -NCO peak at 2270 cm^{-1} show us completion of the reaction. On the Figure 4.6. and Figure 4.7., FT-IR spectrum of 20% urethane modified epoxy acrylate (Si20) before and after reaction are given. It also shows the characteristic -NH stretching band at 3431 cm^{-1} , Si-O-CH_3 band at 1065 cm^{-1} and carbonyl peak at 1722 cm^{-1} .

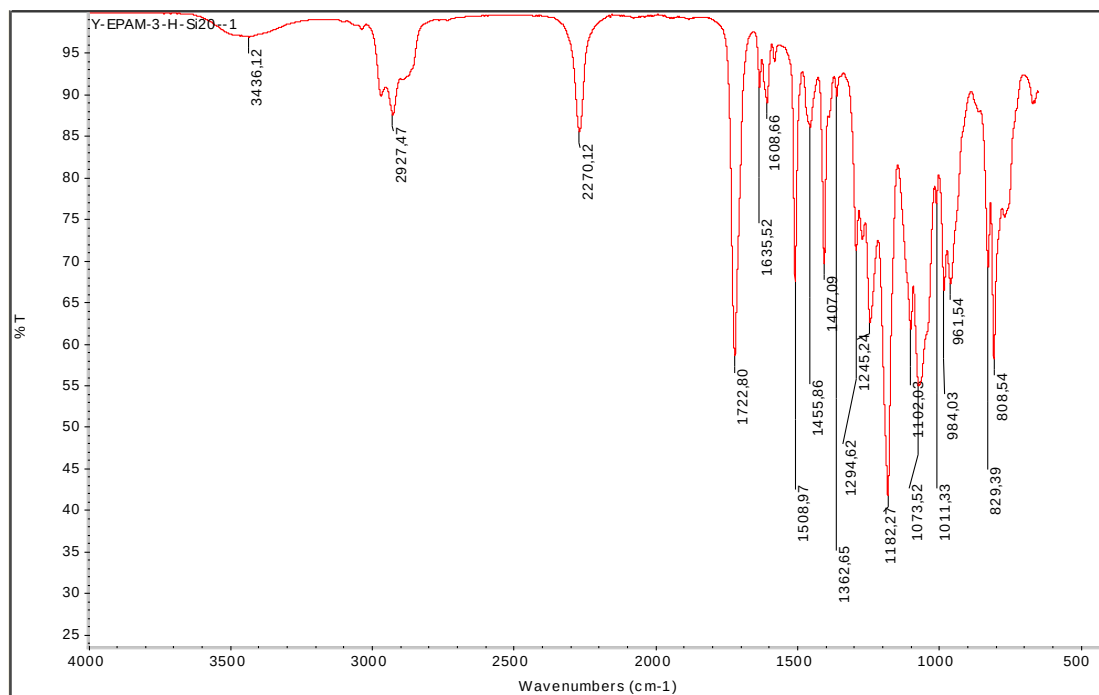


Figure 4.6: IR Spectra of Si20 synthesis, before reaction

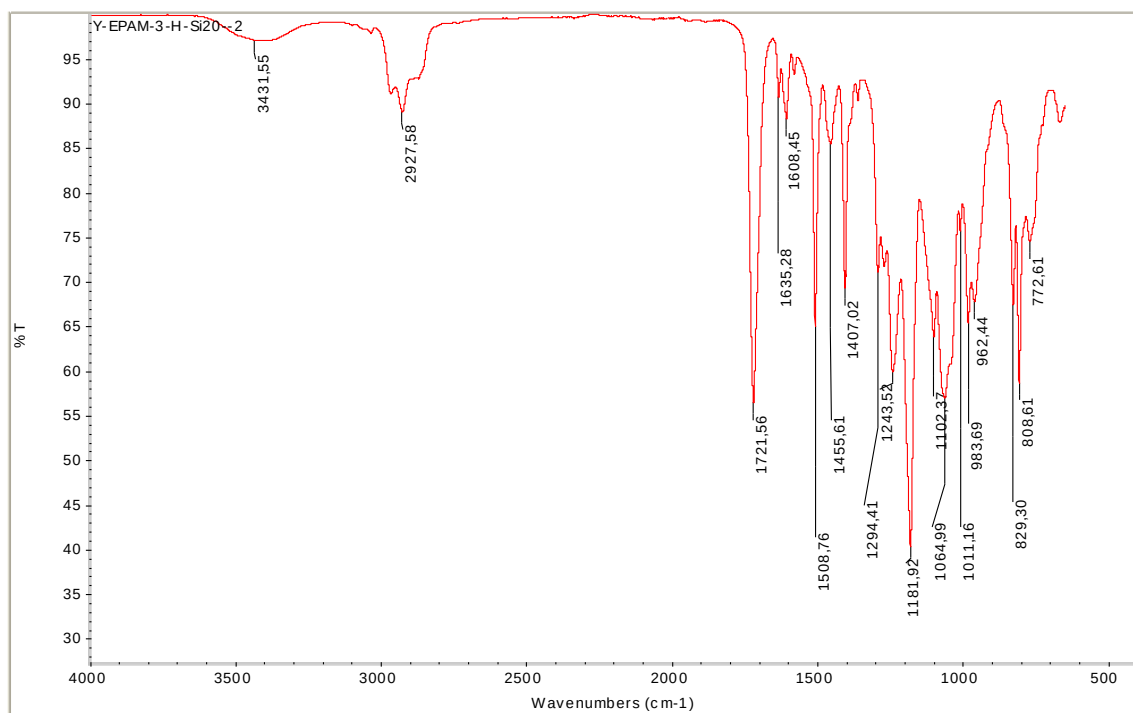


Figure 4.7: IR Spectra of Si20 synthesis, after reaction

The reaction characterization was supported by NMR analysis.

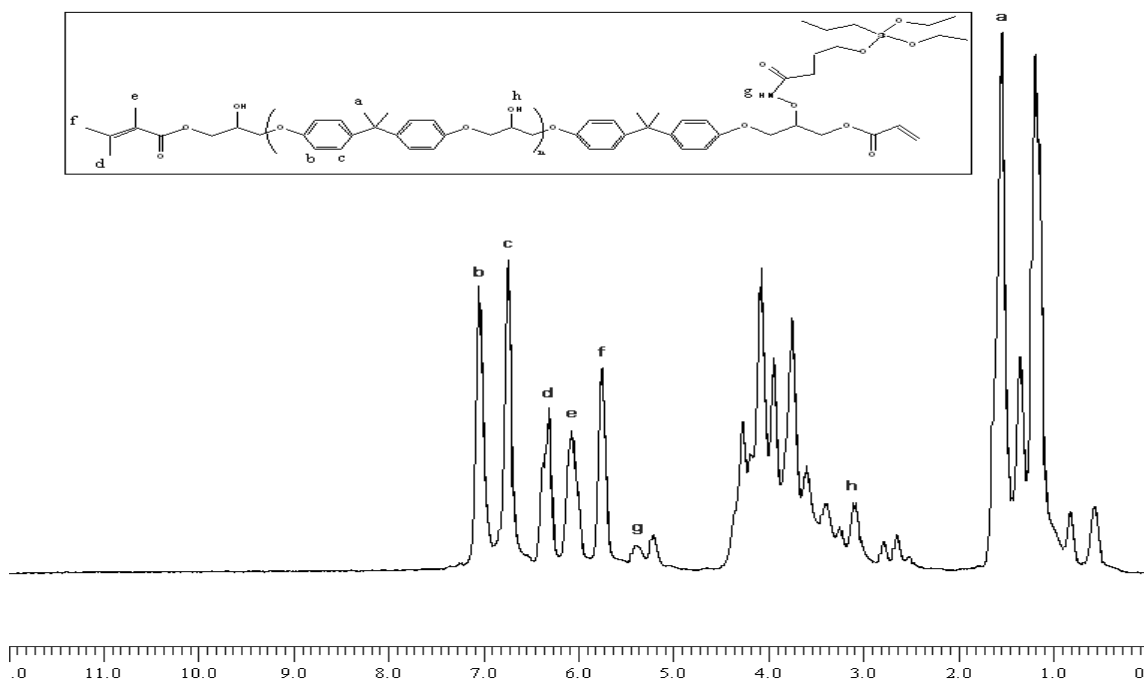


Figure 4.8: ^1H -NMR spectrum of Si20

^1H -NMR spectrum of Si20 was taken in CDCl_3 as shown in Figure 4.8. According to the spectrum, -NH signal at 5,4 ppm shows the formation of urethane linkage.

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 Thermal Gravimetric Analysis

TGA analysis were carried out in a nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$ between 30°C and 900°C for analysing thermal stabilities of the epoxy acrylate films. Figure 4.9., 4.10. and 4.11. are showed TGA curves for free films of different formulations.

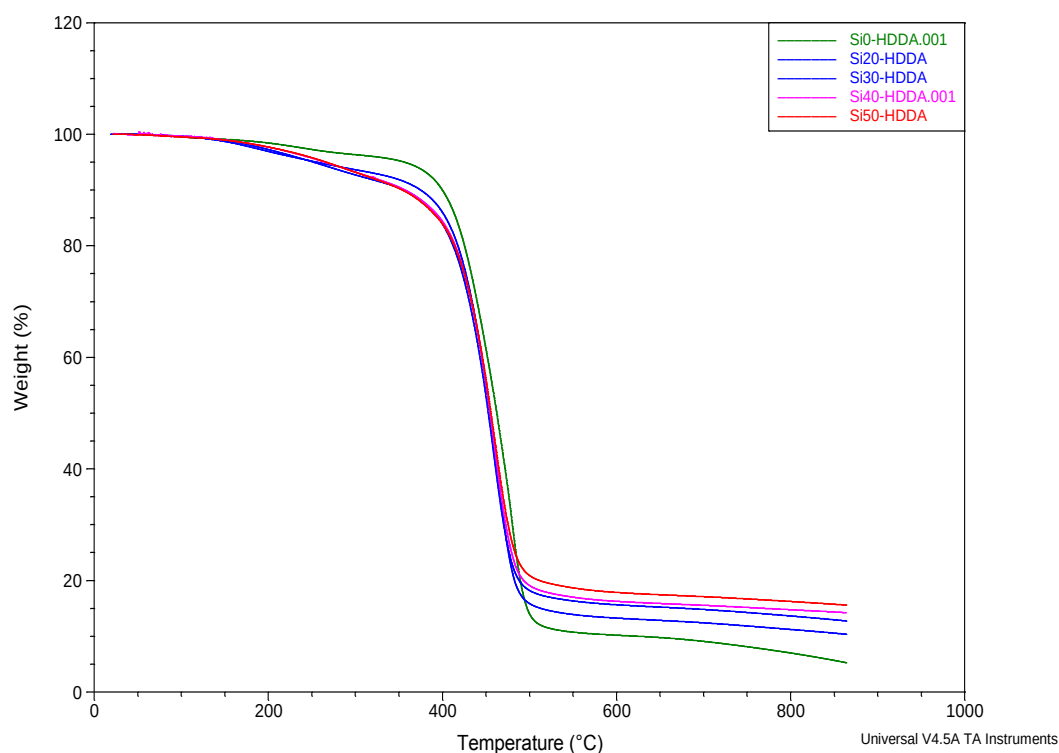


Figure 4.9: TGA thermogram of epoxy acrylate with HDDA

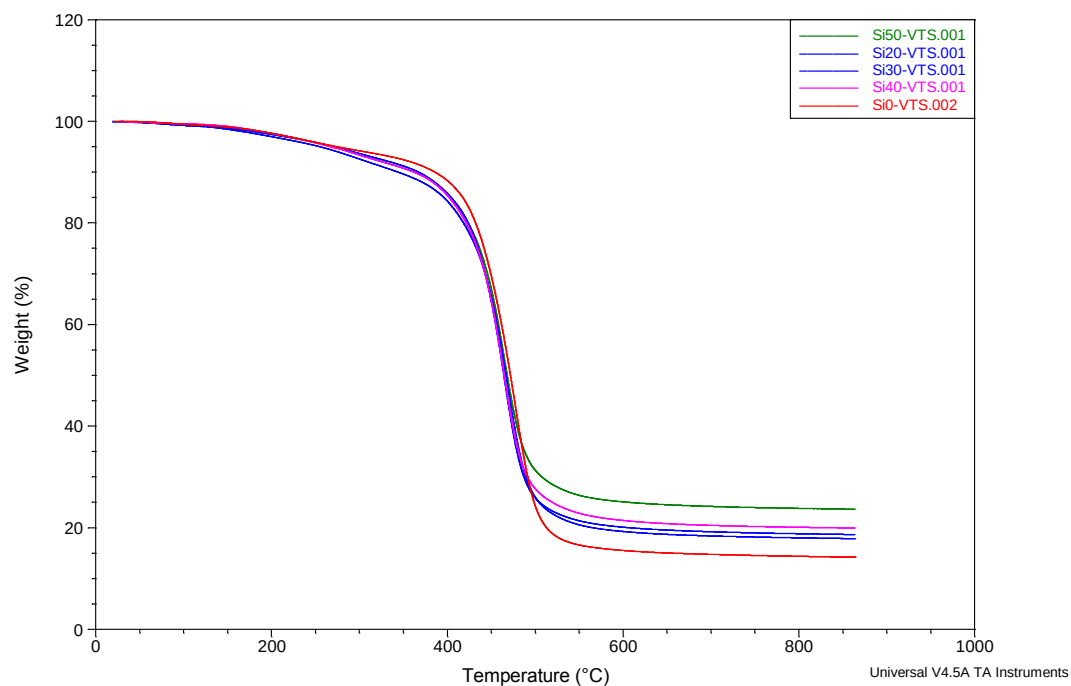


Figure 4.10: TGA thermogram of epoxy acrylate with VTS

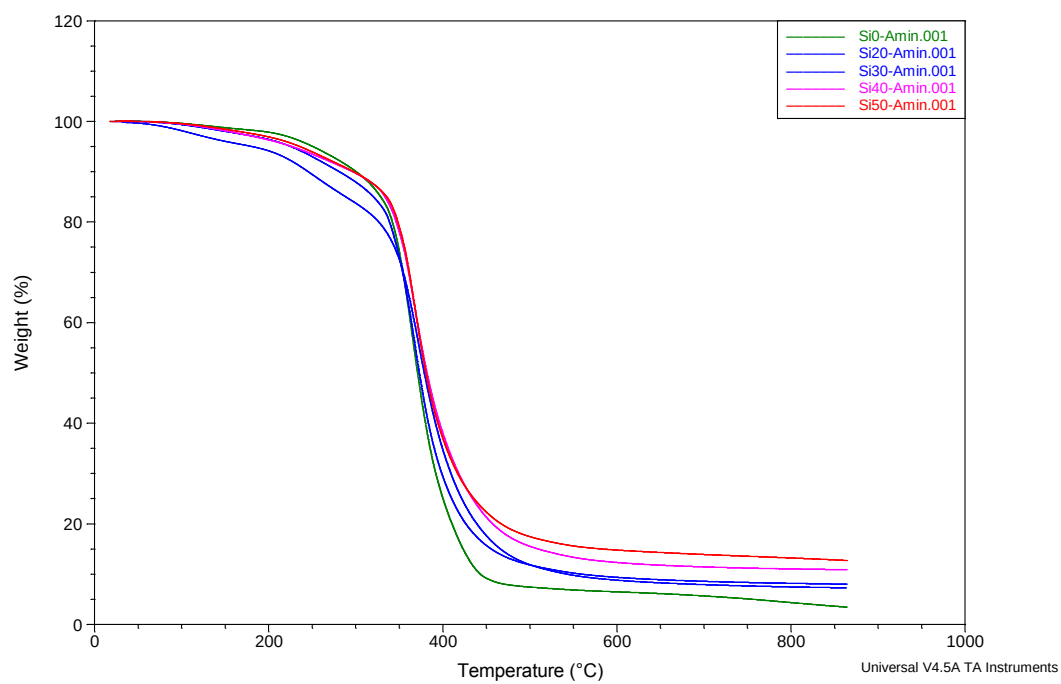


Figure 4.11: TGA thermogram of epoxy acrylate with Amin

TGA thermograms of the hybrids and the results are collected in Table 4.1., 4.2. and 4.3. All samples show a small weight loss around 125 °C implying the release of volatile degradation products such as unreacted photoinitiator and reactive diluent. All samples exhibited a 10% weight loss at around 350 °C followed by a rapid loss over the temperature range 390–440 °C. It can be observed that thermal stability of hybrid networks was caused to a little decrease in thermal stability. This is because silane groups prevent polymerization, so crosslinking degree is low it makes material poor stable against heat. Thermogravimetric analyses showed that with increasing the silane content, final weight shifted to higher values. The delay in degradation caused by the siloxane moiety may be attributed to the steadiness of inorganic structure, which may stabilize the epoxy acrylate resin.

Table 4.1 : TGA analysis values of HDDA system

TGA analysis					
Resin	Si0	Si20	Si30	Si40	Si50
Agent	HDDA	HDDA	HDDA	HDDA	HDDA
%10 weight loss temperature(°C)	400.38	384.31	375.36	366.54	365.36
%50 weight loss temperature(°C)	472	466.51	462.52	459.7	456.07
Final weight loss temperature(°C)	863.86	863.85	863.94	863.8	864
Residue (%)	5,27	10,37	12,75	14,24	15,6

Table 4.2 : TGA analysis values of VTS system

TGA analysis					
Resin	Si0	Si20	Si30	Si40	Si50
Agent	VTS	VTS	VTS	VTS	VTS
%10 weight loss temperature(°C)	386.16	373.51	367.21	362.47	361.28
%50 weight loss temperature(°C)	471.47	460.73	456.18	454.37	447.92
Final weight loss temperature(°C)	864.39	863.67	863.11	863.51	863.63
Residue (%)	14,22	17,86	18,67	19,96	23,66

Table 4.3 : TGA analysis values of Amine system

TGA analysis					
Resin	Si0	Si20	Si30	Si40	Si50
Agent	Amine	Amine	Amine	Amine	Amine
%10 weight loss temperature(°C)	300.85	293.98	294.34	278.93	276.11
%50 weight loss temperature(°C)	370.76	377.87	371.95	381.42	381.42
Final weight loss temperature(°C)	863.67	863.31	864.07	864.1	864.27
Residue (%)	3,456	7,278	8	10,89	12,73

In amine system, different from the uv curing system, thermal stability is lower. %10 weight loss is seen at around 290 °C. In addition, because of low silane content, final residu is the lowest of all curing system.

4.3.2 Gel Content

This test was applied to measure polymerization degree of system. This procedure was proceeded mentioned in section 3.5.10. Gel content values are listed in Table 4.4.

Table 4.4: Gel content of cured films

Gel Content(wt%)			
	HDDA	VTs	Amine
Si0	99,9	99,2	99,2
Si20	99,6	99,17	99,17
Si30	99,55	99,1	99,1
Si40	99,45	98,8	98,8
Si50	99,17	98,5	98,5

This results show us, polymerization systems and formulations are suitable for our materials. Unreacted part of cured materials are mostly under wt. 1% . This value was increased with the silane content. Because of steric hinderance of silane group, curing of acrylates and other groups were get harder, so the gelation of these compound is low. However, because of high polymerization degree, amin system has high gel content value.

4.3.3 Solvent Resistance

This test was appiled according to section 3.5.9. the solvents and the results were listed in tables.

Table 4.5 Solvent resistance of Si0 coatings

Resin	Si0	Si0	Si0
Agent	HDDA	VTs	Amine
Solvents	Weightloss(%) /Appearance	Weightloss(%) /Appearance	Weightloss(%) /Appearance
Buthanol	- / good	- / good	- / good
DMSO	<1 / good	<1 / good	- / good
Xylene	<1 / good	<1 / good	<1 / good
Methanol	- / good	- / good	- / good
Acetone	- / good	- / good	- / good
Chloroform	- / good	- / good	- / good
%10 H ₂ SO ₄	- / good	- / good	- / good
%10HCl	- / good	- / good	- / good
%10NaOH	- / good	- / good	- / good

Table 4.6: Solvent resistance of Si20 coatings

Resin	Si20	Si20	Si20
Agent	HDDA	VTs	Amine
Solvents	Weightloss(%) /Appearance	Weightloss(%) /Appearance	Weightloss(%) /Appearance
Buthanol	- / good	- / good	- / good
DMSO	<1 / good	<2 / good	- / good
Xylene	<1 / good	<1 / good	<1 / good
Methanol	- / good	<1 / good	<1 / good
Acetone	- / good	<1 / good	- / good
Chloroform	- / good	- / good	- / good
%10 H ₂ SO ₄	- / good	- / good	- / good
%10HCl	- / good	- / good	- / good
%10NaOH	- / good	- / good	<1 / good

Table 4.7: Solvent resistance of Si30 coatings

Resin	Si30	Si30	Si30
Agent	HDDA	VTs	Amine
Solvents	Weightloss(%) /Appearance	Weightloss(%) /Appearance	Weightloss(%) /Appearance
Buthanol	- / good	- / good	- / good
DMSO	<1 / good	<2 / good	- / good
Xylene	<1 / good	<1 / good	<1 / good
Methanol	- / good	<1 / good	<1 / good
Acetone	- / good	<1 / good	<1 / good

Table 4.7 (contnd): Solvent resistance of Si30 coatings

Chloroform	- / good	- / good	- / good
%10 H ₂ SO ₄	- / good	<1 / good	- / good
%10HCl	- / good	- / good	- / good
%10NaOH	- / good	- / good	<1 / good

Table 4.8: Solvent resistance of Si40 coatings

Resin	Si40	Si40	Si40
Agent	HDDA	VTS	Amine
Solvents	Weightloss(%) /Appearance	Weightloss(%) /Appearance	Weightloss(%) /Appearance
Buthanol	- / good	- / good	- / good
DMSO	<2 / good	<2 / good	- / good
Xylene	<1 / good	<1 / good	<1 / good
Methanol	<1 / good	<1 / good	<1 / good
Acetone	<1 / good	<2 / good	<1 / good
Chloroform	- / good	- / good	- / good
%10 H ₂ SO ₄	- / good	<1 / good	- / good
%10HCl	- / good	- / good	- / good
%10NaOH	- / good	- / good	<1 / good

Table 4.9: Solvent resistance of Si50 coatings

Resin	Si50	Si50	Si50
Agent	HDDA	VTS	Amine
Solvents	Weightloss(%) /Appearance	Weightloss(%) /Appearance	Weightloss(%) /Appearance
Buthanol	- / good	- / good	- / good
DMSO	<2 / good	<3 / good	<1 / good
Xylene	<1 / good	<1 / good	<1 / good
Methanol	<1 / good	<1 / good	<1 / good
Acetone	<1 / good	<2 / good	<1 / good
Chloroform	- / good	- / good	- / good
%10 H ₂ SO ₄	<1 / good	<1 / good	<1 / good
%10HCl	- / good	- / good	- / good
%10NaOH	- / good	- / good	<2 / good

4.3.4 Contact Angle Measurement

The value of the contact angle of a liquid on a film is a direct reflection of the surface wettability. Contact angles of water were measured on plexiglass plate coated with fifteen different epoxy acrylate films which were cured. For each measurement one drops of water was tested on the surfaces and results are tabulated in Table 4.10

Table 4.10 : Contact angle results

Water Contact Angle			
	HDDA	VTs	Amine
Si0	66,87	68,59	73
Si20	67,38	69,35	74,15
Si30	68,77	70,21	75,12
Si40	69,08	72,7	78,27
Si50	71,61	73,3	81,63

As can be seen in Table 4.10., the epoxy acrylate coating with no modification has a fairly polar surface and shows a water contact angle of 66.87°. Upon 50% of modification with 3-isocyanatopropyl trimethoxysilane (IPTEOS), the contact angle shows a shift to 71.61°. This is an expected behavior assuming that pendant triethoxysilanes make the surface more hydrophobic. It is also seemed in amin curing system, contact angles are higher than uv curing system inspite of including low silane content. That can be estimated, hydrophobicity of surface is not only responsible from polarity, there is also polymerization degree effect. In amin curing system, polymerization degree is higher than other and this is caused to more rigid and so more shrinkage surface of coatings. This is explain why amin curing system has high contact angle.

4.3.5 Gloss Tests

Gloss of the coated plates were measured at an angle of 20°, 60° and 85°. For gloss test, plexiglass plates were coated as mentioned in section 3.3. results are given in table 4.11.

Table 4.11: Gloss test values of coated films

	HDDA		VTS		Amine	
	20 ⁰	60 ⁰	20 ⁰	60 ⁰	20 ⁰	60 ⁰
Si0	172	150	175	154	133	133
Si20	173	152	173	155	137	135
Si30	169	153	172	158	139	139
Si40	168	155	170	160	143	142
Si50	166	156	167	163	144	147

The measurement at 85⁰ is for matt surface, so these values were neglected. It is actually the ability of a surface to reflect light into the specular direction. The factors that affects 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 we can see the decrease in gloss with increasing content of silane. Hybrid particles are spreaded through the coating surface, so that is caused the surface become more rough. As a result, gloss is decreasing.

4.3.6 Pendulum Hardness Tests

König pendulum hardness tests are applied after all formulations coated plexiglass plates.

Table 4.12 : Pendulum hardness results

Pendulum Hardness			
	HDDA	VTS	Amine
Si0	95	98	107
Si20	99	102	111
Si30	101	104	114
Si40	104	105	118
Si50	105	108	122

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. The hybrid resin used to coat Plexiglas panels, has an increased hardness of about 5–9%, depending

onto coating formulation and annealing time. The increase in the hardness can be attributed to alkoxysilane pendant group's content. As can be seen in table 4.12., increasing silane content was caused to improve hardness. We can see this effect all cured formulations. In addition, it can be estimated that because of the rigidity of amin system, pendulum hardness values are higher than uv curing system.

4.3.7 Pencile Hardness

Pencil hardness test was applied on plexiglass plates mentioned in section 3.5.8. This test is applied to understand hardness of the surface in addition to pendulum hardness. In table 4.13., results are listed. We can see the little increase in pencil hardness value with the increase in silane content. Because of there is no big changes in silane content, pencil hardness of formulations nearly same. Furthermore, amine system has high hardness value because of its rigidity.

Table 4.13: Pencil hardness of coated films

Pencil Hardness			
	HDAA	VTS	Amine
Si0	>4H	>5H	>5H
Si20	>4H	>5H	>5H
Si30	>5H	>5H	>6H
Si40	>5H	>6H	>6H
Si50	>5H	>6H	>6H

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 HDAA system are given in Table 4.14.

Table 4.14: Stress-Strain analysis of HDAA system

	Tensile strength at yield (N)	Elongation at break (%)	Young's modulus (Mpa)
Si0-HDAA	120	7,97	12,06
Si20-HDAA	138	13	13,8
Si30-HDAA	172	17,8	16,6
Si40-HDAA	160	15	13
Si50-HDAA	112	10	11,3

As can be seen in Table 4.14., Young's modulus of unmodified epoxy resin is 12,06 Mpa. Until 30% modified coating, there are an increase in young's modulus. Tensile strength and elongation are also increased. The hybrid coatings with higher inorganic content behave as hard and strong. More than 30% modification, all tensile properties show a decreasing. This show us, there is a limit point of composite materials. After this point, increase in silane content is not effect the tensile properties, on the contrary, that can be caused to decrease in properties. According to table, 30% modification is our limit point.

Table 4.15: Stress-Strain analysis of VTS system

	Tensile strength at yield (N)	Elongation at break (%)	Young's modulus (Mpa)
Si0-VTS	134	11,8	13,7
Si20-VTS	160	18	17,9
Si30-VTS	152	17,2	16,5
Si40-VTS	136	15	12,6
Si50-VTS	108	12,4	11

Curing films of VTS and Amin also were carried out tensile test. All system include different silane ratio, so all of them have different limitation point. In table 4.15, we can see tensile test results of VTS system. Because of silane ingredient of vinyltriethoxysilane, limitation point is lower than HDDA system. 20 % of modification is the limit point of VTS system. After that point all tensile properties getting lower with increasing silane content. In addition, in same modification ratio of VTS and HDDA system, VTS system is higher than HDDA. This is caused from high silane content of VTS system in same modification ratio.

Table 4.16: Stress-Strain analysis of Amine system

	Tensile strength at yield (N)	Elongation at break (%)	Young's modulus (Mpa)
Si0-Amine	152	16,2	14,47
Si20-Amine	162	17,6	16
Si30-Amine	174	18,4	18,1
Si40-Amine	181	19	19,9
Si50-Amine	173	17,5	17,5

In amine system, there is differences from VTS and HDDA system. This is also has limitation point at 40 % of modification ratio. Silane content of amine system is more lower than other system, so tensile properties show small changes. All values are higher than other two system. This is estimated because of high crosslinking degree and extra condensation reaction of epoxy-amine-acrylic system.

5. CONCLUSIONS

In this study, a series of UV and thermal curable organic–inorganic hybrid coatings were prepared based on a bifunctional oligomer bearing diacrylate and trimethoxysilane functionalities. Fifteen different epoxy acrylate coating formulations were prepared and checked about their chemical, thermal and mechanical properties.

FT-IR and ^1H -NMR were used to characterize the structure of the hybrids. The thermal properties were elucidated by thermogravimetric analysis (TGA).

Incorporation of trimethoxysilane functionalities into the organic coating decreases the thermal stability. It is estimated that silane groups prevent crosslinking.

Crosslinking degree have important effect on chemical properties. Gel content test helps to measure the percentage of unreacted monomers and oligomers. In analysis results, high silane content reduces polymerization, so the values become low..

Solvent resistance test proves the high chemical stability of our materials against lots of solvents. The results of contact angle test also support that the silane groups make film surface more hydrophobic when compared with pure epoxy resin film. On the contrary, gloss test values show decreasing because of rough surface.

Upon increasing silane content improve hardness of cured films. Pendulum hardness and pencil hardness test prove this estimation. Most of hybrid materials have limitation point. Until this point, tensile properties show increasing with high silane content. Over this values, behaviour of materials become same, sometimes decrease. In tensile test, it can be seen the limitation point and this effect on the cured films.

REFERENCES

- [1] **Dogon, X.**, 1990: *International Technology Assessment Health Care*, **6**, 369-377.
- [2] **Peter, S.**, 1985: Posterior Composite Resin Dental Restorative Materials, *Netherlands*, 47-60.
- [3] **Kim, O., Shim, WJ.**, 2001: *Journal of Polymer Resin*, **8(1)**, 49-57.
- [4] **Salamone, JC.**, 1996: Encyclopedia of Polymeric Materials, *CRC Press, New York*, vol. **3**.
- [5] **Potter, WG.**, 1970: Epoxide Resins , *Springer, New York*.
- [6] **Nobert, M., Simone, K.**, 2004: *Int. Journal of Nanotechnology Opinion*, **1**, 1-2.
- [7] **Kickelbick, G.**, 2003: *Progress in Polymer Science*, **28**, 83-114.
- [8] **Soppera, O., Croutxe-Barghorn, C., Carre, C., Blanc, D.**, 2002: *Surf. Science*, **186**, 91-99.
- [9] **Wu, C. S., Liu, Y. L., Chiu, Y. S.**, 2002: *Polymer*, **43**, 4277-4288.
- [10] **Wang, W. J, Perng, L. H.**, 2000: *Polymer*, **41**, 6113.
- [11] **Tanaka, Y.**, 1973: Epoxy Resin: Chemistry and Technology, New York.
- [12] **Shell Development Company**, 1983: Resin Structural Reference Handbook, *Shell Development Company, Texas*.
- [13] **Gillham, J.K.**, 1986: Encyclopedia of polymer science and engineering, 2nd edition, *John Wiley New York*, pp. 519-524.
- [14] **Lee, H. Neville, K.**, 1967: *Handbook of Epoxy Resins*, New York.
- [15] **Min, B.G., Stachurski, Z. H.**, 1993: *Polymer*, **34**, 3620.
- [16] **Scherzer, N.**, 1994: *Journal of Appl. Polymer Science*, **51**, 491.
- [17] **Rezaifard, A.R., Hodd, K.A.**, 1993: Toughened Plastics I, *Advances in Chemistry Series*, **233**, 381.
- [18] **Malinovskii, M.F.**, 1965: Epoxides and their derivatives, Section II., *Israel Programme for Scientific Translation*, pp. 38-101.
- [19] **Tanaka, Y.**, 1988: Epoxy Resin, Chemistry and Technology, (to Ameron International Corporation), *C. A. MarcelDekker, NewYork*, pp. 735-742.
- [20] **Lwowski, W.** 1984: Comprehensive Heterocyclic Chemistry, **W. Pergamon Press, Oxford**, 7,pp. 1-16.
- [21] **Halton, B., Worden**, 1991: Advance in Ring Strain in Organic Chemistry, *J.Polym.Sci.*, **10**, 1-17.

- [22] **Lewars, E.G.**, 1984: *Comprehensine Heterocyclic Chemistry*, W. Pergamon Press, 7, 114-118.
- [23] **Frost, A. A., Pearson, R. G.** 196: *Kinetics and mechanism* 2nd ed., Wiley, New York, pp. 288-307.
- [24] **Sankar, G., Nasar, A.S.**, 1972 *Materials and Technology*, Petroleum and Organic Chemicals Longman, pp. 322-324.
- [25] **McAdams, L. V. And Gannon, J. A.** 1986: *Ency. Polymer Science Engineering*, Vol. 6, Wiley Interscience, pp. 222-382.
- [26] **Batzer, H. And Zahir, S. A.**, 1977: *J. Appl. Polymer Science*, 21, 1843-1857.
- [27] **Kopf, P. W.** 1988: *Enc. Polymer Science Eng.*, Wiley Interscience, 11, 45-95.
- [28] **Tess, R. W.** 1988: In *Epoxy Resins, Chemistry and Technology*, 2nd edition, ed., C. A. Marcel Dekker, pp. 735-742.
- [29] **Bellenger, V., Verdu, J., Francillette, J. And Hoarau, P.** 1986: *Polymer Communication, Journal of Polymer Science*, 27, 279-281.
- [30] **Schottner, G.**, 2001: *Hybrid Sol-Gel-Derived Polymers: Applications of Multifunctional Materials. Chem. Mater.*, 13, 3422–3435.
- [31] **Sharp, K.G.**, 1998: *Inorganic/organic hybrid materials.*, *Adv. Mater.*, 10, 1243–1248.
- [32] **Haas, K.H.**, 2000: *Hybrid inorganic-organic polymers based on organically modified Si-alkoxides.*, *Adv. Eng. Mater.*, 2, 571–582.
- [33] **Gómez-Romero, K., Cuentas G., Lira, M., Casan, N.**, 2005:, *Hybrid nanocomposite materials for energy storage and conversion applications. J. Mater. Sci.*, 40, 1423–1428.
- [34] **Godovsky, D.Y.**, 2000: *Device applications of polymernanocomposites.*, *Adv. Polym. Sci.*, 153, 163–205.
- [35] **Wright, J.D., Sommerdijk, N.**, 2000: *Sol-Gel Materials: Their Chemistry and Biological Properties*, Taylor & Francis Group, London.
- [36] **Schubert, U., Hüsing, N.**, 1995: *Hybrid Inorganic-Organic Materials by Sol-Gel Processing of Organofunctional Metal Alkoxides. Chem. Mater.*, 7, 2010–2027.
- [37] **Schottner, G.**, 2001: *Hybrid Sol-Gel-Derived Polymers: Applications of Multifunctional Materials, Chem. Mater.*, 13, 3422–3435.
- [38] **Spectrometric Identification of Organic Compounds**, 4th edition. New York: John Wiley & Sons, 1981, p. 166.
- [39] **Thermal Analysis of Polymers**, *Encyclopedia of Polymer Sceince and Technology*, 2005.
- [40] **Madorsky, S.L.**, 1964: *Thermal Decomposition of Organic Polymers*, Wiley-Interscience, New York.
- [41] **Kwok, D.Y., Neumann, A. W.**, 1999: *Contact angle measurement and contact angle interpretation, Adv. in Coll.and Interf. Sci.*, **81**, 167-249.

- [42] **Young, T.**, 1805: An Essay on the Cohesion of Fluids, *Philosophical Transactions of the Royal Society of London*, **95**, 65-87.
- [43] **Goldschmidt, A., Streitberger, H.J.**, 2003: BASF Handbook on Basics of Coating Technology, BASF Coatings AG, Münster, Germany.
- [44] **Bayramoglu, G., Kahraman, M. V., Kayaman, N., Gungor, A.**, 2006: Synthesis and characterization of UV-curable dual hybrid oligomers based on epoxy acrylate containing pendant alkoxy silane groups, *Progress in Organic Coatings*, **57**, 50-55.

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