İSTANBUL TECHNICAL UNIVERSITY « INSTITUTE OF SCIENCE AND TECHNOLOGY

MODIFICATION OF POLYCARBONATE SURFACES VIA UV CURABLE SOL GEL METHOD

M.Sc. Thesis by
Tayyibe ÖZDEMİR, B.Sc

Department : Polymer Science and Technology

Programme: Polymer Science and Technology

AUGUST 2006

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(515041027)

Date of submission : 28 July 2006

Date of defence examination: 8 August 2006

Supervisors (Chairmans): Prof. Dr. Ayşen ÖNEN

Prof.Dr. Atilla GÜNGÖR

Members of the Examining Committee Prof.Dr. Ahmet AKAR (İ.T.Ü.)

Prof.Dr. Melek TÜTER (İ.T.Ü.)

Assoc. Prof.Dr. Nilgün KIZILCAN (İ.T.Ü.)

AUGUST 2006

İSTANBUL TEKNİK ÜNİVERSİTESİ « FEN BİLİMLERİ ENSTİTÜSÜ

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YÜKSEK LİSANS TEZİ

Tayyibe ÖZDEMİR

(515041027)

Tezin Enstitüye Verildiği Tarih : 28 Temmuz 2006

Tezin Savunulduğu Tarih : 8 Ağustos 2006

Tez Danışmanları: Prof. Dr. Ayşen ÖNEN

Prof.Dr. Atilla GÜNGÖR

Diğer Jüri Üyeleri: Prof.Dr. Ahmet AKAR (İ.T.Ü.)

Prof.Dr. Melek TÜTER (İ.T.Ü.)

Doç.Dr. Nilgün KIZILCAN (İ.T.Ü.)

AĞUSTOS 2006

ACKNOWLEDGEMENT

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

I would like to thank my advisors;
To Professor Dr. Ayşen ÖNEN, sharing her knowledges and experiences with me generously, forfor her guidance, inspiration throughout this research, and for the opportunity to work in her research group, and To Professor Dr. Atilla GÜNGÖR, for his good suggestions, and support.

Special thanks go to Prof. Dr. İ.Ersin SERHATLI for her good suggestions, invaluable help, and support .

Many thanks go to my colleagues in this great research group for their assistance and friendship.

I would like to give my speacial thanks to my friend, Raşit İÇYER, for his caring, patience, help, understanding, physical and emotional support.

Finally, I would like to offer the most gratitude to my parents for their patience, understanding, moral support and encouragement during all stages in the preparation of this thesis.

August, 2006 Tayyibe ÖZDEMİR

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ABBREVIATIONS

BA	**:**	Buthyl Acrylate
BME	**:**	Benzoine Methly Ether
DBTDL	**:**	Dibuthyltindilaurate
DEAP	**:**	Diethoxyacetofenon
EA	**:**	Epoxyl Acrylate
EB	**:**	Electron Beam
FT-IR	**:**	Fourier Transformed Infrared Spectroscopy
HDDA	**:**	Hegzane Diol Di Acrylate
IPTEOS	**:**	3-isocyanatoprophyl Triethocy Silane
ISC	**:**	Intersystem Crossing
IOP	**:**	Inorganic-Organic Polymers
MM	**:**	Multifunctional Monomer
OIP	**:**	Organic-Inorganic Polymers
PI	**:**	Photoinitiator
PVB	**:**	Polyvinylbutyral
TEA	**:**	Triethylamine
TEOS	**:**	Tetraethoxysilane
TMPTA	**:**	Trimethylol Propane Triacrylate
TMOS	**:**	Tetramethoxysilane
TGA	**:**	Thermogravimetrical Analysis
UMEA	**:**	Urethane Modified Epoxy Acrylate
UV	**:**	Ultra-Violet
VOC	**:**	Volatile Organic Compound

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SYMBOLS

$\mathbf{A_0}$	**:** Original area
λ	**:** Wavelength
M	**:** Monomer
P	**:** Polymer
R	**:** Radical

MODIFICATION OF POLYCARBONATE SURFACES VIA UV CURABLE SOL GEL METHOD

SUMMARY

Environment and public health concerns have forced the coating industry to develop and produce coating products with low or zero volatile organic compound (VOC) emissions. These constraints and energy problems leaning against petroleum that occurred in 1970'; caused development is the production of curable coatings. UV curable coatings have %100 solid content, lower energy consumption, better quality skills and cause less environmental pollution. With the effect of international environment protection deals, market of these kind of coating is being increased %5-7 in each year.

Sol-gel method depends on, formation of inorganic network with hydrolysis and condensation of metal alkoxides followed by a reactionof polymerisable groups on inorganic network with thermal or high energy radiation. Compared with polymer coatings, the hybrid sol-gel films also manifest some advantages such as low optical propagation loss, high chemical and mechanical stabilities as well as good compability with different surfaces to be coated. Besides that hybrid materials have low water absorption and vapor permeability.

In this study, UV curable urethane modified epoxy acrylate oligomer (UMEA) will be synthesized. Formulations that containing UMEA which was modified in different ratio, acrylate and photoinitiator will be prepared. These samples will be cured under UV light.By coating this formulation on polycarbonate, it's surface properties will be improved against external effects.

POLİKARBONAT YÜZEYLERİN UV IŞINLARIYLA SERTLEŞTİRİLEN SOL JEL METODU İLE MODİFİKASYONU

ÖZET

Çevre ve halk sağlığı kuruluşları, kaplama endüstrisinde çok düşük ya da sıfır uçucu organik emisyona sahip kaplama ürünleri geliştirmeleri ve üretmeleri konusunda büyük baskılar uygulamaktadır. Bu baskılar ve 1970'ler de ortaya çıkan petrole dayalı enerji sorunlarının etkisiyle farklı boyut kazanmış ve kaplama endüstrisinde yeni tekniklerin geliştirilmesine neden olmuştur. Bu gelişmelerden en önemlisi şüphesiz ki UV ışınları ile sertleşebilen kaplamaların üretilmesidir. UV ışınları ile sertleşebilen kaplamalar %100 katı içeriğine sahip, daha düşük enerji tüketimine neden olan, daha kaliteli ve en önemlisi çevre dostu kaplamalardır. Bu tür kaplamaların Pazar payı uluslararası çevre korunması antlaşmalarının da etkisi ile her yıl %5-7 oranında artmaktadır.

Sol-jel yöntemi, metal-alkoksitlerin hidroliz ve kondenzasyonu ile bir inorganik ağ oluşturulması, ardından inorganik bağın bağlı olduğu polimerize olabilen grupların termal ya da yüksek enerjili ışıma yardımıyla reaksiyon vermesine dayanır. Organik polimer kaplamalarla kıyaslandığında, hibrit sol-jel filmleri yüksek kimyasal ve mekanik dayanıklılık, yüksek optik özellikler, farklı kaplama yüzeylerine karşı daha iyi uyumluluk gösterirler. Bunların dışında hibrit malzemeler düşük su absorbsiyonu ve su buharı geçirgenliğine de sahiptirler.

Bu çalışmada, UV-ışınları ile sertleşebilen üretan modifiye epoksi akrilat (UMEA) oligomeri sentezlenecektir. Farklı modifikasyon derecesine sahip UMEA oligomeri, akrilat ve foto başlatıcı ile formülasyonlar hazırlanacaktır. Hazırlanan formülasyon polikarbonat yüzeyler üzerine kaplanarak UV lamba altında sertleştirilecektir. Polikarbonatın yüzey özelliklerinin dış etkilere karşı iyileştirilmesi sağlanacaktır.

1. INTRODUCTION

UV-curable coating applications have gained wide interest, due to their advantages such as lower energy consumption, less environmental pollution, lower process costs, high chemical stability and very rapid curing even at ambient temperatures [1-3]. In the field of UV curing industries, epoxy and epoxy acrylate derivatives have been widely used as coatings, structural adhesives and advanced composite matrices [4]. What distinguishes epoxy resins from the other polymers is their excellent chemical and solvent resistance, good thermal and adhesion properties, versatility in cross-linking. On the other hand, UV-curable 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 [5].

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.

Sol-gel method depends on, formation of inorganic network with hydrolysis and condensation of metal alkoxides followed by a reaction of polymerization groups on inorganic network with thermal or high energy radiation.

UV-curable hybrid coatings represent a major class of hybrid materials. This kind of formulations consist of one or more than one photosensitive organic groups, usually unsaturated C=C bonds, which can be polymerized under UV radiation. The organic oligomer can be functionalized with pending functional groups forming a second network [6].

This thesis deals with preparation of novel bifunctional resin prepared by the reaction between UV-curable epoxy acrylate oligomers and 3-isocyanatopropyltriethoxysilane (IPTEOS). The hybrid networks are characterized by analysis of various properties such as hardness, gloss, adhesion test and stress-strain test. The thermal behavior of coatings is also evaluated.

2. THEORETICAL PART

2.1 Photopolymerization

Photopolymerization is defined as the reaction of monomers or reactive oligomers to produce polymeric structures by light-induced initiation (excitation of a photoinitiator) and subsequent polymerization. Fundamental research and practical applications of photopolymerization have evolved significantly over the past few decades leading to a better understanding of the mechanisms of the reaction and to numerous industrial applications [7]. This technology is now commonly utilised to perform the ultrafast drying of protective coatings, varnishes, printing inks and adhesives, and to produce the high-definition images required in the manufacture of microcircuits and printing plates. Highly crosslinked polymers are readily synthesised by photoinitiated polymerisation of reactive telechelic oligomers [8].

UV-radiation curing has become a well-accepted technology which has found a large variety of industrial applications because of its distinct advantages. Lightinduced polymerization of multifunctional monomers is indeed a powerful method to achieve, selectively in the illuminated areas, a quasi-instantaneous transformation of a liquid resin into a solid polymer [9].

Radiation technology is widely applied in industrial fields as an important polymerization or cross-linking process [10]. Radiation curing is a production technique of fast transformation of specially formulated liquids into solids by electromagnetic wave irradiation. It has been an important technique in the coating, adhesives, and ink industry. Even though the main driving force for using radiation curing is environmental protection, the radiation process has benefits in productivity, quality and manufacturing cost, etc. over the thermal processes. Primary radiation sources are infrared, microwave, radio frequency, UV, and electron-beam. The first three initiate thermal curing, whereas the last two initiate via electronic excitation and ionization. UV and electron beam are most commonly employed due to their fast and high curing abilities [7].

The light-induced polymerization of liquid multifunctional monomers and oligomers is one of the most efficient methods to produce quasi- instantly highly crosslinked polymer networks at ambient temperature [11]. Highly crosslinked polymers have been produced within few seconds by photoinitiated polymerization of multifunctional acrylic monomers and oligomers.

Photopolymerization requires three essential elements:

- Electromagnetic radiation (*hv)*.
- Chromophore group containing photoinitiators
- Monomer/Oligomers with unsaturated moieties i.e. styrene, acrylate

Besides its great speed, this technology (radiation curing) offers a number of advantages, such as solvent-free formulation, low energy consumption, ambient temperature operations and tailor-made properties of the photopolymer [12].

2.1.1 Absorption of Light

For a system to be sensitive to light it must be able to absorb it and then use it to generate species which will either initiate polymerization or undergo a crosslinking reaction. The role of the photoinitiator (A) is to generate reactive species that will initiate polymerization whereas a photosensitier (D) is a compound, which will energise a species that will in turn lead to the production of reactive species as shown in Figure 2.1.

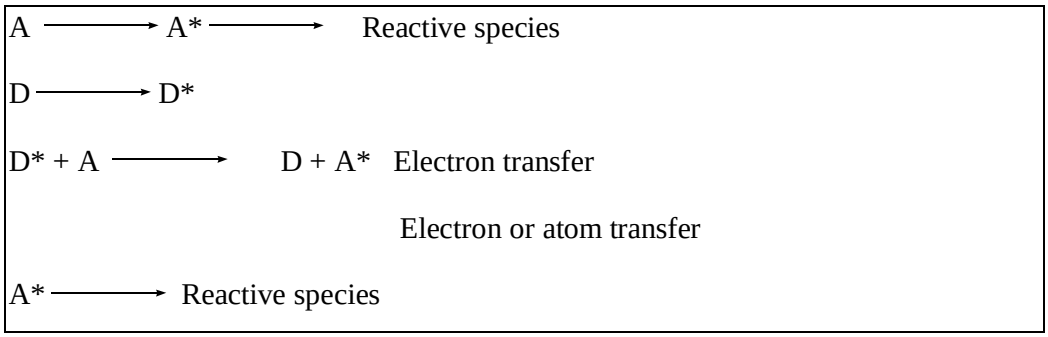


Figure 2.1: Generation of Reactive Species

In crsslinking reactions (which change the physical properties of the polymer) a photo active group (P) is energised by absorption of light and then undergoes reaction of new bonds. Such system can also in many cases be sensitised by energy transfer (either singlet or triplet energy transfer depending on the system being used).

In this process, the sensitier D absorbs the radiation thereby populating an excited state which can hand on its energy to the species P in a process that generates the desired excited state of P as shown in Figure 2.2

$$P \longrightarrow P^* \longrightarrow P\text{-}P \text{ New bond formed}$$

$$D \longrightarrow D^*$$

$$D^* + P \longrightarrow P^* + D \text{ Energy transfer}$$

$$P^* + P \longrightarrow P\text{-}P$$

Figure 2.2: Generation of Excited State of P

The absorption of light by a molecule is determined by the types of bonding which link the various atoms together. When a photon is absorbed, the energy is used to promote an electron from either a bonding molecular or non-bonding molecular orbital to an antibonding orbital. As a consequence, UV visible absorption spectroscopy is often referred to as electronic absorption spectroscopy. For the commonly used initiators, photosensitisers and photosensitive groups encountered in radiation curing, bonding molecular orbitals are usually π-orbitals and non bonding n-orbitals. Usually, electrons from these orbitals are promoted into a π* antibonding orbital. Consider the carbonyl group. As shown in Figure 2.3 it possesses both π and n-bonding orbitals.

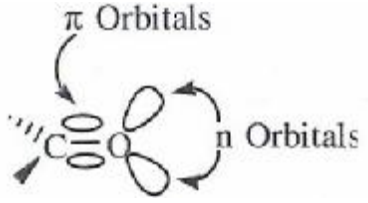


Figure 2.3: The n and π Bonding Orbitals Present in Carbonyl Group

Absorption of light may lead to the promotion of an electron from the π or n-bonding orbital. For absorbtion of a photon to occur its energy must match exactly the energy required to bring about the electronic transition i.e. it is a quantized process.

The electronic absorption spectrum of a typical ketone, e.g. benzophenone in solution reveals the presence of two types of transition (Figure 2.4).

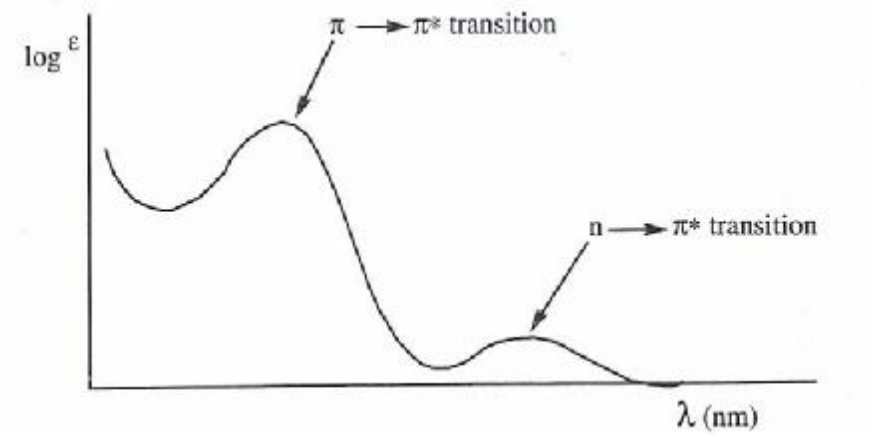


Figure 2.4: Absorption Spectrum of Benzophenone

The absorption of a photon is so rapid that spin is conserved and consequently an exited singlet state is produced. Due to magnetic interactions between the electrons in the half-occupied orbitals and the nucleus, spin inversion may occur and a triplet state be produced (Figure 2.5)

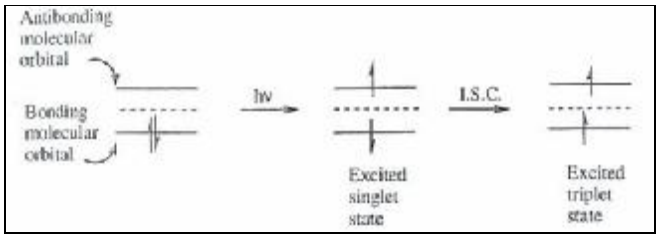


Figure 2.5: Diagrammatic picture showing how excited singlet and triplet states are produced

The process of spin inversion is termed intersystem crossing (ISC) and is usually relative to the process of absorption, slow (~10^{-9} secs). For the triplet state to relax back to the ground state, spin inversion must occur and since this is slow, triplet states often have long lifetimes (10^{-8}-10^{-3}secs). Excited singlet states relax to the ground state by a process not involving spin inversion (termed internel conversation) as a consequence, they have relatively short lifetimes (10^{-12}-10^{-9}secs). When two transitions are present in a molecule a photon may be absorbed leading to the population of the higher energy transition. Normally this excited singlet state which may then undergo intersystem crossing etc. We can summarise all these processes by means of a Jablonski diagram (Figure 2.6).

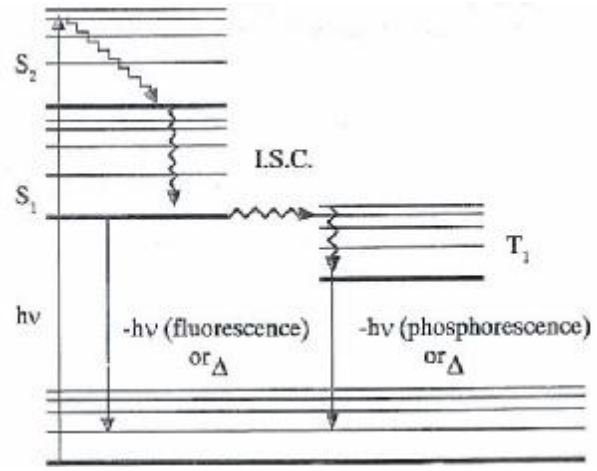


Figure 2.6: Jablonski Diagram

In this case of benzophenone, S_2 would be populated via $\pi \longrightarrow \pi^*$ transition and S_1 via an $n \longrightarrow \pi^*$ transition. From Figures 3 and 4 it can be seen that absorption of the radiation at 254nm will populate and S_2 state energy loss will occur leading to the population of S_1 and T_1 states and as a consequence, not all the absorbed radiation is available for the photochemical reaction. Nevertheless absorption of the light at these shorter wavelengths is particularly usefull in improving cure at the coating-air interface

Mentioned has been made that it is normal for triplet states to have longer lifetime than excited singlet states. A consiquance of triplet states having a long lifetime is that they are more likely to undergo bimolecular reactions than the shorter lived excited singlet states. The rate of a bimolecular reaction between an excited state A* and a ground state molecule M is dependent upon the lifetime of A*, the concentration of M, the rate constant for the process and the viscosity of the medium; thus high rates are favoured by A* having a longer lifetime, M being present at high concentration and the medium having a low viscosity. If the reaction of A* with M leads to initiating radicals (a Type II photoinitiator system) derived from M, the efficiency of the process will decrease as a photoinitiated polymerization process proceeds since the viscosity of the reaction mixture increase as reaction progresses. Previously, when sensitisation was being discussed, it was noted that the energy transfer process is a bimolecular process and hence the efficiency of sensitisation is also dependent upon the viscosity of the medium and it will decrease as cure

progresses. Energy transfer can also lead to energy wastage. In radiation curing many Type II initiators have relatively long lifetimes. [13]

2.2 Radiation Curing

The transformation of a reactive liquid into a solid by radiation, leading to polymerization and into in most cases also to crosslinking is termed curing. Infrared, microwave and radio frequency radiation initiates thermal curing, whereas ultraviolet (UV) and electron beam (EB) irradiation via electronic excitation and ionisation lead to non- thermal. *UV (EB) radiation curing defined as: the fast transformation of 100% reactive, specially formulated liquids into solids by UV photons or ele*trons.

This simple defination refers to the well-known fact that organic molecules become electronically excited after energy absoption. Energies between 2 and 8 eV are typically needed to transform organic molecules from the ground to an excited state. The excited molecules are able to undergo chemical reactions which may lead to chemically reactive products, which initiate the fast formation of liquid into a solid.

On the coating market radiation-curables are competing not only with solvent based systems but also with high solids, water-based and powder coatings. In all coating application radiation-curables have the lowest market share but the highest growth rate. [14]

2.2.1 UV Curing

The simplest type of UV curing formulations for producing a clear surface coating will contain the following ingredients

- Photoinitiator: 1-15 % w/w
- Reactive diluent (mono and multifunctional monomer: ~55% w/w
- Prepolymer (oligomer or binder): ~30% w/w

UV curing is typically a process that transforms reactive diluent and mono and multifunctional oligomers into a crosslinked polymer by a chain reaction initiated by reactive species (free radicals or ions), which are generated by UV irradiation. Most monomers do not produce initiating species with sufficiently high yields when they are exposed to UV light, so that a photoinitiator must be added to the formulation.

Once initiated, the chain reaction will develop very much like in a conventional thermal polymerisation, except for the much larger rates of initiation that can be reached by intense illumination.

The overall process is represented schematically in Figure 2.7.

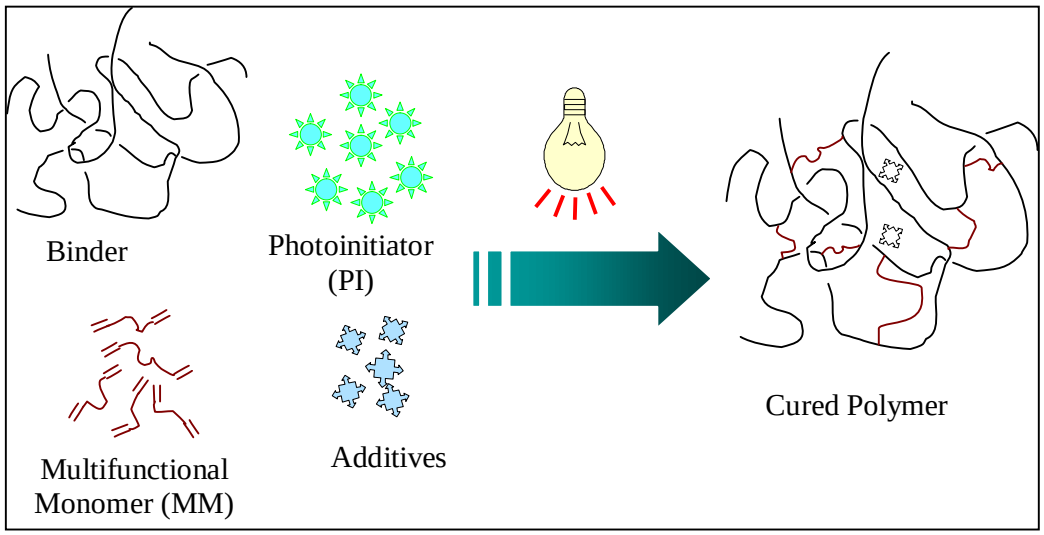


Figure 2.7: Compenents of UV Curable Resins

2.2.1.1 Photoinitiators

Conveniently, initiators are classed by the type the of polymerization system they initiate i.e. free radical, cationic or anionic. Widely two classes of photoinitiators are used in UV free radical curing; those that undergo unimolecular bond cleavage and those that undergo bimolecular hydrogen abstraction from some other molecule [15]. Figure 2.8 shows those two type initiation processes.

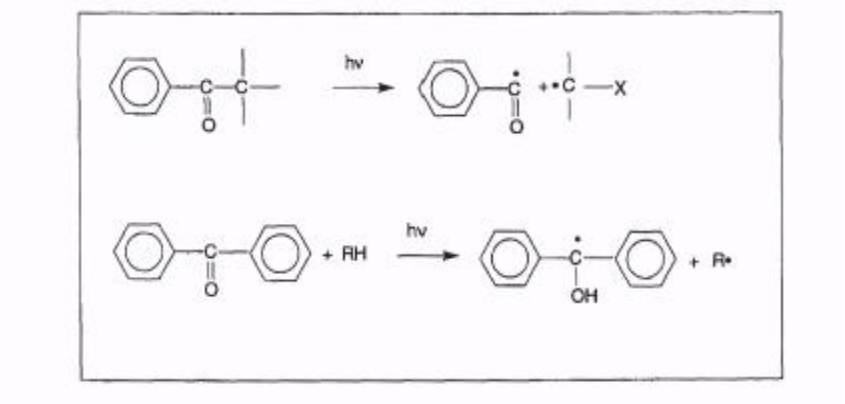


Figure 2.8: Two Types of Photoinitiation

Free radical initiators have been subdivided into Norrish Type I and Type II reaction.

Type I Initiator

Type I initiators or those compounds which upon irradiation undergo a cleavage reaction to generate two radicals.

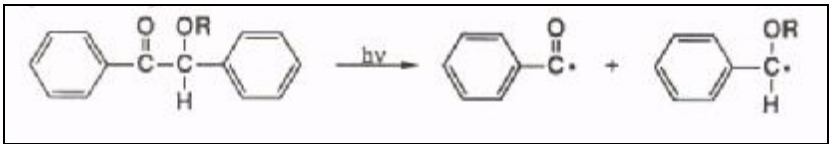


Figure 2.9: An example of Type I (bond cleavage) Photoinitiation

The cleavage reaction generates two radical species and usually (although not always) only one of these is reactive. In general, reaction occurs from the excited triplet state of the ketone. The cleavage reaction is often so facile that it occurs very rapidly and consequently it is the cleavage reaction, which determines the triplet lifetimes and as a consequence the cleavage reaction does not suffer from oxygen quenching.

Benzoine, benzoine ethers, hydroxyphenylketones and acylphosphineoxides were one of the earliest Type I systems to be used in radiation curing.Benzoyl radical will initiate the polymerization of acrylates, methacrylates, styrene etc and in many cases rate constants are available. The considerable debate as to whether or not the-sobstituted benzyl radical is an initiator. It seems to be a relatively unreactive radical and this feature means that its most likely role in the curing of acrylates etc. is as a chain terminator. [13]

Type II Initiator

Type II initiator systems are based on compounds which when excited ultimately lead to atom or electron abstraction from a suitable donor molecule thereby producing a carbon centred radical which acts as the initiating for the polymerization.[13]

Thioxanthones, such as 2-isopropylthioxanthone, are used when their high absorption in the very near UV is desirable to permit absorption in the presence of pigments or dyes that absorb UV strongly in the shorter UV range. Widely used hydrogen donors are tertiary amines with hydrogens on carbon atoms.

2.2.1.2 Reactive Diluents

The monomers range from mono to multi functional, most commonly mixtures of mono-, di-, and trifunctional acrylates. The monomers are also called reactive diluents. Multifunctional oligomer contributes to high rate of cross-linking, owing to its polyfunctionality and in large measure, controls the properties of the final coating due to the effect of the backbone structure on such properties as abrasion resistance, flexibility, and adhesion. Their viscosity is too high alone and monomers are required to reduce viscosity for application. Multifunctional acrylate monomers also give fast cross-linking owing to polyfunctionality, but have lower viscosities than an oligomer. Viscosity is lowered further by monofunctional acrylates, but the rate of cross-linking is reduced. The extent conversion of the double bonds is also affected by the choice of components; in general terms, extent conversion increases with an increase in monofunctional monomer, presumably because the small monomer molecules can diffuse through the film during the reaction. Various type of multifunctional acrylate monomers have been used; examples are trimethylol-propane triacrylate, pentaerythritol triacrylate, 1,6-hexanediol diacrylate, and tripropyleneglycol diacrylate [15]. Care must be taken in handling them because many are skin irritants and some are sensitizers.A range of monofunctional acrylates have been used. Those with lowest molecular weight tend to reduce viscosity most effectively, but may be too volatile.

2.2.1.3 Prepolymer (oligomer or binder)

Binder or resins are essense relatively low molecular weight polymers of synthetic or naturally occuring materials. They are conventionally used in surface coatings and inks to give the final coating film its desired end use properties and appearance. Radiation curable oligomers or prepolymers are generally much lower in molecular weight that conventional resins. They normally consist of one, or at most, a few repeat units. Upon interaction with indicient radiation they can be combined (“polymerized”) to give a higher molecular weight structure and this is usually crosslinked. The terms, “oligomer” and “prepolymer”, are often used interchangeably in the radiation curable coatings and inks industry, and are considered as being distict from “monomers”.

A general property of prepolymers is that they are typically viscous liquids, frequently too high viscosity for direct application as films. Thus viscosity control becomes a major concern to the formulator of coatings of inks. In most cases, low viscosity monomers or reactive diluents are used to reduce the viscosity of radiation curable formulations.

The rapid growth of radiation curable ink and coatings industries can largely be attributed to the commercial availability of a large variety of acrylated (or methacrylated) prepolymers or oligomers. These provide the basic film forming properties of the cured material. Commercial raw material suppliers have incorporated acrylate functionality into a variety of backbone structures, from a broad range of different basic raw materials. Thus, classes of available oligomers include epoxy acrylates, acrylated oils, urethane acrylates, polyester acrylates, acrylic acrylates and speciality products, such as acrylated silicone oils and acrylated amines. Another type includes unsaturated polyesters, which is contain internal carbon-carbon double bonds. Other free radical non-acrylate systems (such as polyene/thiols) involve different chemistry. [16]

Epoxy Acrylate

Epoxy acrylates are widely used 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.

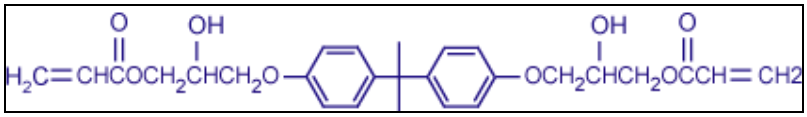


Figure 2.10: Bisphenol A Epoxide with Acrylic Acid.

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.

Arcrylated 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 [17].

Urethane acrylate

Urethane acrylates are produced by reacting polyisocyanates with hydroxyl alky acrylates, usually along with hydroxyl compounds, to produce the desired set of properties. Urethane acrylates are the most expensive of the acrylates. There are many different types of urethane acrylate oligomers having variations in the following parameters.

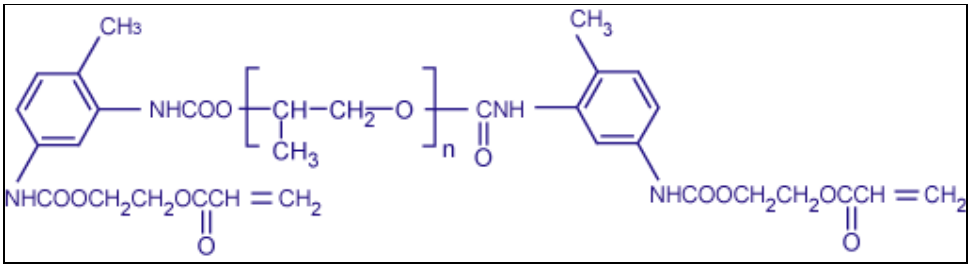


Figure 2.11: Typical Urethane Acrylate Oligomer

Functionality - Varies from one to six. Lower functionality results in lower reactivity, better flexibility, and lower viscosity. Monofunctional urethane acrylates are low viscosity, specialty products used to improve adhesion to difficult substrates and to improve flexibility. High functionality products (4 and higher) have niche applications as well. They are used to improve reactivity, scratch resistance, chemical resistance, and other physical properties. Because of their high viscosity, they are generally blended with other resins.

Isocyanate - Four types of isocyanates are used for urethane acrylates. Monoisocyanates are used for monofunctional acrylates only. Diisocyanates are the most widely used and can be divided into aliphatic diisocyanates and aromatic diisocyanates. The incorporation of an aromatic diisocyanate makes the resulting coating harder and abrasion resistant. The higher cost aliphatic diisocyanates are slightly more flexible. However, they are non-yellowing. Aliphatic urethane acrylates are used for topcoats, optical fibers, flexible packaging, etc. Polymeric isocyanates are used for higher functionality urethane acrylates.

Polyol - The polyol is the backbone of the urethane acrylate. They are essentially polyether or polyester with functionality ranging from two to four. Polyether urethane acrylates are generally more flexible, provide lower cost, and have slightly lower viscosity. Polyester urethane acrylates have less hydrolytic stability but are non-yellowing [17].

Polyester Acrylate

The wide choice of polyester acrylates available enables a broad range of demands on the coating to be met. They are generally low viscosity resins that require no reactive diluents. Polyester acrylates provide performance properties between those

of urethane acrylates and epoxy acrylates. A disadvantage of some types of polyester acrylate is their irritancy. This is particularly true for low molecular weight, highly reactive resins.

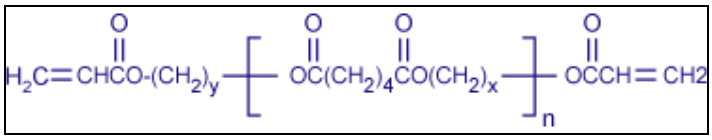


Figure 2.12: Reaction product of acrylic acid with dibasic acid/aliphatic diol-based polyester

Polyester acrylates vary in functionality, chemical backbone and molecular weight. The influence of the functionality is similar to that for the urethane acrylates. The chemical backbone has a large influence on properties such as reactivity, color stability, hardness, reactivity, etc. Typically, the higher the molecular weight, the higher the flexibility and viscosity and the lower the reactivity [17].

Advantages and disadvantages of prepolymers were compared at Table 2.1

Table 2.1: Advantages and Disadvantages of Prepolymers

Type	Advantages	Disadvantages
Epoxy-Acrylate	§ good cure properties § good chemical resistance § excellent adhesion	§ high viscosity § poor weatherability
Urethane-Acrylate	§ good cure properties § flexible and curable § good chemical resistance § balanced properties	§ relativley expensive § high viscosity
Polyester-Acrylate	§ cheap § balanced properties	§ low chemical resistance

There are two major classes of UV-curable systems, which differ basically by their polymerisation mechanism:

- Photoinitiated cationic polymerisation of multifunctional epoxides and vinyl ethers.
- Photoinitiated free radical polymerisation of multifunctional monomers, mainly acrylates or unsaturated polyesters.

Cationic Initiated UV Curing

In cationic UV cure coatings strong acids are photogenerated to initiate chain growth polymerization. When the idea of using cationic polymerization for crosslinking coatings is mentionedit has been thought of infeasible. It is thought that cationic polymerization being carried out at very low temperatures in the rigid absence of water to achieve high molecular weight. However, in coatings the objective is not to make high molecular weight linear polymers, but to crosslink polyfunctional reactants. The reactions that terminate cationic polymerizations still give crosslinks. Therefore cationic polymerization can be carried out in coating films even in the presence of water.

Cationic photoinitiators are onium salts of very strong acids. Iodonium and sulphonium salts of hexafluoroantimonic and hexafluorophosphoric acids are examples. Homopolymerization of oxirane groups is the major type of cationic polymerization used commercially. Epoxy resins are commercially widely used in cationic photoinitiated UV curing.

Free Radical Initiated UV Curing

In these coatings, free radicals are photogenerated and initiate polymerization by adding to vinyl double bonds, primarily acrylates. Those free radical generators are photoinitiators.

Free radicals are readily produced upon UV irradiation of aromatic carbonyl compounds, either by homolytic cleavage of C-C bonds, or by hydrogen abstraction from a hydrogen donor molecule [7]. Figure 2.13 shows the comparison of Radical and cationic UV cure systems.

Radical	Cationic
wide variety of raw materials	more limited raw materials
inhibited by oxygen	not inhibited by oxygen
not inhibited by high humidity	inhibited by high humidity
not inhibited by basic materials	inhibited by basic materials
full cure in seconds	full cure in hours
adhesion - less	adhesion - greater
shrinkage - greater	shrinkage - less
depth of cure - greater	depth of cure - less
initiator for EB cure - no	initiator for EB cure - yes

Figure 2.13: Comparison of Radical and Cationic UV Cure Systems [18]

2.3 Sol-Gel Chemistry And Technology

A process that has, in the past years, gained much notorirty in the glass and ceramic fields is the sol-gel reaction. This chemistry produces a variety of inorganic networks from silicon or metal alkoxide monomer precursors. Although first discovered in the late 1800s and extensively stuided since the early 1930s, a renewed interest surfaced in the early 1970s when monolithic inorganic gels were formed at low temperatures and converted to glasses without a high temperature melting process. Through this process, homogeneuos inorganic oxide materials with desirable properties of hardness, optical transparency, chemical durabilty, tailored porsity, and thermal resistance, can be produced at room tempratures, as opposed to the much higher melting tempratures required in the production of conventional inorganic glasses [19]. The specific uses of these sol-gel produced glasses and ceramics are devided from the various material shapes generated in the gel state, i.e., monoliths, films, fibers and monosized powders [20]. Many specific applications include optics, protective and porous films, optical coatings, window insulators, dielectric and electronic coatings, high temperature superconductors, reinforcement fibers, fillers and catalyst.

The sol-gel process, as the name implies, involves the evolation of inorganic networks through the formtion of a colloidal suspension (sol) and gelation of the sol

from a network in a continuous liquid phase (gel). The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. Metal alkoxides are most popular because they react readily with water. The most widely used metal alkolxides are the alkolxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). However, other alkoxides such as aluminates, titanates, and borates are also commonly used the sol-gel process, often mixed with TEOS.

At the functional group level, three reactions are generally used to describe the sol-gel process: hydrolysis, alcohol condensation, and water condensation. This general reaction schme can be seen in Figure 2.14.

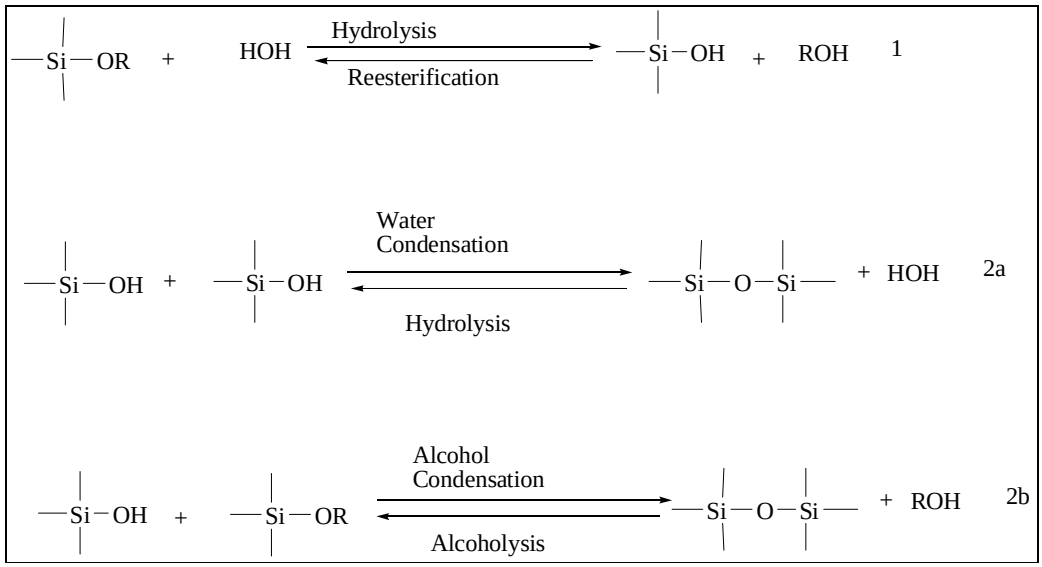


Figure 2.14: Sol-gel reaction schemes

Generally speaking, the hydrolysis reaction (2a), through the addition of water, replaces alkoxide groups (OR) with hydroxyl groups (OH). Subsequent condensation reactions (2a and 2b) involving the silanol groups (Si-OH) produce silaxane bonds (Si-O-Si) plus by-product water or alcohol. Under most conditions, condensation commences before hydrolysis is complete. However, conditions such as, pH, H_2O /Si molar ratio (R), and catalyst can force completion of hydrolysis before condensation begins. Additionally, because water and alkoxides are immissible, a mutual solvent such as an alcohol is ulilized. With the presence of this homogenizing agent, alcohol, hydrolysis is facilitated due to the miscibility of the alkoxide and water. As the number of siloxane bonds increases, the individual molecules are bridged and jointly aggregate in the sol. When the sol particles aggregate, or inter-knit into a network, a

gel is formed. Upon drying, trapped volatiles (water, alcohol, ate.) are given off and the network shrinks as further condensation can occur. It should be emphasized, however, that the addition of solvents and certain reaction conditions may promote esterification and depolymerization reactions according to the reverse in Figure 2.14

However, the characteristics and properties of a particular sol-gel inorgnic network are related to number of factors that affect the rate of hydrolysis and condensation reactions, such as, pH, temperatures and time of rection, reagent concentrations, catalyst nature and concentration, H_20/Si molar ratio (R), aging temperature and time, and drying. Of the factors listed, above, pH, nature and concentration of catalyst, H_20/Si molar ratio (R), and temperature have been identified as most important. Thus, by controlling these factors, it is possible to vary the structures and properties of the sol-gel derived inorganic network over wide ranges.

2.4 Hybrid Inorganic/Organic Polymers

Combining inorganic and organic structures on a molecular scale to form composites of polymer or glasslike materials is a challenging task due to very different formation reactions inorganic and organic networks. So for example the classical glass and ceramic processing at high temperatures does not allow to incorporate organic structures due to their limited thermal stability. However by using soft chemical processes in solution this was made possible in the last 20-30 years and huge variety of hybrid material compositions have emerged in the mean time [21]. According to Allcock for polymerized basically two types of hybrids can be distinguished:

Inorganic-organic polymers (IOP): They have inorganic elements in the main chain/network (example inorganic glasses) and may also have organic side groups. When organic groups are reactive, additional organic crosslinking/polymerization is possible. If classical sol-gel processing [22] of modified metal alkoxides is followed by organic polymerization or crosslinking the resulting hybrid materials are called ORMOCER®s.

Organic-inorganic polymers (OIP): These materials have C- atoms in the main chain/network and may contain inorganic elements in side groups connected to the organic network. Here also additional inorganic crosslinking is possible. Examples

for these polymers are based f.e on silylated organic oligomers/polymers, the organic network is previously formed in the precursor molecule.

Both IOP and OIP are examples of hybrid polymers. The idea of both of these concepts is to obtain a synergistic effect between inorganic and organic phases, not achievable otherwise by physical mixing of macroscopic phases as is usually made in classical composites. Since the structural units used for the controlled formation of hybrid polymers are in the range of some nm up to maybe 10 nm [23] they can be called nonascalled or even moleculer composites. There are other types of hybrid polymers with weak bonds (van-der-Waals, hydrogen bonds) between inorganic and organic phases, which are described [24].

2.4.1 Structural Units, Precursors and Processing of Hybrid Materials

Hybrid polymers can be composed of structural units which span the whole range of more inorganic glass like up to compositions with a high concent of organic networks similar to carbon based polymers as can be seen in Figure 2.15. All structural units are connected via strong covalent bonds. The building principle of these hybrid polymers is based on different types of precursor molecules. These precursors can be classified by their network forming or modifying roles [25]. Various polymerization, polycondensation or crosslinking reactions are possible. Basically four different types of precursors can be used for the synthesis of hybrid polymers.

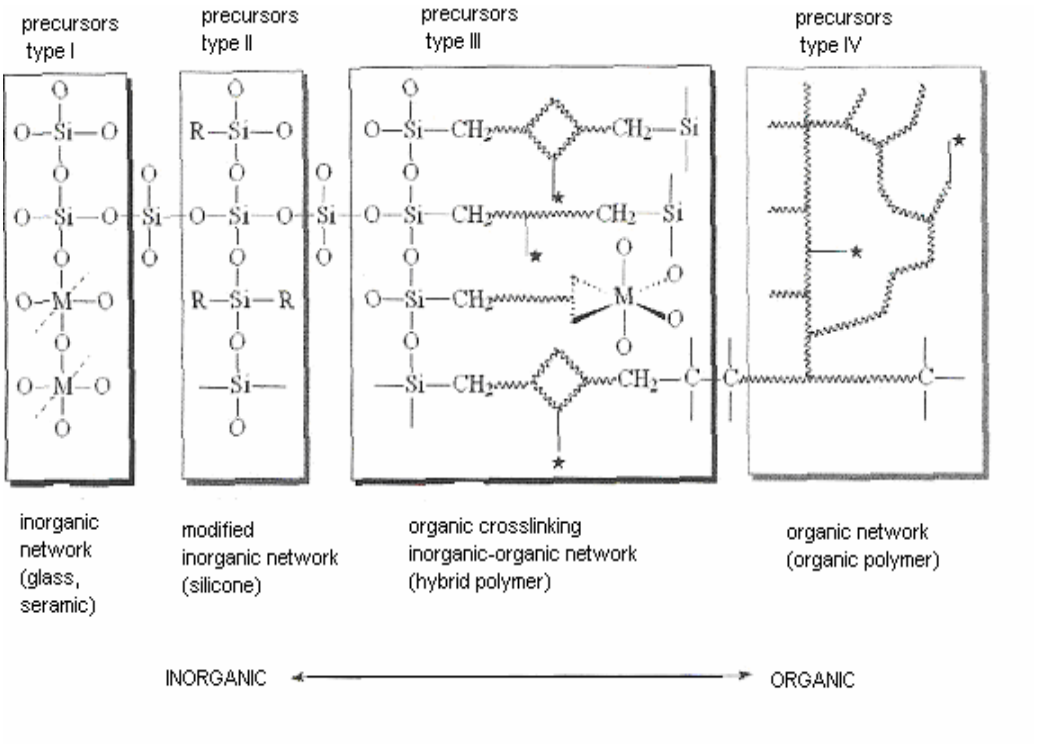


Figure 2.15: Structural Units of Hybrid Inorganic-Organic Polymers (ORMOCER®s, Ceramers) and Precursor Types Used for Preparation (*: additional functional groups).

Type 1: inorganic network formers, alkoxides of Si (Tetramethoxysilane TMOS, Tetraethoxysilane TEOS), Al (Al-tri-sec-butylate), Ti (Ti-isopropylate), Zr (Zr-butylate), etc.

Type 2: inorganic network formers with organic non-reactive modification. Due to the hydrolytic stability of the Si-C bond a wide variety of organic groups are available for the modification of the inorganic networks.

Type 3: forming inorganic network with reactive organic modification for crosslinking/polymerization reactions or organic monomers/polymers with silylated end groups for crosslinking/condensation via inorganic Si-O-Si bonds. These precursors are key elements for hybrid polymers.

Type 4: organic monomers which can react via chemical crosslinking or polymerization reactions with the modified metal alkoxides.

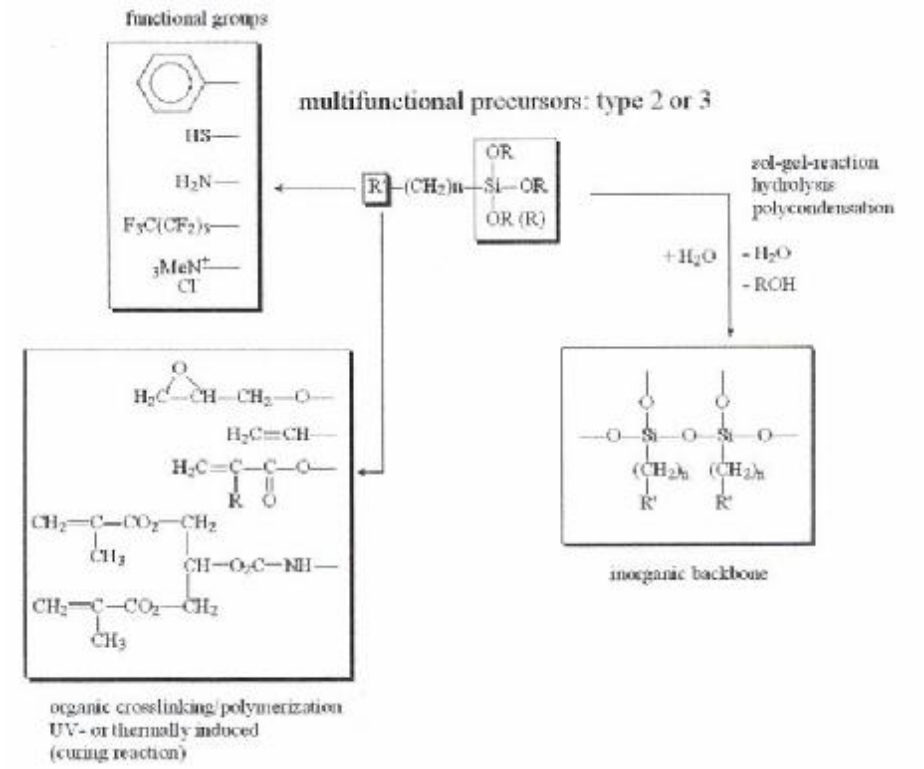


Figure 2.16: Multifunctional Precursors (Type 2 or 3) for ORMOCER® Synthesis

Figure 2.16 Shows examples for type 2 and 3 precursors. These precursors are multifunctional molecules in more than one reactive site and they have more than one type of reactive site (inorganic and organic).

The formation of the inorganic silica type or more general metal oxide network follows the classical sol-gel-route [22]. The reaction step in case of Si alkoxides $Si(OR)_4$ (R: Methyl, Ethyl, Propyl) are as follows:

Hydrolysis:

$$\equiv Si-OR + H_2O \longrightarrow \equiv Si-OH + ROH \qquad (2.1)$$

Polycondensation:

$$\equiv Si-OH + HO-Si\equiv \longrightarrow \equiv Si-O-Si\equiv + H_2O$$

$$\equiv Si-OH + OR-Si\equiv \longrightarrow \equiv Si-O-Si\equiv + ROH \qquad (2.2)$$

Condensation with other metal alkoxides (Ti, Al, Zr) is possible at this stage. Due to varying reaction rates of hydrolysis as given in equation 2.1 and polycondensation of

different alkoxides, as given in equation in 2.2, care has to be taken that true cocondensation takes place leading to homogeneous materials

Due to varying reaction rates of hydrolysis and polycondensation of different alkoxides care has to be taken that true cocondensation takes place leading to homogeneous materials. For the synthesis of ORMOCER®s this is the first processing step followed by organic crosslinking or polymerization. The thermel crosslinking of the organic groups is done at the temperatures between 80 and 180^{o}C or via UV-induced reactions. If OH-functionalized polymers like vinyalcohol/styene copolymers (molecular weight around 1200 g/Mol) or polyvinylbutyral-PVB (molecular weight 60000 g/Mol) are used around 10-20% of all available OH-groups are silylated (f.e by the reaction of isocyanatosilane with the OH-functions) prior to the sol-gel reaction step. In this case mainly water based dispersions of the hybrid polymers can be achieved, which are self-curing systems without the need for additional thermal energy. By condensation with acrylate group containing silanes UV-curable systems can also be synthesized. The remaining OH-groups of the hybrid polymer play an important role due to their polar nature in order to generate stable water based systems. These systems can be used as specially pigmented coatings for facades. Other interesting compositions can be synthesized using silylated polyaniline in order to incorporate electronic conductivity into the composite [26].

2.4.2 Advantages of Hybrid Materials

- Good adhesion to various glass surfaces
- Unlimited color palette
- Easy reproducibility of the colors
- Finishing by conventional wet painting procedures
- Low curing temperatures (< 200 °C)
- Economical even for smaller batches
- Toxicologically safe
- Additional decorative effects possible (color gradients, partial coloration)
- Chemical resistance against various media

- High productivity
- Enegy saving
- Partly solvent-free processing [27]

2.5 Tests on Coated Plates

2.5.1 Pendulum Hardness

There are two methos which can be used to assess pendulum hardness, namely Konig and persoz, but as the former is widely used it will serve to illustrate to technique.

The Koning pendulum suspension points rest on a small arae of samples. The time taken for the angular amplitutide of oscillations to decrease from 6^0 to 3^0 from the vertical is recorded and used as a measure of hardness that is the longer the dampening takes the harder the material. Adjustments can be made to time taken by altering the position of the weight on a threaded rod. In this way the instruments can be calibrated so that the time taken when the substate is a glass plate is 250 seconds. Possible errors caused by draughts are eliminated by enclosing the pendulum in a case, which can also allow the humidity to be controlled. The release mechanisms which lower the pendulum onto the sample are operated from outside the case. Most quoted results are mean of a number of measuremets taken at various places over the surface. The small area sampled allows adventitious surface deflects to be avoided but necessitates measurements over other areas to enable representative results to be obtained

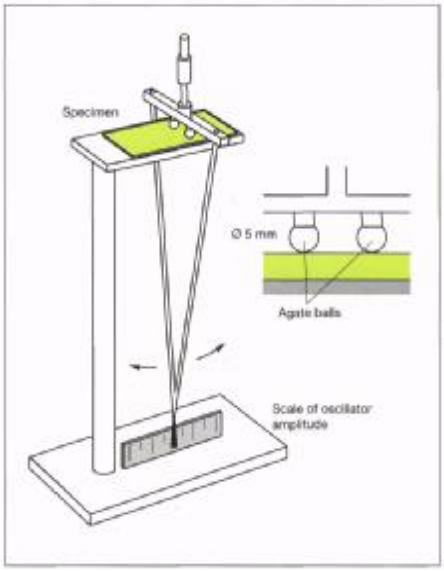


Figure 2.17: König pendulum hardness tester [28]

2.5.2 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 illumineted 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 realiable procedure with samples manifesting different gloss to also set various angles of incicidence and reflection for the measuring beam. Owing to the higher proportion of reclection light with larger angles of incidence matt surfaces are measured with a large angle of incoming light (85^o), semi-gloss ones are measured with a medium angle (60^o) and high-gloss ones with only a very small angle (20^o) . Modern devices contain all 3 measuring geometries and can be used universally by switching to the various ranges.

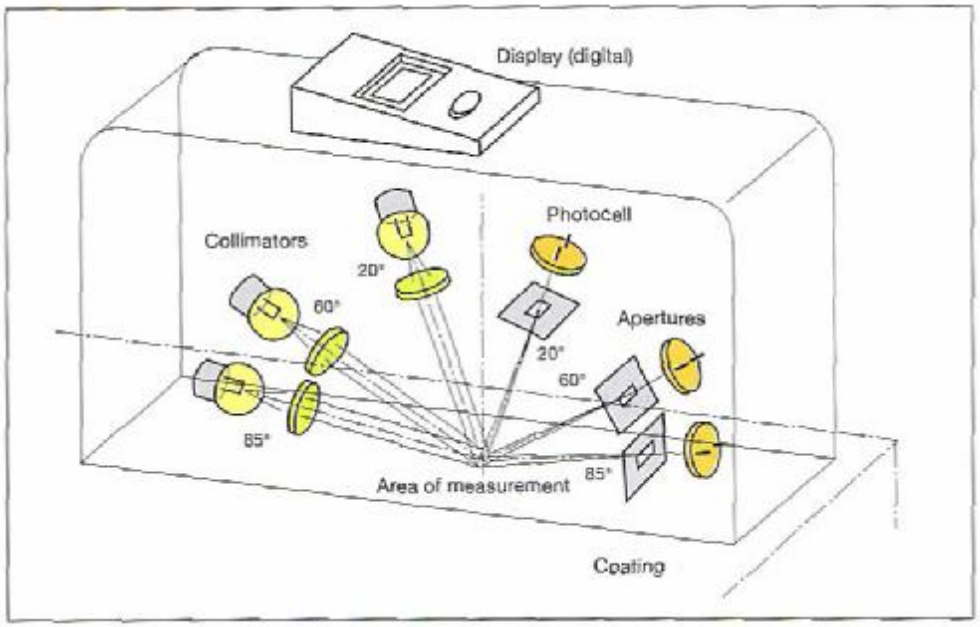


Figure 2.18: Scheme of a Measurement Device for Glass at Different Angles [28]

2.5.3 Adhesion test

The tecnology of adhesion has been studied for decades. One prerequisite for good adhesion is good contact between the adhesive or coating and the substrate. If this is fulfilled the adhesion can occur by one or more of the follwing mechenisms.

i) Mechanical-the coating fills microscopic crevices on the substrate surface and solidifies in them, so that a fully interlocked system is achieved.

ii) Physical- Van de Waals forces, hydrogen bonds and even electrostatic attractions occur between the coating and the substrate.

iii) Chemical-constituents of the coating bond chemically to the surface, hence bond cleavage is required in order to separate the coating and the subsrate. This case tends to be rares than the first two.

The above practice has been elaborated and given official sanctions by testing organisations. For instance the shape should be stuck to an area upon which a grid of 6x6 or 11x11 lines has been enscriebed. The tape is pulled off as before and the number of squares removed is counted. The percentage remaining is then quoted. Alternatively to the ASTM recommend a grading system between 5 and 0 in which 5 is equal to no coating removed and 0 equivalent to more than 65% removed [29]

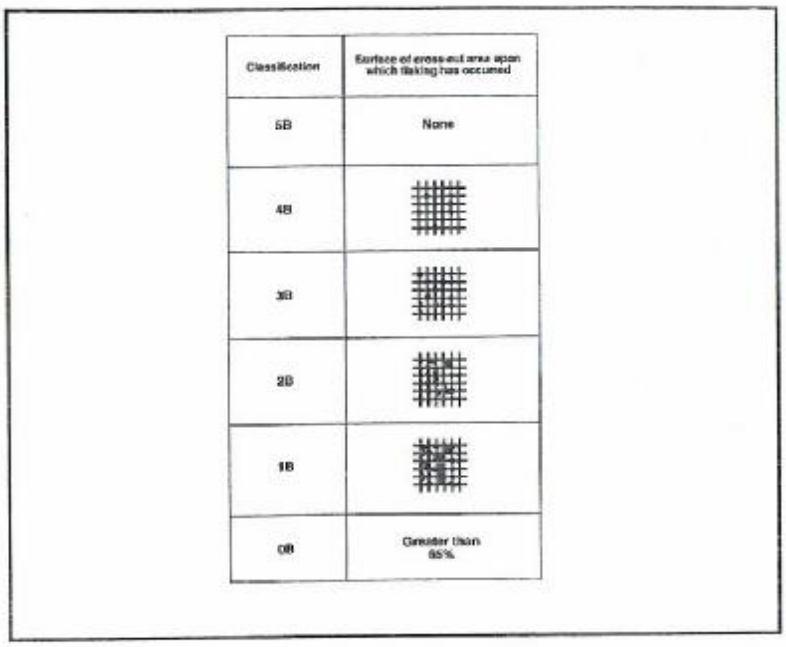


Figure 2.19: Adhesion Failures

2.5.4 Tensile Properties

The behaviour of a coating, when it is subjected to tensile stress, can be measured given of course that it can be separated from the substrate to which it was initially applied. The proviso for this that the film must have sufficient strength to be

handled. Realese paper is ofen used as the substrate so that free films can be obtained. Parameters such as modulus, elongation at break point and strength can all be evaluated using a tensile tester, such as an Instron. The modulus is a mesure of the stress (Force/unit cross section) required to elongate the coating a given distance. A high modulus is characteristic of a strong rigid substance. Break strength or tensile strength is the greatest stress a coating can withstand before ripping occurs and elongation is the degree to which the coating can be stretched prior to taering. The result of the test, as with virtually any other, is dependent upon temperature and relative humidity.

Tensile stress σ as an area-related force is directly proportional to elongation Δl in relation to initial length 1, the ε-value. The proportionality factor E in the appropriate stress-strain diagram is the modulus of elasticity by definition and given in equation 2.3. [28].

$$\sigma = F/A \qquad \sigma = E.\,\varepsilon \qquad \varepsilon = \Delta l / l \qquad (2.3)$$

Where,

F: Tensile force

A: Cross-sectional area

σ: Tensile stress

l: Initial length

Δl: Elongation

ε: Tensile strain

E: modulus of elasticity

The units of tests are for tensile stress is kg/mm^2, for tensile strain is unitless (mm/mm) and for elastic modulus is same as for tensile stress (kg/mm^2).

2.5.5 Weathering Test

Panels should be prepared so that they are representative of the production line and exposed on vertical fences facing both North and South and they should not be shielded for longer than 2 hours after sunrise and 2 hours before sunset. A control should always be included for comparision and the criteria used to judge performance should include degree of loss of gloss, amount of cracking and degree of chalking.

Outdoor exposure of coating on metal takes a similar from in that panels era exposed on racks at 45^{o} South and vertically North. The north facing panels are subject to more wind and rain, the south facing panels to more of the sun's rays. In order to accelerate the effect of sunlight, panels can be exposed in Florida or Arizona. Performance is again judged on colour change, gloss retention, degree of chalking and, if the samples are badly degreded, degree of cracking. The amount of corrosion is measured by the number and size of blisters near a scribe deliberately scored into the coating, exposed edges, bends and fasteners [29]

3. EXPERIMENTAL WORK

3.1 Materials

3.1.1 Monomers

Epoxy Resin (shell)

Marepoks-1790 was used to as a epoxy resin.

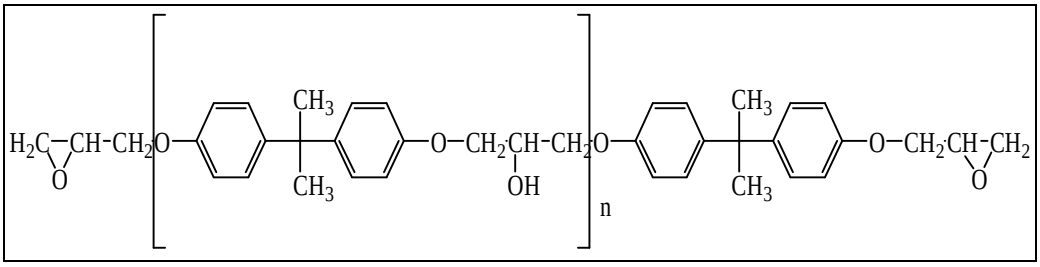


Figure 3.1: Epoxy Resin

It was used without further purification.Epoxy value is 0.515-0.540 mgKOH/g. Density of epoxy resin is 1.12 g/ml at 20^{o}C

Hekzane Diol Di Acrylate(HDDA)

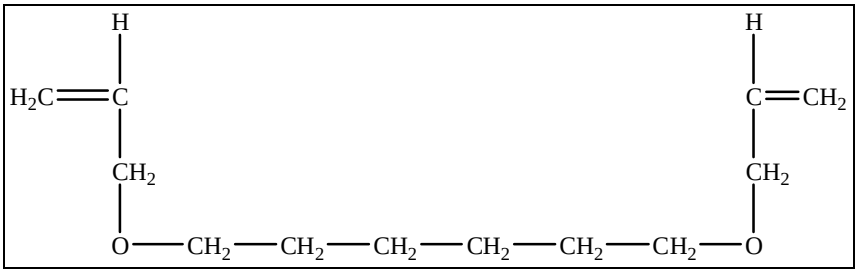


Figure 3.2: Hekzane Diol Di Acrylate (HDDA)

Photomer®4006-F (Trimethylol Propane Triacrylate) (Sartomer)

Trimethylol Propane Triacrylate (TMPTA) is a trifunctional acrylic monomer.

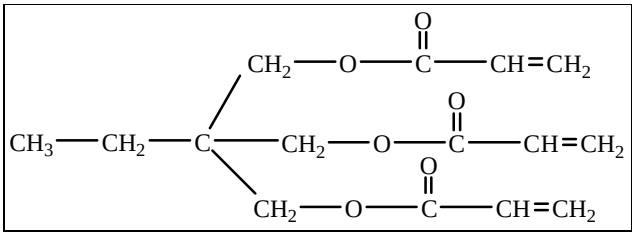


Figure 3.3: Trimethylol Propane Triacrylate

3.1.2 Other Chemicals and Reagents

Triethylamine (TEA) (Acros)

It was used without further purification.

Acrylic Acid (henkel)

It was used without further purification.

3-(isocyanatopropyl) triethoxysilan (IPTEOS) (Fluka)

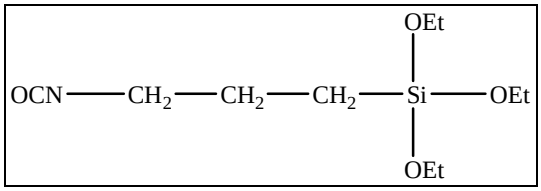


Figure 3.4: 3-(isocyanatopropyl) Triethoxysilan (IPTEOS)

It was used without further purification. Density is 1.0002 g/ml.

Dibutyltinlaurat (DBTDL, T12 Catalyst) (henkel)

It was used without further purification.

Irgacure 184 (1-Hydroxyphenylketone) (Ciba Speciality Chemicals)

1-Hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184) which is a alpha clevage type photoinitiator.

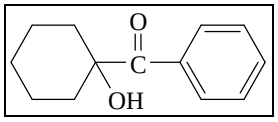


Figure 3.5: Hydroxy Cyclohexyl Phenyl Ketone

3.2 Equipments

3.2.1 Infrared Spectroscopy

Infrared spectra were recorded on Schimadzu 8300 spectrophotometer.

3.2.2 Ultra-Violet Spectrophotometer (UV)

The UV spectra of products were determined by Pharmaspec UV-1700 Shimadzu spectrophotometer.

3.2.3 UV Curing Machine

A conveyor type UV curing machine (EMA) was used photoinitiated polymerization of formulations. EMA UV curing machine is shown at Figure 3.1.

UV Lamp: medium pressure mercury UV lamps, 120 W/cm



Figure 3.6: EMA UV Cure Machine

3.2.4 Osram UV- Lamp (300 W)

High pressure UV-lamp was used to irradiate the hybrid free film.

3.2.5 Thermogravimetrical Analysis (TGA)

Thermal gravimetrical analysis was performed on a TA TGA Q50 instrument

3.2.6 Polycarbonate plates (Birleşik Akrilik Sanayi)

Polycarbonate plates (75 mm x 100 mm x 2 mm) were coated with different formulations. They were used for evaluation of pendulum hardness, gloss and adhesion.

3.2.7 Glass Mold

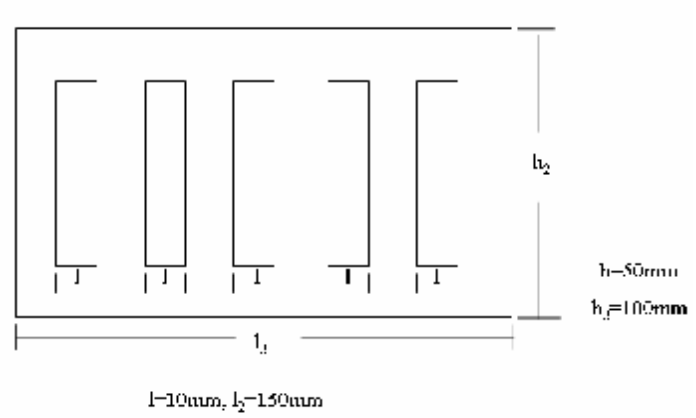


Figure 3.7: Glass Mold for Preparation of Free Film

Each divided part, made by HF, surfaces were smoothened by abrasion.

3.2.8 Tensile Loading Machine

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

3.2.9 Pendulum Hardness Tester

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

3.2.10 Glossmeter

BYK-Gardner (Micro-TRI) glossmeter is used. Gloss is measured at angle of incidence 20^{o}, 60^{o} and 85^{o} .

3.2.11 Cross-cut Adhesion Tester

Zwick Z010 Tensile tester machine is used for adhesion testing

3.3 Synthesis of Resin

3.3.1 Synthesis of Epoxy Acrylate

The reaction was carried out in a three-neck 500 mL round-bottom flask equipped with mechanical stirer, nitrogen inlet, water condenser, termometer and dropping funnel as shown in Figure 3.8. 100 g Marepoks-1790 and 2 ml triethlyamine (TEA) added into flask, stirred until obtaining a homogenious mixture. The reaction mixture was stirred for 30 min and heated to 70^{o}C under the nitrogen inlet. 33.3 ml Acrylic acid (33.3 mL) was then added dropwise into the system during 30 min. After one hour 2 ml TEA was added and reaction mixture was kept 80^{o}C and stirred for 4 hours. The product was clear viscous liquid. To reduce the viscosity of the neat resin 20 wt.% HDDA (27.67 mL) was added and stirred well. Completion of reaction was checked by infrared spectroscopy (Figure 4.3) .

3.3.2 Synthesis of Modified Urethane Epoxy Acrylate

The reaction was carried out in a three-neck 500 mL round-bottom flask, equipped with mechanical stirrer, nitrogen inlet, water condenser, thermometer, and dropping funnel. All glassware was kept in the oven overnight and reaction system was cooled under nitrogen to remove humidity. The preparation of UMEA-30 is given as example. 12 g epoxy acrylate (80:20 EA:HDDA, wt.%) was charged into a flame-dried three-necked and equipped with a nitrogen inlet and a dropping funnel and stirred at 40^{o}C until a homogenious mixture was obtained with a nitrogen inlet and dropping funnel. 2.98 ml 3-(isocyanatopropyl) triethoxysilan (IPTEOS) was added dropwise to the reaction mixture to modify %30 of hydroxyl groups in epoxy acrylate resin theoretically. Disappearance of the characteristic -NCO peak at 2275 cm^{-1} in the FT-IR spectrum confirmed that the reaction was completed. 20 wt.% HDDA (3.3 mL) was added to product and stirred well. The reaction product was kept under nitrogen atmosphere in a close tight dark colored tube in the refrigerator and wrapped with aliminum folio for preventing photopolymerization. The same experimental method was also used for the synthesis of urethane modified epoxy acrylates with hydroksil modification ratio of %10, %20, %50.

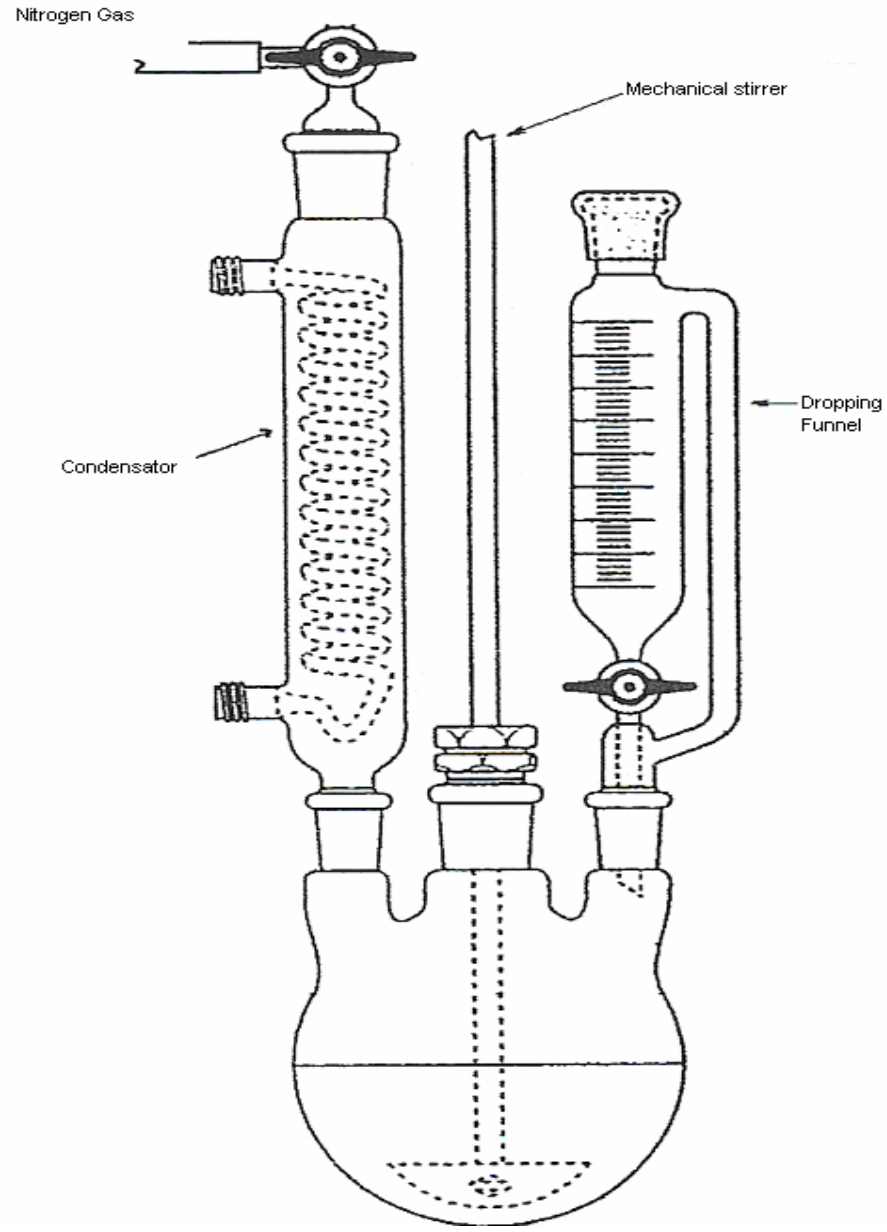


Figure 3.8: Reaction System for the Synthesis of Resin

3.4 Application

Modified epoxy acrylate containing UV-curable formulations were prepared by mixing (UMEA) 70 wt.%, Photomer® 4006F (27 wt.%) and photoinitiator (3 wt.%) The composition of formulations is given in Table 3.1

Table 3.1 Composition of Hybrid Systems

Sample Code	Modification Ratio (%)	Standard solution (10g)		
		Modified Resin (g)	Photomer 4006F (g)	Photoinitiator (g)
UMEA0	0	7	2,7	0,3
UMEA10	10	7	2,7	0,3
UMEA20	20	7	2,7	0,3
UMEA30	30	7	2,7	0,3
UMEA50	50	7	2,7	0,3

3.4.1 Preparation of Hybrid Coatings

I. Free Films: Glass molds were cleaned with acetone .Hybrid free films were prepared by pouring the light sensitive viscous liquid formulations on to a surface modified glass mold (10mm x 50mm x 1mm) as shown in Figure 3.7. In order to prevent the inhibiting effect of oxygen, the resin in the mold (Figure 3.2) was covered by a transparent 100 µm thick Teflon ^{TM} film before irradiation with a high pressure UV-lamp (OSRAM, 300 w). Then placed under UV lamp (distance: 15 cm) and irradiated for 1 minute. Teflon ^{TM} film was used to obtain a smooth surface. The films taken out from the mold and the edges were smoothened with zero number sandpaper and kept for using strain-stress test.

II. Coated Polycarbonate plates: Firstly temporary polyethylene coating films were pulled away by force from polycarbonate plates surface. Then, dusts sticked on the surface were cleaned with methanol wetted fiber cloth. After than polycarbonate plates were put on a smooth surface. 1 or 1.5 g of formulations mentioned in Table 3.1. were dropped on the plate. The surface was coated with a film by pulling a glass rod from one side to another. Wet films cured by UV machine, whose conveyor speed was 2 m/min and power of lamp was 13.2 amper.

3.5 Sol-Gel process

All coated samples were kept in water for 10 minutes. They were taken out , dried and kept in oven at 90^{o}C for 6 hours.

3.6 Analysis

3.6.1 Test Methods of Coated Polycarbonate Plates

Gloss test ASTM D523-80, adhesion test ASTM D3359-78, pendulum hardness test DIN 53157 and UV weathering test were applied to coated plates according to related methods mentioned in Part 3.2.

3.6.2 Test Metods of Free Films

3.6.2.1 Thermal Gravimetric Analysis (TGA)

Weight loss was recorded by TGA at heating rate of 20 ^{0}C/min under nitrogen atmosphere between 25^{0}C and 600 ^{0}C.

3.6.2.2 Tensile Properties

The thickness of the test samples of free films were taken as average from 4 different points with micrometer. Each end point of the films were holded with tensilone machine's jaws. Distance between each jaws were set up carefully. The speed of jaws were 5 mm/min. This application was continued until yield point. Mechanical tests were done for 4 free films for each formulation. Elongation at break, strength at break and modulus were calculated.

3.6.2.2 Weathering Test

UV Atlas 2000 type equipment was used for weathering tests.

4. RESULTS AND DISCUSSION

In this study improvement of physical and mechanical properties of UV-curable epoxy acrylate protective coatings was aimed. For this purpose urethane modified epoxy acrylates with varying modification degrees were synthesized and employed for the coating of polycarbonate plates via UV curing.

4.1 Synthesıs of Epoxy Acrylate and Modified Urethane Epoxy Acrylate

Epoxy acryrate and urethane modified epoxy acrylate were synthesized respectively according to the methods described in 3.3. Epoxy oligomers were reacted with acrylic acid to yield hydroxyl containing epoxy acrylates via oxyrane ring opening reaction (Figure4.1). Completion of reaction was cheched by FT-IR spectrum. It also shows the characteristic O-H streching band at 3446 cm^{-1}, carbonyl streching band at 1720 cm^{-1} and C=C stretching band at1508 cm^{-1} as shown in Figure 4.3.

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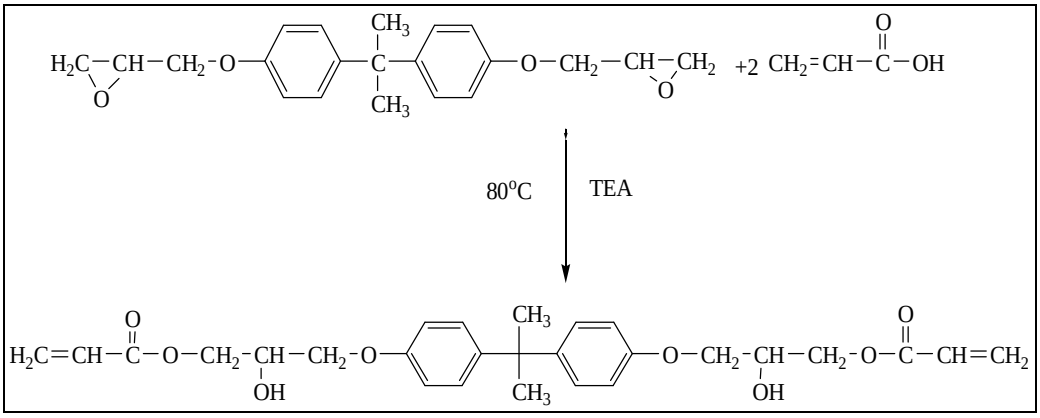


Figure 4.1 Synthesis of Epoxy Acrylate (EA)

These epoxy acrylates were modified by reacting with (3-isocyanatopropyl) triethoxysilan (IPTEOS) (Figure 4.2).

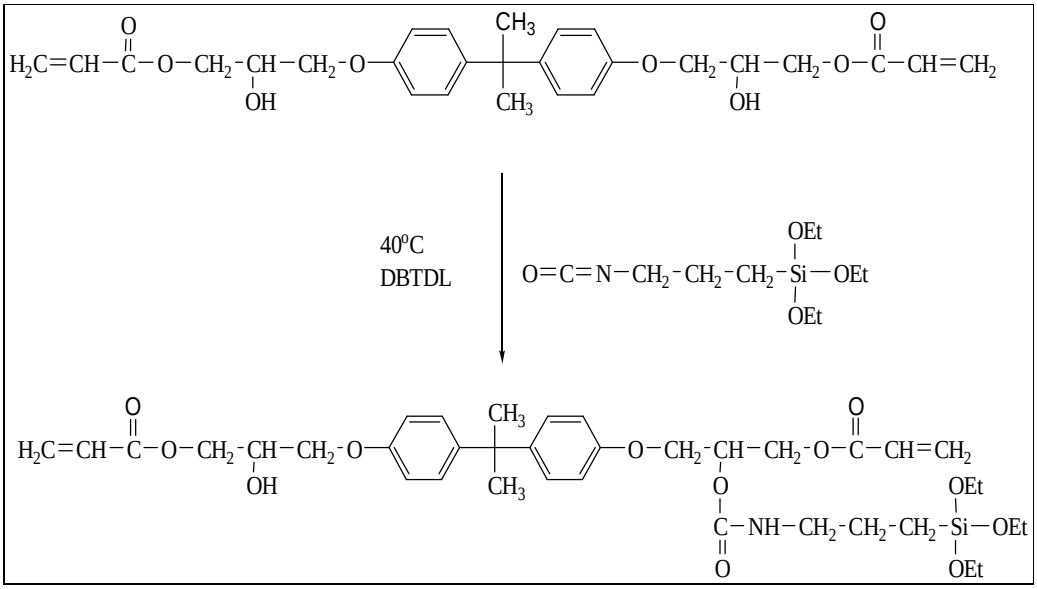


Figure 4.2 Synthesis of Urethane Modified Epoxy Acrylate (UMEA)

Progress of reaction and formation of urethane epoxy acrylate (UMEA) was followed by the disappearance of characteristic absorption band at 2275cm^{-1}(-NCO group's band) in the infrared spectrum. It also shows the characteristic N-H streching band at 2929 cm^{-1}, carbonyl streching band at 1721 cm^{-1} and Si-O-CH_3 band at 1181 cm^{-1} as shown in Figure 4.4.

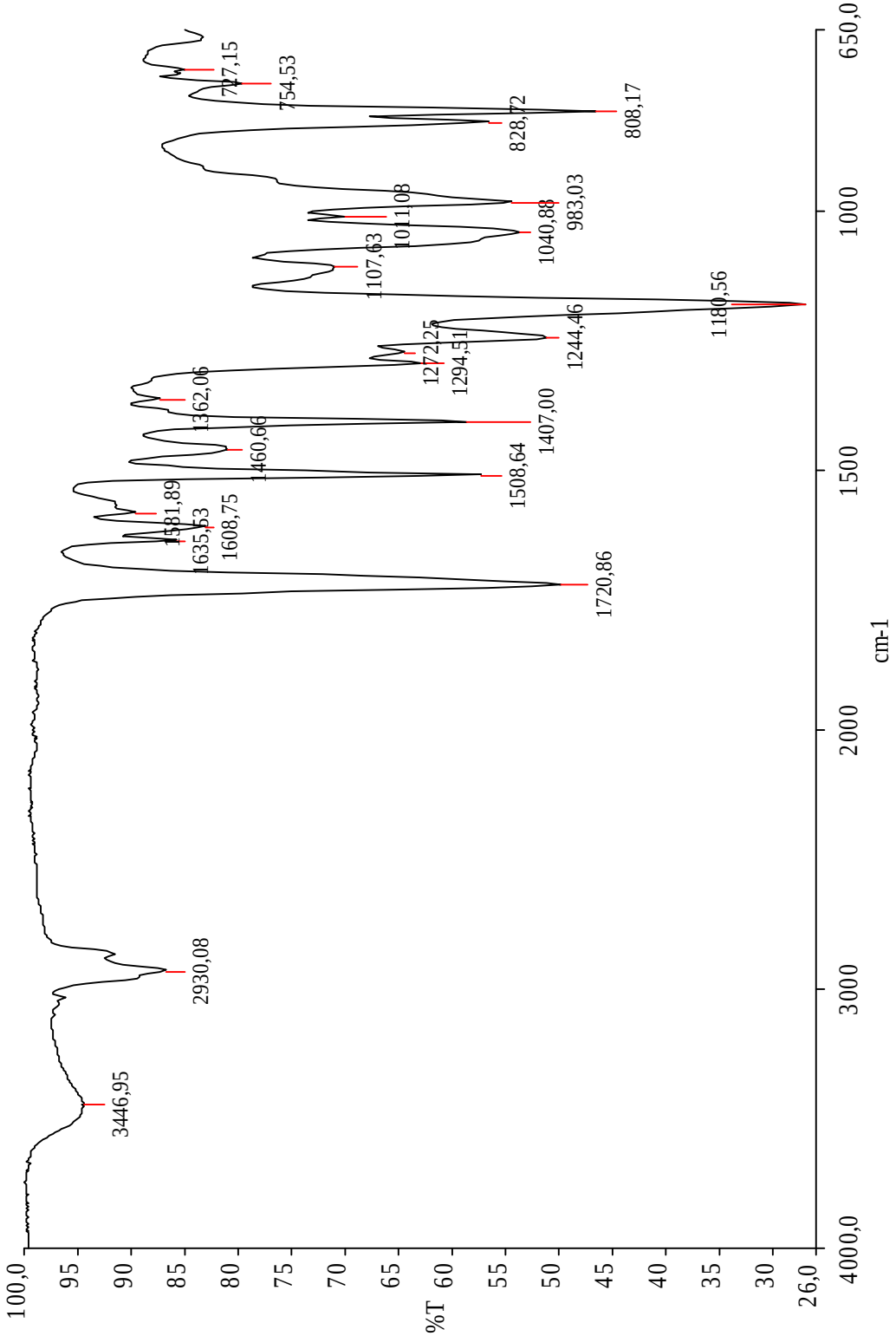


Figure 4.3 FT-IR Spectra of UMEA-0

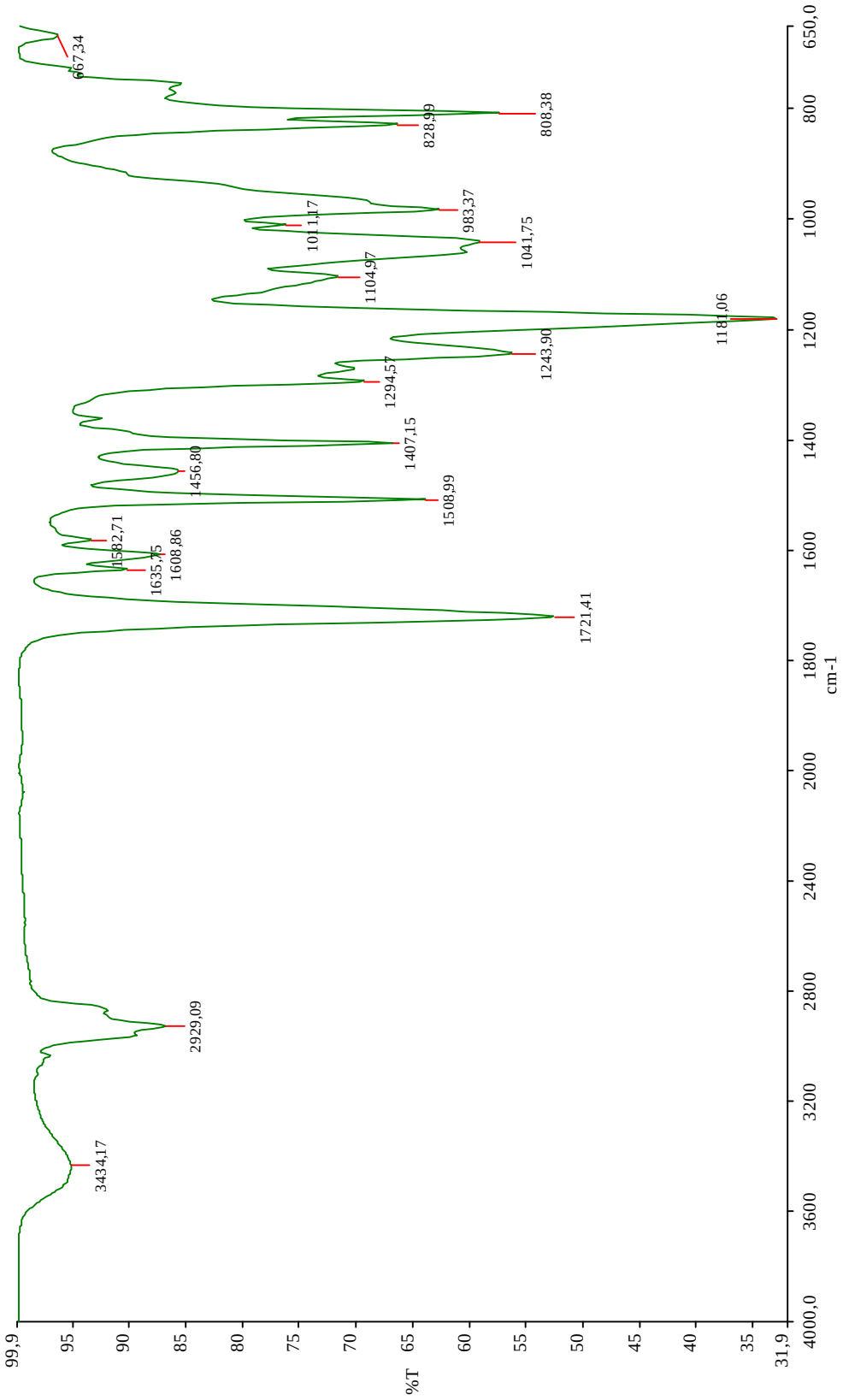


Figure 4.4 FT-IR Spectra of UMEA-10

4.2 Characterızatıon of Coatings

Various physical and mechanical characteristics of hybrid coatings before and after annealing were tested

4.2.1 Pendulum Hardness Test

The time which passed for the growing faint of pendulum on the polycarbonate test plates are shown as second on Table 4.1. The hardness of the uncoated poycarbonate plate is 132 Köning

Table 4.1 Hardness of samples

Sample	Modification Ratio (%)	Hardness(König)	
		Before Annealing	After Annealing
UMEA-0	0	138	138
UMEA-10	10	140	145
UMEA-20	20	139	140
UMEA-30	30	140	142
UMEA-50	50	139	142

The hardness of coating is the most important factor affecting the abrasion and sctratch resitance. Hard coatings give better resistance, whereas abrasion resistance is also affected by surface friction [30]. Chain flexibility and crosslinking degree of network play a major role in the value of hardness [31]. As can be seen in Table 4.1, Polycarbonate panels have an increased hardness of about 3-9% after the annealing. Condensation of alkoxysilane groups leads to the formation of Si-O-Si bonds thus increasing the crosslinking density and hardness values respectively.

4.2.2 Gloss Test

Gloss of the coated plates were measured at an angle of 20^{o}, 60^{o} and 85^{o}. The gloss value of UV cured polycarbonate plates was measured and then these plates were subjected to thermal application for 6 hours. Results of gloss tests for UV cured polycarbonate plates before and after annealing is given in Table 4.2.

Table 4.2 Gloss of samples

Sample Code	Modification Ratio (%)	Post-cure(h)	Gloss		
			20°	**60°**	**85°**
UMEA-0	0	0	183	147	112
		6	183	147	112
UMEA-10	10	0	182	148	110
		6	184	154	114
UMEA-20	20	0	119	116	107
		6	129	131	94
UMEA-30	30	0	178	151	113
		6	179	150	113
UMEA-50	50	0	169	145	112
		6	158	138	107

Coating's gloss is complex phenomenon resulting from the interaction between light and the surface of coating [32]. The influence of post-curing on the gloss can be clearly seen in Table 4.2. Gloss of the unmodified epoxy acrylate (UMEA-0) coatings are not changed by annealing. Upon annealing at 20°C for 6 hours, the gloss of UMEA-10, UMEA-20 and UMEA-30 coatings shifts to higher values. On the other hand, the gloss of UMEA-50 coatings is decreasing with post-cure time. The result shows that after a critical point, increasing the SiO_2 content diminishes the gloss as shown in Figure 4.8 and 4.9.

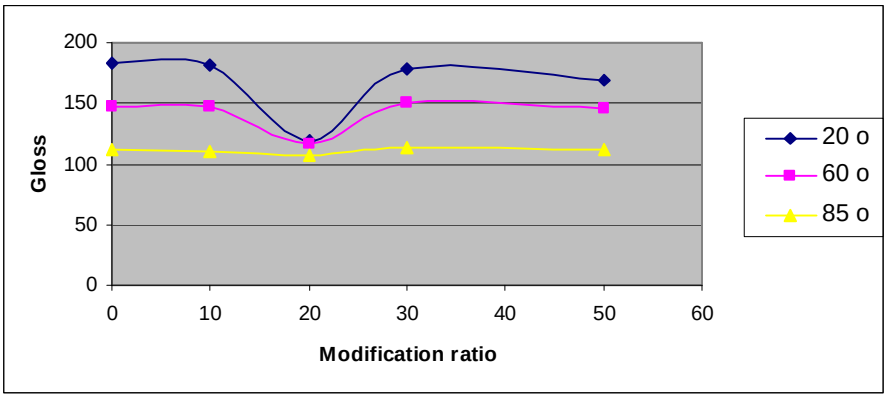


Figure 4.5 Gloss of UV Cured UMEA Films (Before annealing)

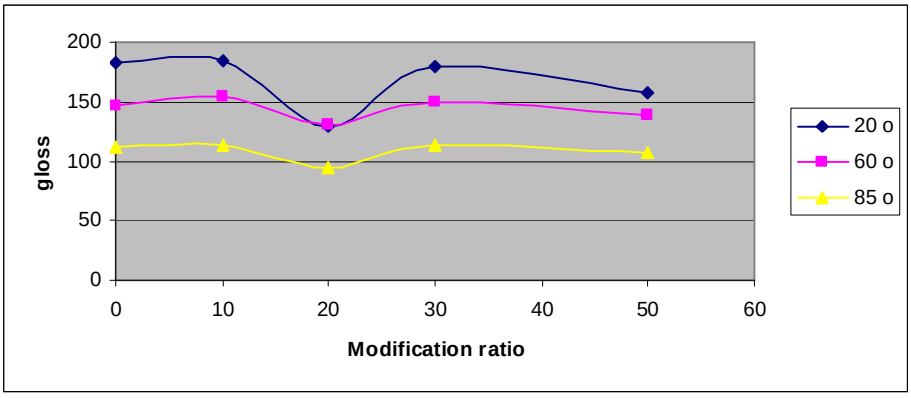


Figure 4.6 Gloss of Cured UMEA Films (After annealing)

4.2.3 Adhesion Test

Parallel lines with 2 mm distance to each other are drown on the coated plates surfaces.The band is sticked with 180^{o} on the surfaces then pulled with constant speed. After this application the number of the squares are evaluated as a percent of adhesion. Adhesion did not show much variation with the modification degree and adhesion degree was poor as described in 2.5.3.

4.2.4 Tensile-strength test

The mechanical specification of free films, prepared at 50x10x1 mm dimensions, made clearly with measurement of stress-strain values. Stress resistance and yield values were calculated according to the formulas given in page 26 by evaluating the graphics obtained from tensilon experiments. Stress strain values of UMEA coatings are shown Table 4.3

Table 4.3 Strain-stress analysis

Sample Code	Modification Ratio (%)	Tensile strength (Mpa) σ	Elongation at Break (%) ε	Modules(Mpa)
UMEA-0	0	12.3	1.2	545
UMEA-10	10	13.2	1.4	905
UMEA-20	20	7.7	1.1	880
UMEA-30	30	20.5	1.9	1512
UMEA-50	50	22.6	1.6	1882

Tensile strength of unmodified epoxy acyrale (UMEA-0) is 12.3 Mpa. The coating has a very low elongation value (1.2-1.9%). All samples have no yield value as UMEA coatings are brittle. However the variation in elongation at break is almost negligible. As the crosslinking density of the material increases tensile strength and modulus increases due to the increasing strength of the material. For UMEA-20 stress strain results also show deviation compared to other samples.This can be attributed to the inhomogenity of the matrix and possible phase separation as silane groups were distributed randomly in the matrix. These results demonstrate that hybrid coatings with higher inorganic content behave as hard and strong.

4.2.5 Thermal Gravimetric Analysis (TGA)

Results of thermal gravimetric analysis for modified resins were given in Table 4.4

Table 4.4 TGA analysis of hybrid networks

Sample Code	Modification Ratio (%)	10% weight loss temperature (^oC)	50% weight loss temperature (^oC)	Final weight loss temperature (^oC)	Char (%)
UMEA-0	0	379	400	553	0.7
UMEA-10	10	327	409	573	1.3
UMEA-20	20	347	431	579	1.4
UMEA-30	30	379	438	583	2.5
UMEA-50	50	397	439	591	3.3

The thermal properties of the hybrid coatings were also characterized by TGA in air atmosphere. Result of TGA thermograms of the hybrid materials are collected in Table 4.4. All samples show a small weight loss around 125^oC and these degradation products can be photoinitiator and reactive diluent. One can see that all samples exhibit a 10% weight loss at between 310-380^oC. Thermal stability of urethane modified epoxy acrylate was improved compared with pure epoxy acrylate. Thermogravimetric analyses showed that (Table 4.4) with increasing the silica content, final weight loss temperature shifted to higher values. The final weight loss appearing between 550-590^oC is probably due to the further oxidation of siloxanes.

In this case, char yield (amount of SiO_2) also increases with increasing modification ratio.

4.2.6 Wheathering Test

Annealed coatings were also subjected to weathering test. In Table 4.4 the influence of weathering on the transmittance values at 440 nm can be seen.

Table 4.5 Results of transmittance

Sample Code	Transmittance	After Wheathering Transmittance
UMEA-0	86.5	85.7
UMEA-10	86.4	82.5
UMEA-20	73.6	75.6
UMEA-30	85.4	82.3
UMEA-50	84.5	82.1

Upon weathering at 60^{o}C and 0.55 w/m^2 for 100 hours, transmittance values decreases for each sample. Besides this as modification degree increases transmittance values also shifts to lower values. Transmittance of UMEA-20 decreases because of phase separation.

5. CONCLUSION

In this thesis, a series of UV-curable organic-inorganic hybrid coatings were prepared based on a bifunctional oligomer bearing diacrylate and triethoxy functionalities. Incorporation of triethoxysilan functionalities into the organic coating improve the hardness. Upon increasing inorganic content, the other properties such as gloss, tensile strength and modulus are also improved. The adhesion of coating onto polycarbonate substrate is poor. The thermal stability of hybrids is also higher that of pure epoxy acrylate resin. The enhancement of the mechanical and thermal properties was correlated with an increase in cross-linking density of the system.

REFERENCES

[1] **Inan T.Y., Ekinci E., Kuyulu A., Güngör.,** 1999. Synthesis and characterization of phosphorus-containing methacrylate-based difunctional crosslinkers and their use in UV-curable resin systems, *Journal of Applied Polymer Science*, **73,** 2575-2585.

[2] **Pappas S.P.,** 1978. UV Curing: Science and Tecnology, Tecnology Marketing Corporation, Stanford, USA

[3] **Kayaman N.A., Demirci R., Çakır M., Güngör A.,** 2005. UV-curable interpenetrating polymer networks based on acrylate/vinylether functionalized urethane oligomers. *Radiation Physics and Chemistry*, **73,** 254-262

[4] **Kim J.W., Suh K.D.,** 1998. Amphiphilic urethane acrylate qq heterophasic gel structure: swelling behaviors and mechanical properties, *Colloid and Polymer Science,* **276,** 342.

[5] **Arndt L.W., Junker L. J., Patel S.P., Pourreau D.B., Wang W.,** 2002. Proceedings of the 80th Annual Meeting of Federation of Societies for Coatings Tecnology, October 30 to November 1, 2343-IV-1202.

[6] **Chiang C.L., Ma C.C.M., Wang F.-Y., Kuan H.-C.,** 2003. Thermo-oxidative degradation of novel epoxy containing silicon and phosphorous nanocomposites, *Eur. Polym. J.*, **39,** 825-830.

[7] **Wang, D., Elisseeff J.,** 2004. Photopolymerization, *Encyl. Biomat. Biomed. Eng.*, 1112

[8] **Decker, C.,** 1996. Photoinitiated Crosslinking Polymerization, *Prog. Polym. Sci.*, **21**, 593-650

[9] **Decker C.,** 1998. The Use of UV Irradiation in Photopolymerization, *Polym. Int.*, **45**, 133-141

[10] **Kim B. K., Lee K. H., Kim H. D.,** 1996. Preparation an Properties of UV Curable Polyurethane Acrylates, *J. Appl. Polym. Sci.,* **60**, 799-806

[11] **Studer K., Decker C., E., Schwalm R.,** 2005. Thermal and Photochemical Curing of Isocyanate and Acrylate Functionalized Oligomers, *Europ. Polym. J.,* **41**, 157-167

[12] **Decker C.,** 2002, Photopolymerization of Functional Acrylic Oligomers, *Polym. Int.,* **51,** 1141

[13] **Davidson R. S.,** 1999. Exploring the Science Tecnology and Applications of UV and EB Curing, John Wiley and Sons , London

[14] **Mehnert R.,Pincus A., Janorsky I., Stowe R., Berejka A.,** 1998. UV & EB Curing Tecnology & Equipment Volume I, John Wiley and Sons, London

[15] **Wicks Z. W. Jr., Jones F.N., Pappas S.P.,** 1999. Organic Coatings Science and Technology, 2 nd ed., John Wiley and Sons, Canada

[16] **Webster G.,** 1996. Prepolymers and reactive Diluents Chemistry and tecnology of UV and EB Formulation for Coating, Inks and Paints. Volume II, ., John Wiley and Sons, London

[17] http://www.specialchem4coatings.com/tc/radiation-curing, 2006

[18] **Willard K,** 2000 UV/EB Coating for Automotive Coatings, Tecnical Paper, Rad. Tech. Rep., November/December 2000, 15-20

[19] **Brinker C.J., Scherer G.W.,** 1990. The Physics and Chemistry of Sol-Gel Processing, Newyork

[20] **Brinker C.J., Scherer G.W.,** 1985. Sol Yields Gel Yields Glass: I. Gelatıon and Gel Structure, *J.Non-Crystalline Solids*, **70**, 301-322

[21] **Chow G.M., Gonsalvez K.E.,** 1996. Nanotecnology-Molecularly designed materials, *ACS Symp*. Ser. 622, American Chemical Society, Washington

[22] **Brinker C.J., Schere G.W.,** 1990. Sol-Gel Science, San Diego

[23] **Houbertz R., Schulz J., Fröhlich L., Domann G. and Popall M.,** 2003. *Mater. Res. Soc. Symp. Proc.,* **769,** p.H.7.6.1

[24] **Sanchez C., Ribot F.,** 1993. Molecular design of hybrid organic-inorganic materials, *Journal De Physique,* **3,** 1349-1355

[25] **Haas K.H., Wolter H.,** 1999. Synthesis, properties and applications of inorganic-organic copolymers, *Current Opinion in Solid State and Materials Science,* **4,** 571-580

[26] **Rose K.,** 2002. Organic-inorganic hybrids II, *In Proceeding PRA-conference*, University of Surrey, 28-29 May

[27] http://www.isc.fhg.de/alteseiten/ormocere_e/o3_1_1.html, 2005

[28] **Goldschmidt A., Streitberger H.J.,** 2003. BASF Handbook on Basics of Coating Tecnology, BASF Coatings AG, Münster, Germany.

[29] **Lowe Dr. C.,** 1996. Test Methods for UV& EB Curable Systems Volume IV, John Wiley and Sons, Londan

[30] **Karataş S., Hoşgör Z., Menceloğlu Y. Kayaman A.N., Güngör A.,** *J. Appl. Polym. Sci.* Submitted for publication

[31] **Kahraman M.V., Kuğu M., Menceloğlu Y., Kayaman A.N., Güngör A.,** *J. Non-Cryst. Solids,* submitted for publication

[32] **Soucek M.D.,** 1999. Siloxane modified cycloaliphatic epoxide UV coatings, *Progress in Organic Coatings,* **36,** 89

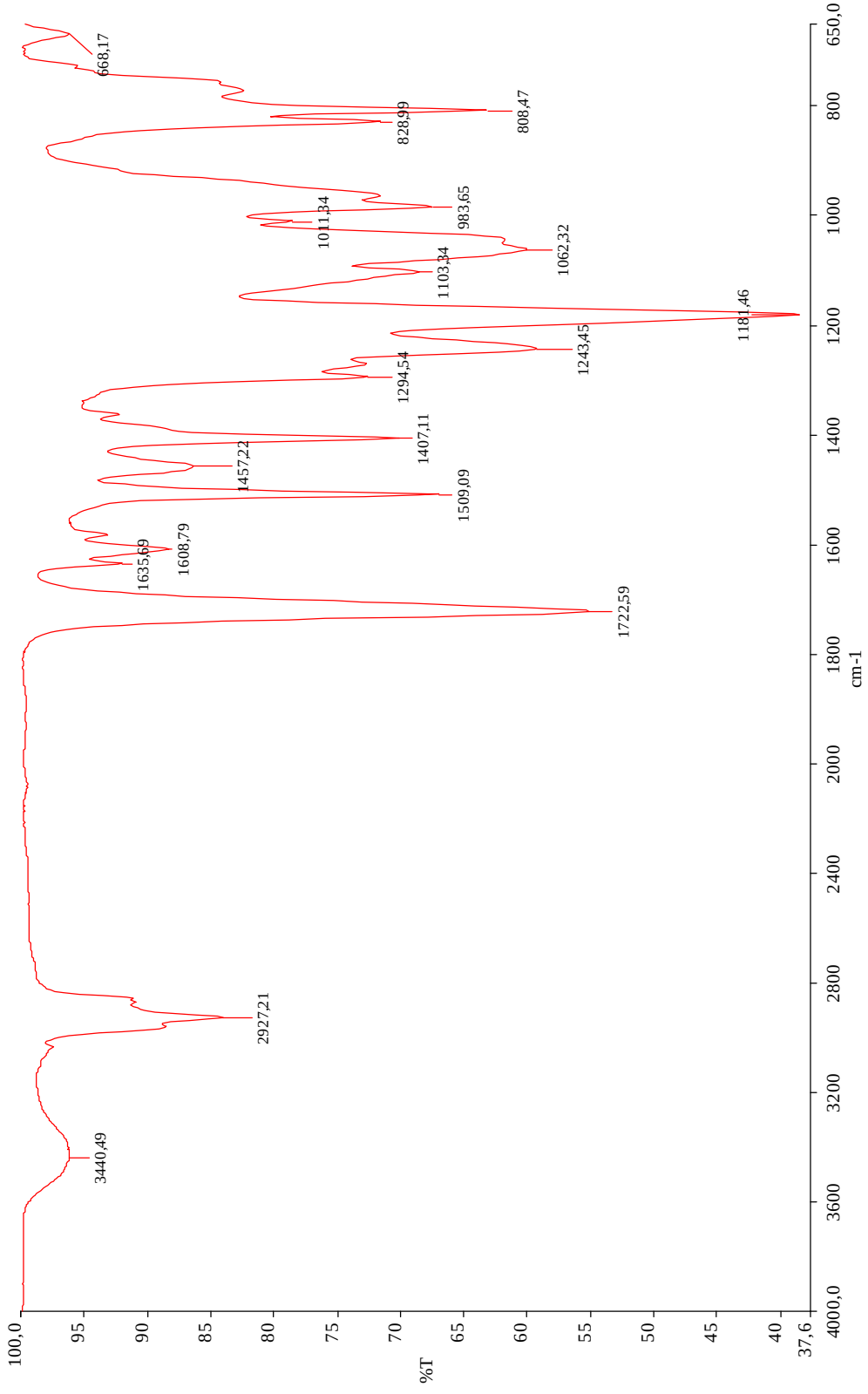


Figure D.1: FT-IR Spectra of UMEA-20

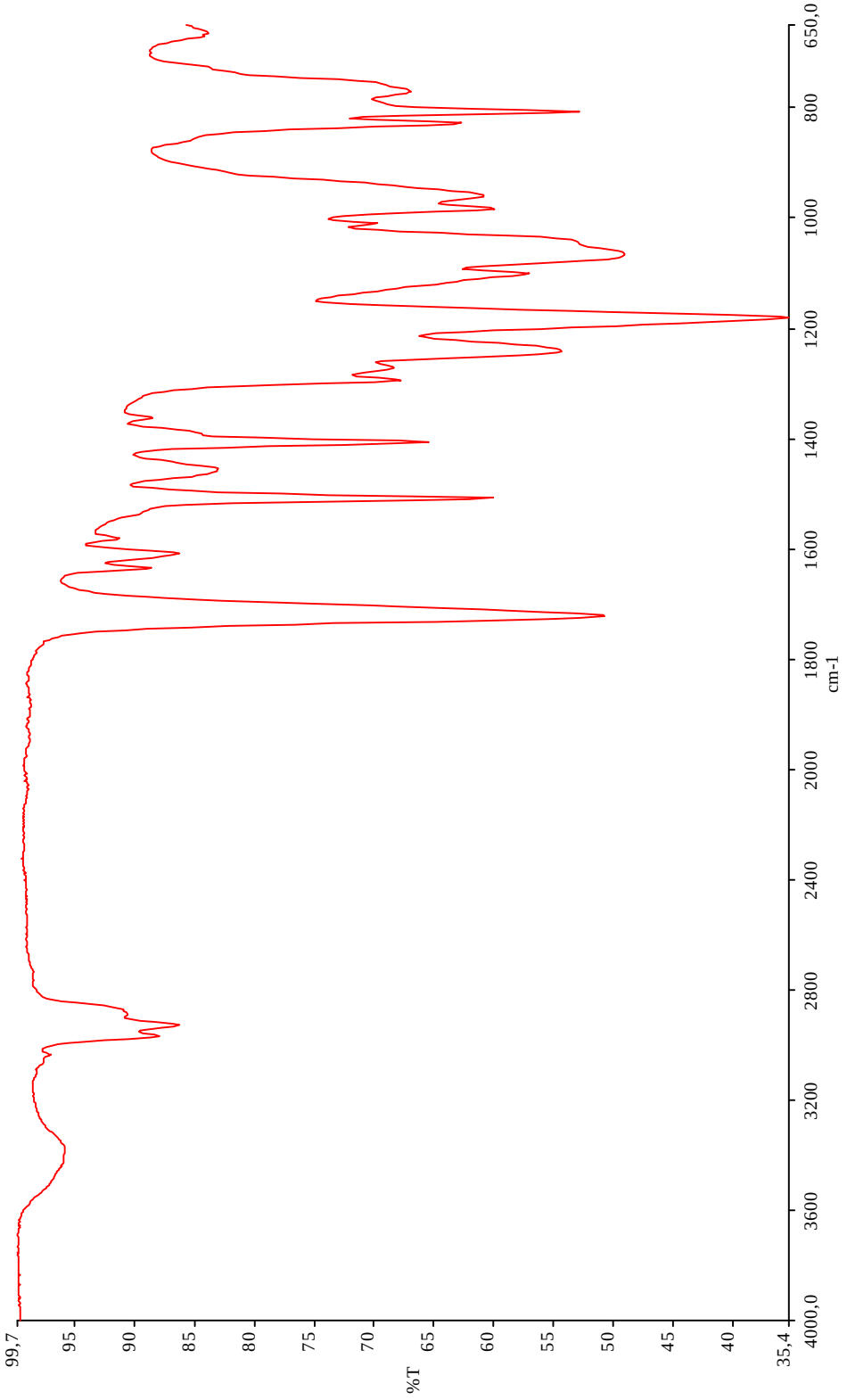


Figure D.2: FT-IR Spectra of UMEA-30

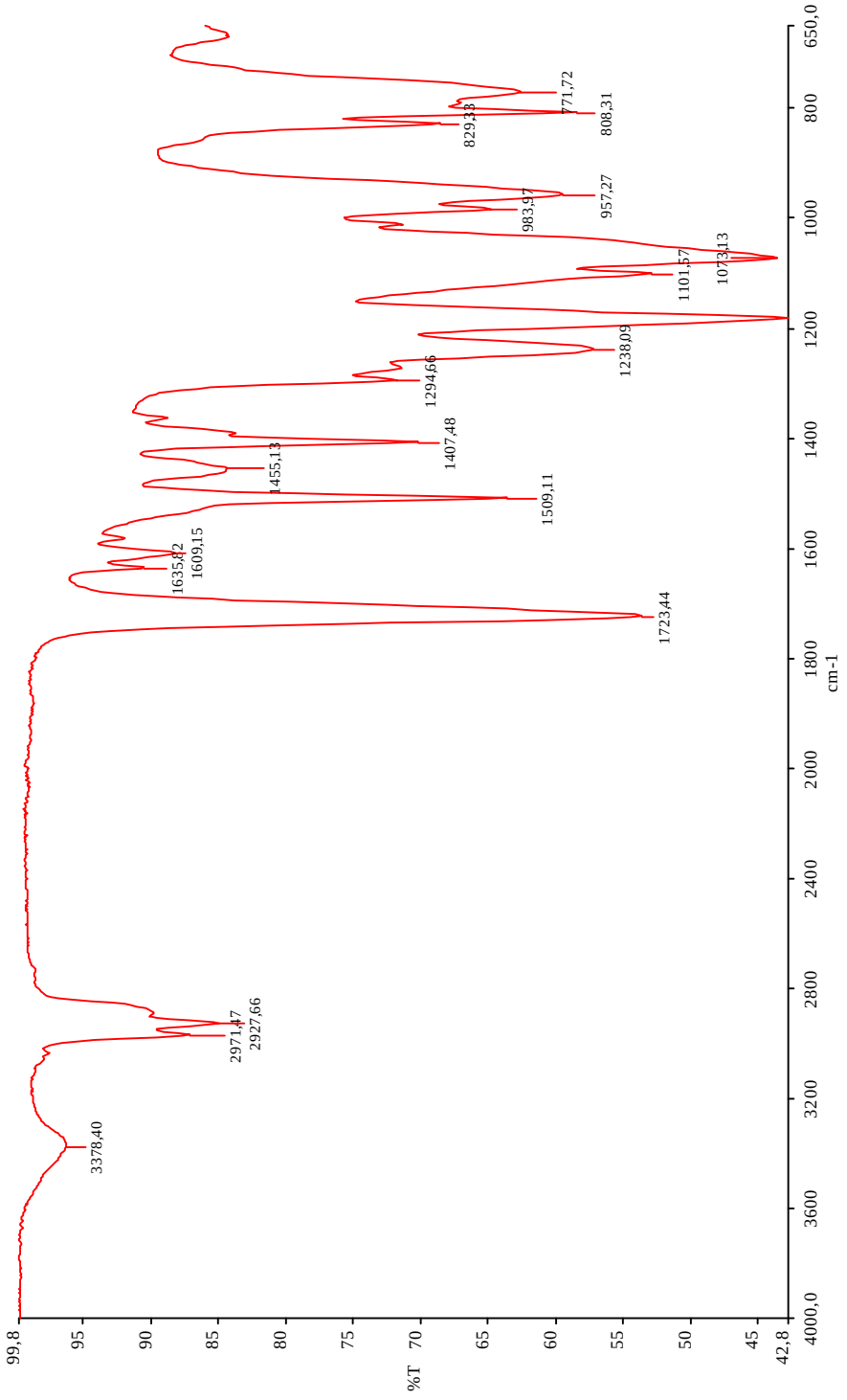


Figure D.3: FT-IR Spectra of UMEA-50

RESUME

Tayyibe ÖZDEMİR was born in Milas in 1980. She was graduated from Milas High School in 1998. She admitted to Marmara University, Teacher of Chemistry Department in 1998 and graduated as a Teacher of Chemistry in 2003

She was accepted as a M.Sc. student to the Polymer Science and Technology Programme of the Institute of Science and Technology of Istanbul Technical University in 2004 in which she is about to graduate.