İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF NOVEL URETHANE ACRYLATE AND THEIR PAPER COATING APPLICATIONS

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

Programme : Polymer Science and Technology

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ÜRETAN AKRİLAT SENTEZİ VE KAĞIT KAPLAMADA KULLANIM ALANLARI

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FOREWORD

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

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Polymer Science & Technology

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ABBREVIATIONS

UA	**:** Urethane Acrylate
PE	**:** Polyester
BFPPO	**:** Bis(4-fluorophenyl)phenyl phosphine oxide
BOHPPO	**:** Bis(4-hydroxyphenyl)phenyl phosphine oxide
BOHEPPO	**:** [(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide
IPDI	**:** Isophorone diisocyanate
HEMA	**:** 2-Hydroxy ethyl methacrylate
UV	**:** Ultra Violet
NMR	**:** Nuclear Magnetic Resonance
TGA	**:** Thermal Gravimetrical Analysis
FT-IR	**:** Fourier Transform Infrared
DPGDA	: Dipropyleneglycoldiacrylate
HDDA	**:** 1,6-hexanedioldiacrylate
TMPTA	**:** Trimetyhlolpropane triacrylate
DBTL	**:** Dibutyl Tinlaurate

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SYNTHESIS OF NOVEL URETHANE ACRYLATE AND THEIR PAPER COATING APPLICATIONS

SUMMARY

Coatings are found almost anywhere in daily life. They are applied in order to provide decorative appearance, and/or protective barrier. The market prospects of future coating technologies are reflecting the environmental concerns about the use of solvents. In radiation curable coatings there isn't solvent emission, hence they are mainly used in industrial applications where governed by VOC (volatile organic carbon) regulations.

One of the major growth areas of recent years, especially in the paste ink field, has been in radiation curing ink. These are inks, and clear lacquers whose components react when exposed to UV light, or when passed through an electron beam, to cure instantly to a solid polymer. UV curable systems used in graphic arts applications are divided into the categories of printing inks, containing pigments or dyes, and clear coat overprint varnishes (OPV).

Radiation curing inks are basically formulated in the same way as any other ink, they are composed of pigment, binder, diluents and additives necessary for specific applications. In these inks, the binders are generally acrylates. The diluents are also acrylates and are non-volatile. The characteristic which is common almost to these inks, and which divides them from other ink systems, is the ability to change almost instantaneously from the fluid phase to a highly cross-linked solid phase by means of a chemical reaction initiated by ultra-violet light.

In this study a new compound was synthesized to use as an oligomer resin in UV curable varnishes for paper coatings. The aim of this thesis was to introduce improving properties for paper coating such as flame retardancy, flexibility, abrasion resistance etc. For this purpose, a new phosphorus containing polyester was synthesized and characterized. This saturated polyester containing terminal hydroxyl groups used as polyester polyol to synthesize urethane acrylate. The polyester-based polyurethane acrylate exhibits high levels of tensile and flexural strength with good abrasion resistance. Also, the incorporation of phosphorus into polymer is expected to introduce flame retardancy, thermal stability to the material. This new material is used in several formulations for coating paper by radiation-curable system. The influence of the oligomeric resin on the mechanical and thermal properties of the coated substrate is studied.

ÜRETAN AKRİLAT SENTEZİ VE KAĞIT KAPLAMADA KULLANIM ALANLARI

ÖZET

Günlük yaşamda yüzey kaplama teknikleri hemen hemen her alanda kullanılmaktadır. Bu ürünler dekoratif görünüm sağlamak ya da koruyucu bir yüzey oluşturmada tercih edilebilirler. Bu piyasa için gelecekteki yüzey kaplama teknolojilerinde kullanılacak solventler çevresel sorun oluşturur. UV ile kürleşen yüzey kaplamalarda solvent emisyonu yoktur, bundan dolayı özellikle VOC (uçucu organik karbon) yönetmeliği uygulanan endüstriyel uygulamalarda kullanılır.

Radyasyonla kürleşen mürekkepler son yıllarda gelişmekte olan bir alandır. Bu mürekkep ve laklar, UV ışınına maruz kaldıklarında ya da elektron demetinden geçirildiklerinde anında kürleşirler ve katı polimerlere dönüşürler. Baskı uygulamalarında kullanılan UV ile kürleşen sistemler pigment ve boyar madde içeren baskı mürekkepleri ve baskı sonrası vernikleme kategorilerine ayrılırlar.

Radyasyonla kürleşebilen mürekkepler temel olarak herhangi bir mürekkep gibi formüle edilirler. Pigmentler, bağlayıcılar, seyrelticiler ve uygulama alanına göre seçilecek katkı maddelerinden oluşurlar. Bu mürekkeplerde bağlayıcılar genellikle akrilatlardır. Seyrelticiler de akrilatlardan oluşur ve uçucu değildirler. Bu tür mürekkeplerin, UV ışınının başlattığı kimyasal reaksiyon ile sıvı fazdan hızlıca yüksek çapraz bağlı katı faza geçebilmeleri, bu malzemelerde ortak olan ve diğer mürekkeplerden ayıran karakteristik bir özelliktir.

Bu çalışmada kağıt kaplamada kullanılmak üzere UV ile kürlenebilir yeni bir oligomer sentezlenmiştir. Bu tezin amacı, kaplamaya alev geciktiricilik, esneklik, aşınmaya dayanım gibi özellikler katmaktır. Bu amaçla fosfor içeren bir polyester sentezlenmiş ve karakterizasyonu yapılmıştır. Hidroksi uç grubu içeren bu doymuş polyesterler üretan akrilat sentezinde poliol olarak kullanılmıştır. Polyester bazlı üretan akrilatlar yüksek gerilim mukavemeti ve aşınmaya dayanım gösterirler. Ayrıca, polimere fosforlu bileşik katılmasıyla malzemeye alev geciktiricilik ve termal kararlılık katılması beklenir. Bu yeni malzeme UV ile kürleşebilir kağıt kaplamada kullanılıp çeşitli formülasyonlara katılmıştır. Oligomerik reçinenin kaplamaya kattığı mekanik ve termal özellikler araştırılmıştır.

1. INTRODUCTION

UV curable coating is also preferred where thermal curing is hardly possible, like curing of coatings on temperature sensitive substrates, like wood, paper and plastics, and in imaging applications, where only selected areas should be polymerized, like in polymer printing plates and photoresists. UV coating provides also low energy consumption, low emission, low capital investment and low space consumption. Radiation curable coating consists of very low molecular film forming agents with a high proportion of polymerisable C-C double bond, which are diluted in the liquid state with reactive monomers or solvents or are combined as aqueous dispersions with photoinitiators and other components to produce a coating formulation appropriate to the relevant application.

Radiation cure coatings cross-link by reactions initiated by radiation, rather than heat. Such coatings have the potential advantage of being identifinitely stable when stored in the absence of radiation. Rapid cure a ambient temperature is particularly significant for heat sensitive substrates, including paper. Then the UV curable material is favorable to use in paper coating.

Although UV radiation has been known to initiate curing for a very long time, the development of UV-curing inks had to wait until resins which both cured and were capable of participating in the print process were developed. UV curable formulations gives dry printing, provide elimination of spray powder which leads to smooth prints and a clean press environment and no solvent emissions. It also gives very high gloss prints achievable, in some cases able to replace lamination. And It is consistent to low odor level because no odorous species generated by post cure chemistry. For these advantages of using UV, inks have ensured a steady growth rate in ink usage. Lamps and installations, which have become simpler, relatively inexpensive and more versatile, have supported this growth. UV-cured inks and lacquers provide the largest volume of the specialized radiation-cured market.

Phosphorus-containing monomers/oligomers used as flame-retardants for UV curable systems have drawn much attention recently, since they generally give off non-toxic and non-corrosive volatile products during combustion [1, 2].

This thesis will concern of the preparation of novel polyester-based urethane acrylate containing phosphorus compound. Then, this component will be used in UV curable formulations for paper coating. And the coated paper will be characterized by various analysis methods such as contact angle, hardness, gloss, and stress-strain test. In addition the thermal behavior of the coating will be investigated.

2. THEORETICAL PART

2.1 Epoxy Resins

2.1.1 Introduction

Epoxy resins were introduced commercially in the United States in the late 1940s. They have gained wide acceptance in protective coatings and electrical and structural applications for a variety of required properties such as chemical resistance, dielectric or insulation properties, low shrinkage on cure, dimensional stability or fatigue resistance, thermal stability, bacteria and fungus resistance, stability or fatigue resistance, thermal stability, bacteria and fungus resistance, water resistance, etc. [3]. Epoxy resins are characterized as compounds or mixtures of compounds that contain one or more epoxide or oxirane groups. The major types of epoxy resins can be classified as cycloaliphatic epoxy resins, epoxidized oils and glycidated resins. The most widely used epoxy resins are diglycidyl ethers of bisphenol A with epiclorohydrin.

2.1.2 Chemistry of Epoxy Resins

The importance of epoxy resins as coating materials arises mainly from the ease with which these resins can be converted to high-molecular-weight materials through curing reactions. Epoxy resins as a class of crosslinked polymers are prepared by a two-step polymerization sequence. The first step which provides prepolymers, or more exactly: preoligomers, is based on the step-growth polymerization reaction of an alkylene epoxide which contains a functional group to react with a bi- or multifunctional nucleophile by which prepolymers are formed containing two epoxy end groups. In the second step of the preparation of the resins, these tetra functional (at least) prepolymers are cured with appropriate curing agents [4].

The most widely used pair of monomers to prepare an epoxy prepolymer are 2,20-bis(4-hydroxyphenyl)propane (referred to as bisphenol-A) and epichlorohydrin, theepoxide of allylchloride. The formation of the prepolymer can be seen to involve

two different kinds of reactions. The first one is a base-catalyzed nucleophilic ring opening reaction of bisphenol-A with excess of epichlorohydrin to yield an intermediate b-chloro alcoholate which readily loses the chlorine anion reforming an oxirane ring. Further nucleophilic ring-opening reaction of bisphenol-A with the terminal epoxy groups leads to oligomers with a degree of polymerization up to 15 or 20, but it is also possible to prepare high molecular weight linear polymers from this reaction by careful control of monomer ratio and reaction conditions [5].

The two ring-opening reactions occur almost exclusively by attack of the nucleophile on the primary carbon atom of the oxirane group [6]. Depending on the conditions of the polymerization reaction, these low molecular weight polymers can contain one or more branches as a result from the reaction of the pendant aliphatic hydroxyl groups with epichlorohydrin monomer. In most cases, however, the chains are generally linear because of the much higher acidity of the phenolic hydroxyl group. At high conversions, when the concentration of phenolic hydroxyl groups drops to a very low level, under the base-catalyzed reaction conditions formation and reaction of alkoxide ions become competitive and polymer chain branching may occur. Polymers of this type with molecular weight exceeding 8000 are undesirable because of their high viscosity and limited solubility, which make processing in the second stage, crosslinking-reaction difficult to perform. The oligomers of the diglycidylether of bisphenol-A (DGEBA) are the most commonly epoxy resins, therefore a great deal of investigations with respect to the processibility behavior before crosslinking is focused on this oligomer [7].

The initial product is the monoglycidyl ether of Bisphenol A. Analogous reaction of the phenolic group of Bisphenol A with NaOH and epichlorohydrin gives the diglycidyl ether of Bisphenol A. The epoxy groups react with Bisphenol A^- to extend the chain, these reactions introduce alcohol groups on the backbone. Continuation of these reactions results in linear polymers, since both the Bisphenol A and epichlorohydrin are difunctional. Bisphenol A epoxy resins are made with excess epichlorohydrin, so the end groups are glycidyl ethers. The reaction is presented in Figure 2.1 [4].

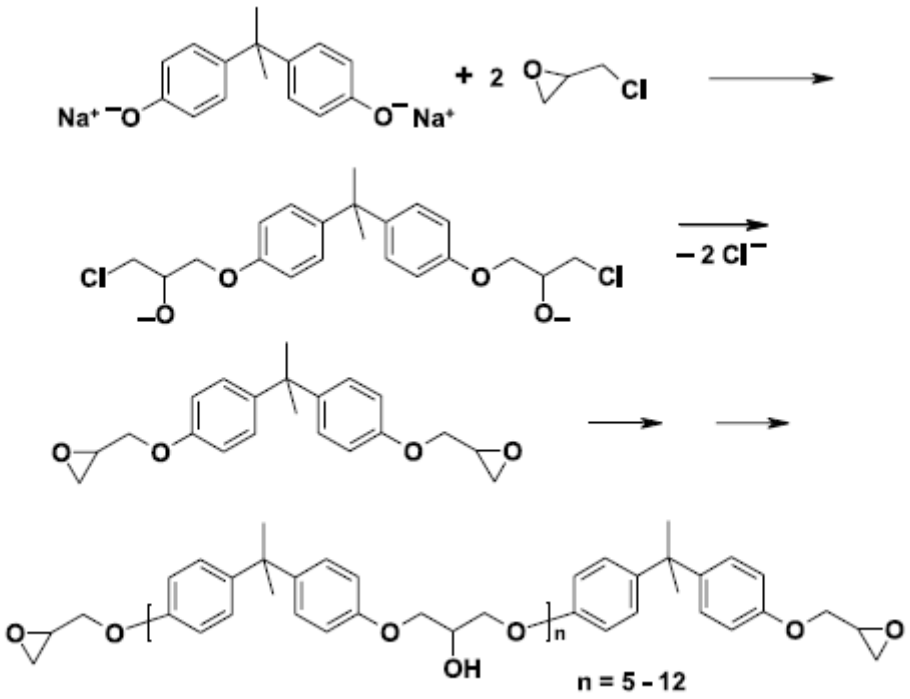


Figure 2.1: Bisphenol A epoxy resin

2.1.3 Epoxy resin types

Generically, epoxy resins can be characterized as a group of commercially available oligomeric materials, which contain one or more epoxy (oxirane) groups per molecule. The epoxy resins most widely used by far in coatings are the bisphenol A based epoxy resins, the generalized structure of which is given in Figure 2.1. In commercial products, the n value ranges from 0 to about 25, although higher-molecular-weight thermoplastic resins having n values of 200 or more are available. As n increases, the epoxy equivalent weight (EEW) increases, as does the number of hydroxyl groups. Thus, epoxy resins with low n values are normally cured by reaction of the epoxy group, whereas those resins with higher n values are cured by reaction of the hydroxyl functionality. Resins having n values less than 1 are viscous liquids; they are used mainly in ambient-temperature cure coatings, electrical castings, flooring, electrical laminates, and fiber-reinforced composites. These applications require liquid resins having good flow and are cured through the epoxy ring. The higher n value resins, particularly those above 3000 molecular weight, are normally used in solution and find their greatest application in heat-cured coatings.

In these resins the concentration of epoxy groups is low, and so they are cured with materials that react with the hydroxyl groups along the backbone [8].

2.1.4 Epoxy Acrylates

2.1.4.1 Introduction

The most widely used oligomers are aromatic and aliphatic epoxy acrylates. Epoxy acrylates are inexpensive highly reactive and produce hard and chemically resistant films. Epoxy acrylates are prepared by the reaction of an epoxy group with acrylic acid. Generally, the reaction produces medium to high viscosity fluids, which have a fast cure rate. The polymerization of monoacrylates produces linear polymers, whereas diacrylates produce branching, and higher-functionality acrylates give rise to cross-linked structures.

2.1.4.2 The Chemistry of epoxy acrylate

Epoxy acrylates, in general, obtained by reacting 1 mol of diglycidyl ether of bisphenol A with 2 mol of acrylic acid and are represented by the general formula as below:

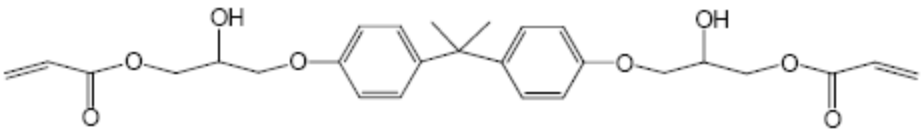


Figure 2.2: Epoxy acrylate general formula

The ring-opening reaction yields the acrylic ester and a hydroxyl group. Various catalysts (e.g. triphenyl phospine) are used, so the reaction is carried out at as low a temperature as possible. Care is required to avoid polymerization of the acrylic acid or esters during the process. Inhibitors are added to trap free radicals. Some inhibitors, notably phenolic antioxidants, are effective only in the presence of oxygen, so the reaction is commonly carried out under an atmosphere of air mixed with inert gas. Variation in reaction conditions and catalyst composition can result in significant differences in the product. The most widely used epoxy resin is the standard liquid bisphenol A epoxy resin (n=0.13), yielding predominantly the acrylated diglycidyl ether of bisphenol A. Epoxidized soybean or linseed oil also react with acrylic acid to give lower T_g oligomers with higher functionality.

2.1.4.3 Types of 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. [9]

Aromatic difunctional epoxy acrylates

They 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

They are essentially epoxidized soybean 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

They 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

They 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

They consist mainly of oligomers with fatty acid modification. They provide good pigment wetting properties and higher molecular weight but lower functionality than other aromatic epoxy acrylates. They are used in printing inks and pigmented coatings.

2.1.4.4 The applications of epoxy acrylates

Both aromatic and aliphatic epoxies and epoxy novolacs are used. Aliphatic epoxy acrylates exhibit lower viscosity and a greater compability range than their aromatic counterparts. Epoxidized oils belonging to the aliphatic epoxide can also be used. The latter types of acrylate oligomers provide good flexibility, lower viscosity, good pigment wetting properties and very low skin irritancy. However, these properties are obtained at the expense of cure rate and chemical resistance properties. Epoxy novolak acrylates are harder materials and have superior resistance properties compared to the standard epoxy acrylates.

The standard epoxy acrylate is a well-known and established raw material. In its undiluted form it is extremely viscous although it is soluble in most monomers and the rate of viscosity reduction is very rapid. Because of their highest reactivity compared to urethane and polyester acrylates, coating used for wood or paper substrates are usually formulated form epoxy acrylates. UV response and curing speeds of these resins varies with their structure. For example, as the distance between the acrylic groups increases, curing speeds and film hardness decrease.

Epoxy acrylate resins are attracting attention because, like conventional epoxy resins, the acrylated epoxies tend to give coatings with good toughness, chemical resistance and adhesion. They have various advantages such as high chemical resistance, high heat resistance, high hardness and high adhesive power. The epoxy component contributes to adhesion to nonporous substrates and enhances chemical resistance of the film [10]. Both, hard and flexible epoxy acrylates are widely used in coating applications such as wood and paper as well as in coatings and inks for difficult substrates. Epoxy novolak acrylates find use in screen printing applications, e.g. for printed circuit boards. Also they are used widely in inks and lacquers for most applications and generally they are used as the main vehicle of a UV curable lithographic ink.

2.2 Polyurethanes

2.2.1 Introduction

Polyurethanes are widely used in coatings, flexible and rigid foams, elastomers, and composites. In an overall sense, the polyurethane business is huge and is concerned with rigid foams, flexible foams prepared in both slab and molded forms, elastomers, including reaction-injection-molded products, and coatings [8]. Polyurethanes are a broad class of very different polymers, which have only one thing in common – the presence of the urethane group:

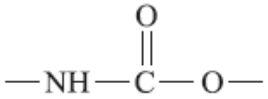


Figure 2.3: Urethane group

2.2.2 The Chemistry of polyurethanes

Polyurethanes are macromolecules in which the constitutional repeating units are coupled with one another through urethane (oxycarbonylamino) groups (Figure 2.4). They are prepared almost exclusively by stepwise addition polymerization reactions of di- or polyfunctional hydroxy compounds with di- or polyfunctional isocyanates.

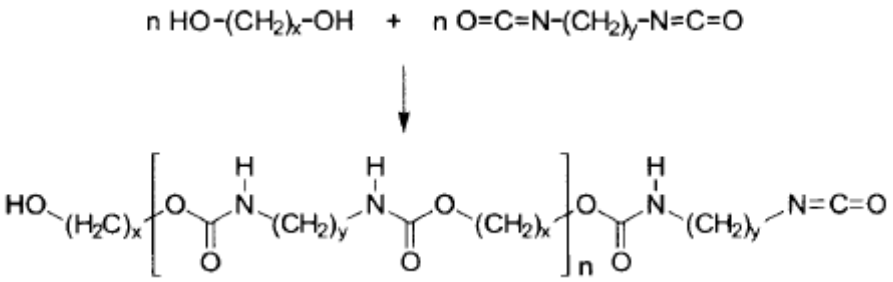


Figure 2.4: Polyurethane general formula

This addition reaction proceeds readily and quantitatively. Side reactions can give amide, urea, biuret, allophanate, and isocyanurate groupings, so that the structure of the product can deviate from that above; such side reactions are sometimes desired. Linear polyurethanes made from short-chain diols and diisocyanates are high melting, crystalline, thermoplastic substances whose properties are comparable with those of the polyamides because of the similarity in chain structure. However, they generally melt at somewhat lower temperatures and have better solubility, for

example, in chlorinated hydrocarbons. The thermal stability is lower than for polyamides: depending on the structure of the polymer, the reverse reaction of the urethane groups begins at temperatures as low as 150-200 °C with regeneration of functional groups; the cleavage of the allophanate groups begins at the still lower temperature of 100 °C. Polyurethanes are predominantly biphasic multiblock copolymers consisting of a sequence of more flexible elastomeric chain segments separated by corresponding hard domains formed by the diurethane groups with intermolecular hydrogen bonds.

A key factor in the preparation of polyurethanes is the reactivity of the isocyanates. Aromatic diisocyanates are more reactive than aliphatic diisocyanates, and primary isocyanates react faster than secondary or tertiary isocyanates. The most important and commercially most readily accessible diisocyanates are aliphatic and colorless hexamethylene-l,6-diisocyanate (HDI), isophorone diisocyanate (IPDI), and aromatic, brownish colored diphenylmethane-4,4′-diisocyanate (MDI), 1,5-naphthalene diisocyanate, and a 4:1 mixture of 2,4- and 2,6- toluenediisocyanates (TDl) [11].

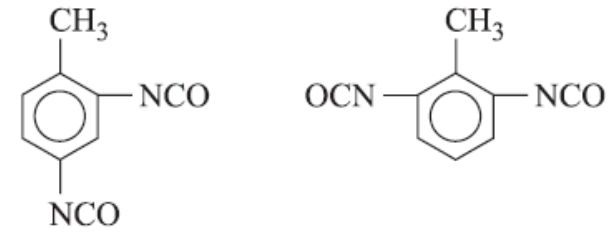
2.2.3 The basic components in urethane technology

2.2.3.1 Isocyanates

Polyurethanes are formed in the reaction of isocyanates with polyols. The most important commercial aromatic isocyanates are toluenediisocyanate (TDI), diphenylmethane diisocyanate (MDI) and naphthalene diisocyanate (NDI), while the important aliphatic isocyanate is hexamethylene diisocyanate (HDI). Cycloaliphatic isocyanates of industrial importance are isophorone diisocyanate (IPDI) and hydrogenated MDI (HMDI).

A number of triisocyanates, such as triphenylmethane triisocyanate, are used in coatings and adhesives. Chemistry and technology of a wide range of isocyanates is given in several books [12, 13].

Toluene diisocyanate is usually supplied as the mixture of two isomers: 2,4-TDI and 2,6-TDI (Figure 2.5) with a ratio 80:20 (called TDI 80) or 65:35 (TDI 65).



2,4-TDI 2,6-TDI

Figure 2.5: 2,4-TDI, 2,6 TDI structures

TDI is a liquid at room temperature, having density 1.22 g/cm^3, boiling point 120 ^{o}C at 1333.22 Pa (1 atm) and melting point 13.6 ^{o}C (TDI 80) or 5 ^{o}C (TDI 65). It is used primarily for flexible foams and different adducts-intermediaries for coatings. Pure MDI is a solid at room temperature, having melting point 39.5 ^{o}C and density 1.18 g/cm^3 at 40 ^{o}C.

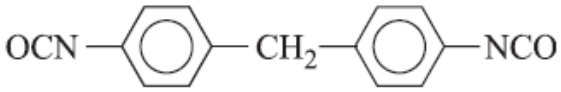


Figure 2.6: MDI structure

In the manufacture of distilled (pure) MDI, a residue is obtained, which contains a mixture of isomers, trimers and isocyanates with a higher degree of polymerization. Such a mixture is a dark brown liquid at room temperature and is called crude MDI or polymeric MDI (PAPI). The dominating species is a triisocyanate with the approximate structure is shown in Figure 2.7.

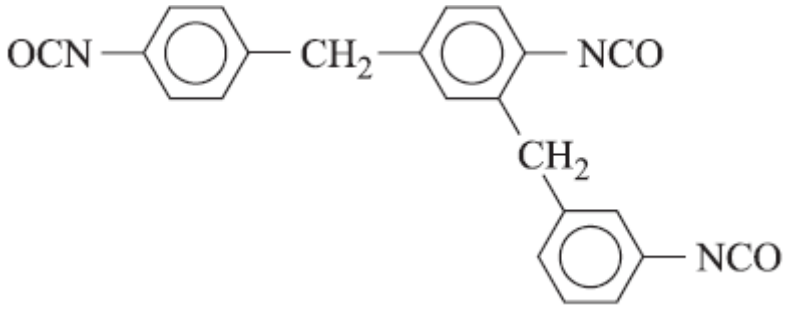


Figure 2.7: Triisocyanate structure

Pure MDI is used mainly for preparation of thermoplastic elastomers, while crude MDI is used for rigid and partly for flexible foams.

Paraphenylene diisocyanate shown in Figure 2.8 is another important isocyanate. It produces excellent elastomers but its use is limited due to a very high price.

Figure 2.8: Paraphenylene diisocyanate structure

Aromatic diisocyanates are not suitable for products that are exposed to irradiation and external influences (such as coatings) because of yellowing. Those applications require aliphatic or cycloaliphatic isocyanates. One popular cycloaliphatic isocyanate is isophorone diisocyanate, a liquid at room temperature (melting point is −60 ^{o}C) having density 1.06 g/cm^3, molecular weight 222 and boiling point 158 ^{o}C at 1333.22 Pa (Figure 2.9).

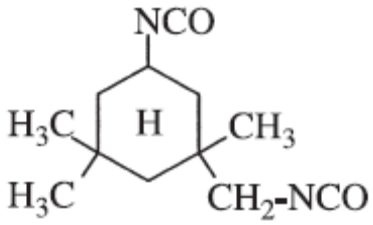


Figure 2.9: Isophorone diisocyanate

The reactivity of an isocyanate group depends on the radical to which it is attached, as well as the position in the molecule. In principle, aromatic isocyanates are more reactive than the aliphatic ones. The reactivity of an isocyanate group in symmetric diisocyanates decreases after the first group has reacted, which should be taken into account [14].

Reactivity also depends on temperature, and sometimes the difference in reactivity of two isocyanate groups may diminish with increasing temperature. This effect is stronger in the cases with higher activation energies.

Reactions of isocyanates can be accelerated either by increasing temperature or adding catalyst. Slowing down the reaction cannot be done by additives if the concentration of isocyanate and polyol is kept constant. Lowering the temperature or diluting the mixture polyol–isocyanate by adding a solvent or neutral diluents would, however, slow down the reaction. Activation energies of the reactions of isocyanates with polyols, as a rule, do not exceed 20–40 kJ/mol. The reaction rates increase with

increasing polarity of the medium (e.g., solvent). The reactivity of different groups, proton donors, with isocyanates decreases in the order: aliphatic NH_2 > aromatic NH_2 > primary OH > water > secondary OH > tertiary OH > COOH. Urea group in R-NH-CO-NH-R is more reactive than amide group, R´CONHR, and amide is more reactive than the urethane group, R-NHCOO-R´. This sequence can be changed if the groups with different steric hindrances are attached.

2.2.3.2 Polyols

Second to isocyanate in the technology of polyurethane preparation is polyol. Most of the polyols used are usually chosen from the general classes of polyesters, polyethers, alkyd resins and acrylics. The structure of the polyol plays a large part in determining the properties of the final product.

Polyether polyols (polypropylene glycols and triols) having molecular weights between 400 and 10,000 dominate in the foam technology. Foams are usually made with triols, which form crosslinked products with diisocyanates, whereas diols dominate in the elastomer technology. Polyether polyols have higher hydrolytic stability than the polyester polyols, but they are more sensitive to different kinds of irradiation and oxidation at elevated temperatures. Polypropylene oxide (PPO) polyols, also called polypropylene glycols (PPG), are cheaper than other polyols. PPG structure can be represented by the formula shown in Figure 2.10.

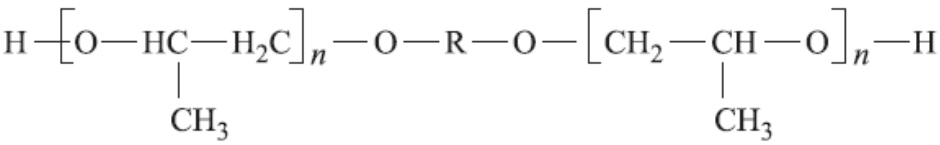


Figure 2.10: Polypropylene glycol (PPG) structure

Group R comes from the starter diol such as ethylene glycol (R= $–CH_2–CH_2–$). If multifunctional starters, such as glycerin, trimethylol propane or sugars are used, the resulting polypropyleneoxide polyol would have the functionality of the starter component.

Due to the weak intermolecular attractive forces (low polarity) and non-crystallizing nature, PPG polyols are liquid at room temperature even at very high molecular weight, unlike polyester polyols, which are often crystalline greases. Weaker interactions on the other hand cause lower strengths of the PPG based urethanes.

Viscosity of polyether polyols is a function of the hydroxyl content (due to hydrogen bonding) and molecular weight. PPO diols have viscosities from 110mPa s (cP) at 20 ^{o}C for the molecular weight of 425 to 1720 mPa s for Mw=4000. Glycerin for example has viscosity above 1000 mPa s at 20 ^{o}C but when propoxylated to Mw=1000 gives a triol with viscosity of about 400mPa s.

Polyether polyols based on polytetramethylene oxide (PTMO), sometimes-called polytetrahydrofurane (PTHF), have better strengths than PPG polyols, mainly due to their ability to crystallize under stress. Their structure is represented in Figure 2.11.

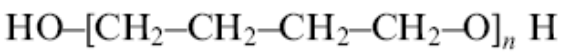


Figure 2.11: Polyether polyol structure

Polyester polyols are an important class of urethane raw materials, with applications in elastomers, adhesives, etc. They are usually made from adipic acid and ethylene glycols (polyethylene adipate) as shown in Figure 2.12.

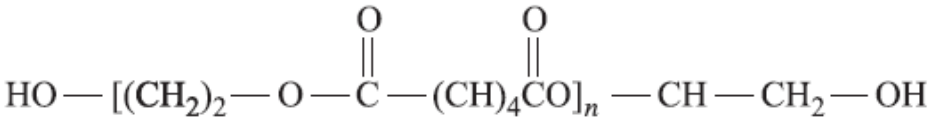


Figure 2.12: Polyester polyol structure

Or they are from butane diol and adipic acid (polybutylene adipate). Both would crystallize above room temperature. In order to reduce their glass transition and destroy crystallinity, copolyesters are prepared from the mixture of ethylene glycol and butane diol with adipic acid. Polycaprolactone diol is another crystallizable polyester diol as shown in Figure 2.13.

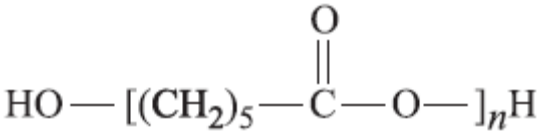


Figure 2.13: Polycaprolactone diol structure

Polyols for coatings, rigid foams, and adhesives may contain aromatic rings in the structure in order to increase rigidity. These polyols may also crystallize, which is important in some applications, e.g., adhesives. Special class of polyols are ‘polymer

polyols' containing usually copolymers of acrylonitrile and styrene or methylmetacrylate attached to the chains of polyether polyols, forming a dispersion. They are used for high modulus products such as froth and integral skin foams, RIM, shoe soles and one-shot elastomers.

An important but less frequently used group of polyols, polybutadiene diols, are mainly used for elastomers:

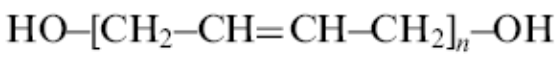


Figure 2.14: Poly-1,4-butadiene (BD) structure

Structural formula (Figure 2.4) shows poly-1,4-butadiene (BD), but 1,2-poly BD and the mixture of the two are also produced.

Castor oil (Figure 2.15) is a natural triol with a typical OH number 160 mg KOH/g (functionality=2.7). Although it has three ester groups, it is not considered a polyester type polyol.

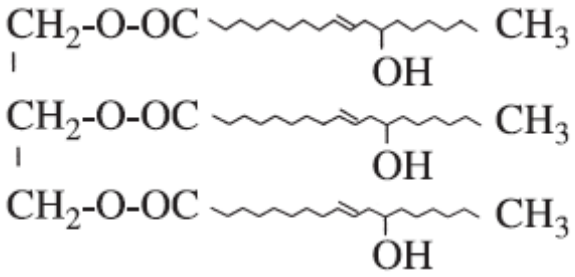


Figure 2.15: Castor oil structure

A new class of polyols from vegetable oils could become a significant player in rigid foam technology. An example is soybean oil based polyols [15, 16]. The structure is shown in Figure 2.16.

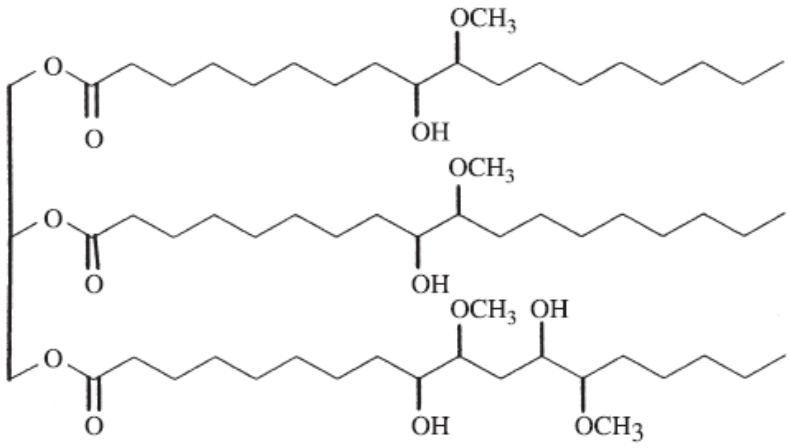


Figure 2.16: Soybean oil based polyol

The advantage of these polyols is their compatibility with hydrocarbon blowing agents, higher hydrophobicity and improved hydrolytic properties of resulting polyurethanes.

They have also better oxidative stability than PPO based polyurethanes, but their viscosity is typically between 2–12 Pa s (2000–12,000 cP). Molecular weight of these polyols is about 1000 and functionality may vary from 2 to 8, but high hydroxyl numbers cause high viscosity. These molecular weights are not sufficient for flexible foams and copolymerization with propyleneoxide and ethylene oxide is necessary to obtain polyols for these applications. Alternative ways of making polyols from triglycerides is by hydrolysis to fatty acids and introduction of OH groups. Although the price of vegetable oils is very competitive with petrochemicals, the number of chemical steps should be minimal in order to have polyols at competitive prices.

2.2.4 Catalysts

Rapid growth of urethane technology can be attributed to the development of catalysts. Catalysts for the isocyanate–alcohol reaction can be nucleophilic (e.g., bases such as tertiary amines, salts and weak acids) or electrophilic (e.g., organometallic compounds).

In the traditional applications of polyurethanes (cast elastomers, block foams, etc.) the usual catalysts are trialkylamines, peralkylated aliphatic amines, triethylenediamine or diazobiscyclooctane (known as DABCO), N-alkyl morpholin,

tindioctoate, dibutyltindioctoate, dibutyltindilaurate etc. Usually a combination of catalysts is required to achieve proper structure and properties, especially in applications such as integral skin foams or reaction injection molding (RIM). The mechanism of the catalysis of isocyanate-alcohol reaction in presence of amines is assumed to proceed through an activated complex between amine and isocyanate as shown in Figure 2.17 [17, 18].

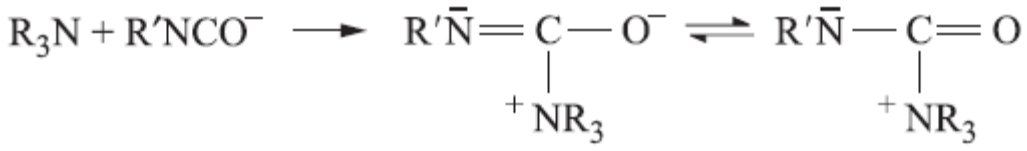
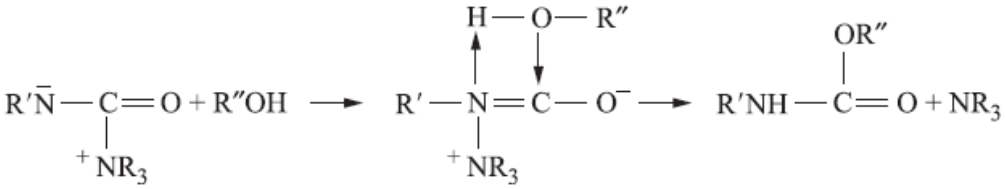


Figure 2.17: The mechanism of the catalysis of isocyanate-alcohol

The complex then reacts with the alcohol to form an intermediary product, which decomposes to give urethane and regenerate the catalyst:



In hydroxyl-containing compounds with higher acidity, a transfer of proton from alcohol to amine is possible. Tin (Sn) catalysts are considerably stronger than amine catalysts, but their mixtures are even more powerful. The reaction rates depend also on the amount of catalyst, which usually is not more than 0.3% in the mixture [19]. The mechanism of metal catalysis is multifaceted and it always involves metal complexes with reacting species, but true nature of the transition states is open to debate [20]. Organometalic catalysts could be lead, zinc, copper, calcium and magnesium salts of fatty acids, such as octanoates or naphthenates. Especially good for application in elastomers are mercury catalysts, since they strongly promote isocyanate–alcohol reaction but are fairly insensitive towards isocyanate–water reaction. Also, they may give long processing (gel) time but once the reaction starts, curing is finished quickly, as required in flooring applications. Gel time can be easily adjusted with catalyst concentration. Unfortunately, mercury is undesirable in many applications.

2.2.5 Polyurethane acrylates

Acrylate-terminated polyurethanes are used in a number of ultraviolet light and electron beam curable formulations. The products are termed "urethane acrylates" or "acrylated urethanes." They are prepared by first forming an isocyanate-terminated prepolymer (Figure 2.18) from a polyol and then end capping the prepolymer with a hydroxy acrylate such as 2-hydroxyethyl acrylate (Figure 2.19). The reactions leading to urethane acrylates are usually carried out in an inert solvent.

In all commercial and most laboratory preparations, there is a significant amount of reaction between the ingredients so that chain extension occurs and molecular weight increases. This causes the final product to have a markedly higher-than expected viscosity. Oligomeric compounds such as these are formulated with triacrylates such as trimethylolpropane triacrylate to provide cross-linking, monomeric acrylates, N-vinyl pyrrolidone, or other compounds for viscosity reduction to provide low-viscosity, essentially 100% solids systems that will cure when exposed to actinic radiation. In formulations, the urethane acrylate is considered as the main ingredient contributing to mechanical properties of the cured film. When the actinic radiation source is ultraviolet light, a photoinitiator (for example, 2,2-diethoxyacetophenone or benzophenone in combination with an amine synergist, etc.) is added as a free radical source. Electron beam curable formulations do not require a photoinitiator. Radiation-cured polyurethanes are often used on plastic substrates that require only low or moderate curing temperatures such as clear overprint lacquers on vinyl decals, electronic circuit boards, *"no* wax" vinyl flooring, and tile. Although radiation-cured colored and pigmented inks and coatings are used in the marketplace, the skill needed in preparing such products, because of difficulty with light penetration or absorption, is readily apparent. [21, 22, 23]

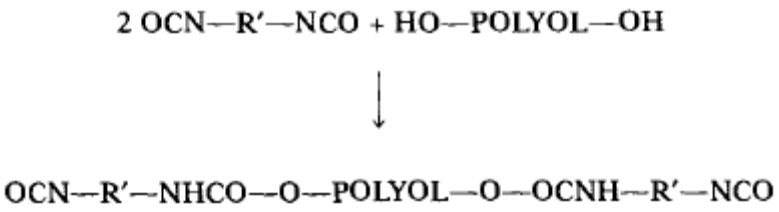


Figure 2.18: Isocyanate-terminated prepolymer

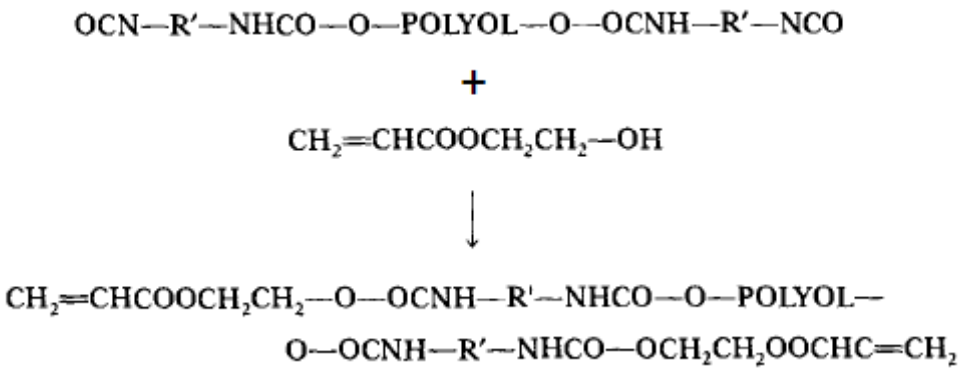


Figure 2.19: Urethane acrylate structure

Acrylated urethane oligomers tend to give coating with a good combination of hardness and elasticity. Any polyol or hydroxy-terminated oligomer can be reacted with excess diisocyanate (OCN-R´-NCO) to yield an isocyanate-terminated oligomer. This oligomer can then be reacted with hydroxyethyl acrylate at ambient or moderately elevated temperature to yield an acrylated urethane oligomer. It has been shown that the gloss retention on exposure to UV of UV cure coating films decreases as the Mw of the diol from which the urethane diacrylate is prepared increases. It is proposed that this reflects a higher crosslink density with the lower Mw oligomers [24]. 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.

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.

Molecular Weight - For di- and trifunctional urethane acrylate, the polyol modifier determines this property.

2.3 UV Coatings

2.3.1 Introduction

Radiation is the term used to describe the passage of energy from a transmitting source to an absorbing body without interaction with any intervening matter. UV radiation has been known to initiate curing for a very long time, although results reported before 1960 may depend upon other mechanisms accelerated by heat produced. [25]

Industrial applications involving radiation processing of monomeric, oligomeric and polymeric substances depend essentially on two electrically generated sources of radiation: accelerated electrons and photons from high-intensity ultraviolet lamps. The difference between these two is that accelerated electrons can penetrate matter and are stopped only by mass, whereas high-intensity UV light affects only the surface. Generally, processing of monomers, oligomers and polymers by irradiation by UV light and electron beam is referred to as curing. This term encompasses chemical reactions including polymerization, cross-linking and surface modification and grafting. The process of conversion of liquid to solid is mainly designed for use on compositions based on nonvolatile monomers and oligomers with molecular weights less than 10,000. These have low enough viscosities to be applied without the use of volatile solvents (volatile organic compound or VOC). This, of course, is very beneficial for the environment — more specifically, the air. In fact, in their

legislative actions, some states have recognized UV/EB curing of coatings, printing inks, paints and adhesives as environmentally friendly [26].

UV/EB processing has another positive side. They both represent a clean and efficient use of electric energy. When compared with water-based technology, another "green" alternative to VOC-based technology, it is found to be far superior in energy consumption. UV irradiation process is the lower-cost option, because the equipment is simpler, smaller and considerably less expensive to purchase and operate.

In industrial irradiation processes, either UV photons with energies between 2.2 and 7.0 eV or accelerated electrons with energies between 100 and 300 kV are used. Fast electrons transfer their energy to the molecules of the reactive substance (liquid or solid) during a series of electrostatic interactions with the outer sphere electrons of the neighboring molecules. This leads to excitation and ionization and finally to the formation of chemically reactive species.4 Photons, on the other hand, are absorbed by the chromophoric site of a molecule in a single event. UV-curing applications use special photoinitiators that absorb photons and generate radicals or protons. The fast transformation from liquid to solid can occur by free radical or cationic polymerization, which, in most cases, is combined with cross-linking. In liquid media, the transformation takes typically 1/100 of a second to 1 second. However, in a rigid polymeric matrix, free radicals or cationic species last longer than a few seconds. A post- or dark-cure process proceeds after irradiation and the result is a solid polymer network [27].

In summary, UV technology improves productivity, speeds up production, lowers cost and makes new and often better products. At the same time, it uses less energy, drastically reduces polluting emissions and eliminates flammable and polluting solvents.

2.3.2 Radiation curing chemistry

The UV light has a wavelength range of 200-400 nm and is a part of the electromagnetic radiation spectrum. UV light is usually characterized by its specific energy emission. Photochemical reactions generally occur through electronically excited states which have definite energy, structure, and lifetime. The total energy of

a molecule at a particular energy state is the sum of electronic excitation energy (E_e), the vibratinal energy (E_v), and the rotational energy (E_r) as follows:

$E = E_e + E_v + E_r$

where,

$E_e > E_v >> E_r$

The intensity of any light absorbed by a light-absorbing species (chromophores) follows Lambert-Beer's Law:

$I = I_0\ 10^{-\varepsilon cd}$

where, I_0 is the intensity of the incident light
I is the intensity of transmitted light
ε is the molar extinction coefficient ($cm^{-1}\ mol^{-1}$)
c is the concentration of absorbing species
d is the optical path length

Absorbance A (or optical density) is defined as $-\log (I/ I_0)$, then $A = \varepsilon cd$.

Typical chromophoric groups for UV light are C = O, ROOH and aromatic groups. These extend the absorption of monomers, oligomers and polymers into the UV light range [28].

The Jablonsky diagram, as Shown in Figure 2.20, can represent the structure of various electronically excited states and the most important photochemical processes involved with these states.

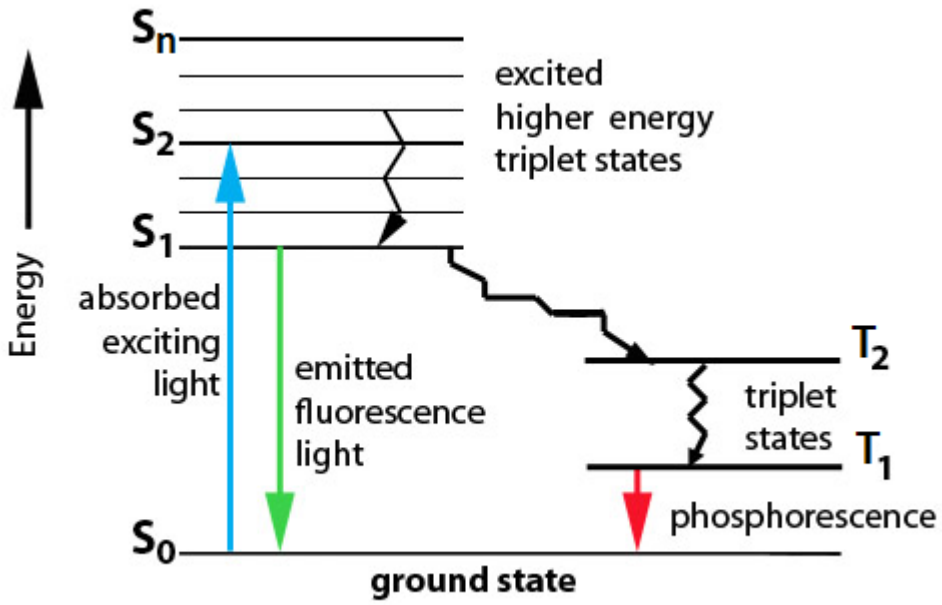


Figure 2.20: Jablonsky Diagram

The ground states of almost all organic compounds have all electron spins paired. Absorption of a photon promotes an electron from the singlet state S_0 to a higher energy singlet state S_1, S_2 … S_n, numbered in the order of increasing energy above the ground state. A change in the spin state of an electronically excited molecule, called intersystem crossing, produces triplet species T_1, T_2 … T_n with two unpaired spins [29]. A triplet state is always lower in energy than the corresponding singlet state. Singlet states may emit light and return to the ground state. To put it simply:

• The absorption of a photon by a chromophore brings about a transition into the excited singlet state.

• Generally, the excited molecule has two possibilities to emit the absorbed energy: It can either return into the ground state by emitting energy by fluorescence or can cross over to the excited triplet state.

• Molecules in the triplet state are biradicals, which can, if the energy is high enough for breaking a bond, form free radicals. The free radicals can then initiate the polymerization and/or cross-linking reaction. The main decay processes to the ground state shown in Figure 2.17, which is essentially an energy diagram for the different electronic states, are:

• Radiative processes:

Absorption: $S_0 + h\nu \rightarrow S_1$

Fluorescence: $S_1 \rightarrow S_0 + h\nu'$

Phosphorescence: $T_1 \rightarrow S_0 + h\nu''$

where h is the Planck's constant and ν, ν′, and ν″ respective frequencies of the absorbed or emitted light.

• Radiationless processes:

Internal conversion: $S_1 \rightarrow S_0$ + heat

Intersystem crossing: $T_1 \rightarrow S_0$ or $S_1 \rightarrow T_1$

The result of a photochemical reaction involving monomers, oligomers and polymers depends on the chemical nature of the material, wavelength of the light and the other components of the system. Ultraviolet, visible and laser light can polymerize functional monomers, cross-link [30] or degrade polymers, particularly in the presence of oxygen [31]. As pointed out at the beginning of this chapter, we will be focusing on the reactions, which lead to useful products.

The UV curing technology is based on the photoinitiated rapid transformation of a reactive liquid formulation into a solid coating film. The initiating species may be a cation, an anion or a radical. The vast majority of UV curable coatings are based on radical producing photoinitiators. The main components of such formulations based on radical polymerizations are:

• Reactive resins containing a plurality of polymerizable double bonds, which govern mainly the desired properties of the final coating;

• Copolymerizable, monomeric diluents, which are responsible for the reduction or adjustment of the viscosity of the formulation, a function taken by the solvent in conventional formulations;

• Photoinitiators or a photoinitiating system containing photoinitiator and photosensibilizer or coinitiators; and, if necessary, other coating additives, like surface active additives, slip additives, fillers, pigments, light stabilizers, etc.

2.3.3 Raw materials for UV coating systems

2.3.3.1 Photoinitiator and photosensitizer

Essentially two types of compounds are used in the UV curing process to absorb the light and generate reactive species. These are photoinitiators and photosensitizers. A

photoinitiator (PI) is a compound-generating reactive species that will initiate polymerization or cross-linking. A photosensitizer (S) is a compound that will energize certain species that will, in turn, lead to production of reactive species. It is a molecule that usually absorbs light at longer wavelengths and transfers energy to a photoinitiator to generate free radicals or ions.

PI → PI* → Reactive species (free radicals or ions), or

S → S*

S* + PI → S + PI* Energy transfer to photoinitiator

Thus, photosensitizers are useful mainly by being capable of extending the spectral sensitivity of certain photoinitiators under specific conditions.

The function of a photoinitiator is:

• Absorbing the incident UV radiation
• Generation of reactive species (free radicals or ions)
• Initiation of photopolymerization

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

The photon absorption follows Lambert-Beer's Law. The number of photons *I* presents at depth *l* from the surface is given as a function of the optical absorbance, A, normalized to the initial number of photons I_0:

$\log(I_0/I) = A = \varepsilon [PI] l$

where [PI] is the concentration of photoinitiator. The quantity l is also termed the photon penetration path.

In general, upon exposure to UV radiant energy, a photoinitiator can generate free radicals or ions, as pointed out earlier. These are generated at a rapid rate and their depth profile corresponds to the inverse photon penetration profile. Similar to electron penetration, the final cure profile often deviates from the initial radical or ion distribution because they can live much longer than the exposure time.

Depending on the type of reactive species generated upon exposure to UV light, photoinitiators are classified as free radical, cationic and anionic.

Free radical photonitiators

The UV curing of certain monomers, such as acrylate, methacrylate and maleate/ vinyl ether systems, is initiated by free radicals. In all practical cases, the initiating radicals are generated from electronically excited photoinitiator molecules [32, 33].

A photoinitiator molecule is excited into the singlet state by the absorption of a photon. The formation of a radical occurs via a triplet state. Radical formation occurs via two possible reaction sequences that are designated as Norrish Type I and Type II reactions. In Type I reaction, the photoinitiator triplet state decays into a radical pair by homolytic decomposition and directly forms radicals capable of initial polymerization. The absorbed radiation causes bond breakage to take place between a carbonyl group and an adjacent carbon. In Type II reaction, triplet states of ketones possessing an α hydrogen preferably react with suitable hydrogen-donating compounds by hydrogen abstraction. The resulting radical pair can be generated either by a homolytic cleavage of the R-H bond or via an intermediate charge transfer complex followed by proton transfer [34]. The lifetime of the excited initiator species is very short, generally less than 10–6 s. During this time, it can be partitioned essentially between two processes: (1) It can decay back to the original state with emission of light and heat or (2) yield a reactive intermediate (free radical or ion) that, in turn, can react with another free radical or initiate polymerization of a monomer [35].

Cationic photoinitiators

Cationic photoinitiators are compounds that, under the influence of UV or visible radiation, release an acid that, in turn, catalyzes the desired polymerization process [36]. Initially, diazonium salts were used, but they were replaced by more thermally stable iodonium and sulfonium salts [37].

Anionic photoinitiators

Tertiary amine salts of ketocarboxylic acids [38] were used initially. Newer systems based on peptide chemistry have been described and used in microlithography [39].

2.3.3.2 Oligomers

Unsaturated polyesters

Unsaturated polyesters were among the earliest commercially available radiation curable systems. Such unsaturated polyesters (UPE), derived by the condensation reaction of maleic or fumaric acid with various diols, dissolved in styrene, were the earliest used UV curable resins. Styrene/unsaturated polyester system is relatively slow but inexpensive and therefore has been used extensively for wood coatings, yet there is a tendency to replace them by acrylates [40]. Because of the toxicity of styrene, these systems are not used extensively any more. Multifunctional acrylates, like TPGDA or TMPTA, have been used instead of styrene as a reactive diluent in UPE resins for adhesives and ink applications. Recently, powder resins based on unsaturated polyesters have been introduced, obtained by mixtures of UPE with vinyl ether polyurethane crosslinkers [41] or mixtures of UPE with allyl ether polyesters [42].

Epoxies

Epoxy resins are mainly used together with cationic photoinitiators. The main advantage of epoxy oligomers is that they are not inhibited by oxygen; however, polymerization is inhibited by the presence of strong nucleophiles such as amines. Since epoxy groups can be attached on differently structured backbones and combined with other photosensitive groups, several tailor-made photosensitive resin alternatives.

The physical properties of these polymers depend upon the backbone structure of the epoxy resin and upon the achieved crosslink density. By comparison, of the glass transition temperatures, T_g, of crosslinked epoxy resins based on bisphenol-A diglycidilether polymerized via thermal, cationic or anionic vs. photoinitiated polymerization, it has been shown that average crosslink densities are similar in all cases and is in the range of 3-5 [43].

Standard acrylate terminated oligomers

The acrylate resins now dominate the market. The schematic structure of the main acrylate terminated resin classes is shown in Figure 2.21.

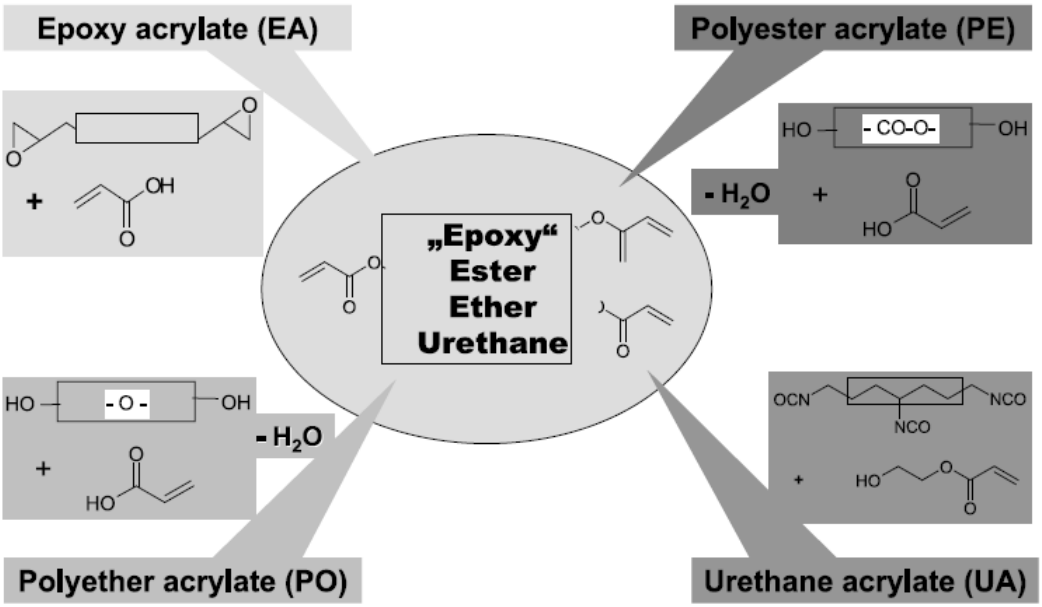


Figure 2.21: Schematic chemical structure of main acrylate resin type

The most widely used oligomers are aromatic and aliphatic epoxy acrylates. Epoxy acrylates are highly reactive and produce hard and chemically resistant films. They are prepared by the reaction of epoxides, e.g., Bisphenol-A diglycidylether, with acrylic acid.

The epoxy acrylates are distinguished by a high reactivity and the cured coatings exhibit good chemical stability. The epoxy component contributes to adhesion to nonporous substrates and enhances chemical resistance of the film [10]. Main uses are paper coatings and inks as well as wood coatings.

Urethane acrylates are simple addition products of multifunctional isocyanates, like toluene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate or their condensation products, e.g., isocyanurates, biurets, allophanates, with polyols and hydroxyalkyl acrylates, for instance, hydroxyethyl acrylate, hydroxybutyl acrylate or pentaerythritol triacrylate. Since the addition reaction proceeds very well, the coatings or ink formulating companies produce a large portion of the urethane acrylates captively. However, also a large variety of different urethane acrylate resins are available by the raw materials suppliers. The applications are mainly on plastics, with the dominant application on PVC floor coverings, wooden parquet, screen inks and optical fibers. These applications require good optical properties and non-yellowing behavior, thus more than 80% of the used urethane acrylates are based on

aliphatic isocyanates. Urethane acrylates with low functionality exhibit a high flexibility and are often based on flexible polyester or polyether diols, which are reacted with bifunctional isocyanates and endcapped with hydroxyalkyl acrylates.

Since the viscosity of the urethane acrylates is relatively high, they are often diluted with reactive thinners like TPGDA or HDDA. However, if the flexibility of the coatings should be increased, rather than using flexible diols, monofunctional diluents, like ethylhexyl acrylate, 2-(2-ethoxyethoxy) ethyl acrylate or trimethylolpropane-formal-monoacrylate are also used. The higher functional urethane acrylates are often used to obtain hard, scratch and chemical resistant coatings.

Besides the good mechanical properties, these aliphatic type urethane acrylates exhibit good weatherability and do not yellow upon exposure to exterior conditions. Thus, they are the preferred class of resins for exterior applications. The structure of the urethane acrylates can be designed to the required properties by choosing the right balance of hard phase and soft phase, by tuning the setscrews molecular weight, glass transition temperature and crosslink density. The compilation of the desired properties of urethane acrylates, however, reveals that the individual measures are often diametrically opposed and that a compromise always has to be made in order to adjust the most desired properties. After UV cure, they produce tough, flexible materials that exhibit good abrasion resistance.

Acrylated polyesters are prepared by reacting the OH group of polyesters with acrylic acid or hydroxy acrylate with acid groups of the polyester structure. Polyester acrylates are often low-viscosity resins requiring little or no monomer [44].They produce coatings and adhesives dominated by the polyester structure used in the oligomer. They are used for pressure sensitive adhesives and also for strong rigid adhesives for metal-to-metal bonding. Amino-modified polyester acrylates show a high reactivity and low skin irritation. The molecular weights of such resins are typically in the range of 500–2000 g/mol.

There is a large variety of polyester acrylates available on the market. These resins are mainly used in wood coatings and paper coatings, and to a lesser extend in inks. The polyester acrylates used in wood coatings are mainly applied in top and undercoats.

Polyether acrylates are produced by esterification of polyetherols with acrylic acid. Amino-modified polyether acrylates have a higher reactivity and low skin irritancy, similar to polyester acrylates. Polyetherols often used are ethoxylated or propoxylated glycerol or trimethylol propane. Such polyether acrylates represent a class of resins of low viscosity, and do not require reactive thinners. They can be used as sole resins as well as reactive diluents.

Several other types of oligomers useful for UV curable systems have been reported in the literature. These systems are especially interesting due to their performance advantages. Dendritic and hyperbranched resins Dendritic polymers have gained attractiveness because of their unique structure as well as unique properties compared to their linear or branched homologues. Miscellaneous resin types Self-initiating UV-curable resins have been introduced recently [45]. They are obtained by the Michael addition-type reaction of beta keto esters to diacrylates. This chemistry is very versatile to the design of new UV-curable resins that do not need an additional photoinitiator. Silicon based oligomeric (meth)acrylates are used in so-called hybrid polymers based on sol–gel reactions, where an inorganic network is obtained via the siloxane condensation and an organic network via the UV or thermal polymerization of reactive groups like acrylates or methacrylates. Dual curing (UV initiated and thermal) resins can be performed by using blends of the classical resins, like acrylate terminated oligomers and polyisocyanates/polyol or melamine–formaldehyde/polyol combinations. In addition, water-based systems and polyenes are some of the other oligomers.

2.3.4 Kinetics of free radical photopolymerization

Photoinitiated free radical polymerization proceeds via three main steps:

1. Initiation

2. Chain propagation

3. Termination

The initiation rate v_i depends on the radical yield per absorbed photon Φ and the number of photons absorbed per second, I_a. The latter quantity is a fraction of I_0, the number of photons per second entering the process zone.

Initiation step: $AB^* \rightarrow \bullet R1 + \bullet R2$ (•R1, •R2 – free radicals)

$$\bullet R1,\ \bullet R2 + M \rightarrow \bullet P1$$

Initiation rate: $v_i = \Phi\ I_a$

In the chain propagation, the monomer is consumed and the propagation rate depends on the monomer concentration [M] and the concentration of polymeric radicals [•P]. The quantity k_p is the propagation rate constant.

Propagation step: $\bullet P_n + M \rightarrow \bullet P_{n+1}$

Propagation rate: $v_p = k_p.[\bullet P_n]\ [M]$

Chain termination occurs by combination or disproportionation of different polymer radicals. The termination rate v_t is proportional to the polymer radical concentration $[\bullet P_n]$ squared, with k_t being the termination rate constant.

Other possible chain termination processes are chain transfer and reaction of polymer radicals with inhibitors and radical trapping.

Termination step: $\bullet P_n + \bullet P_m \rightarrow P_n - P_m$

or $P'_n - P_m$ (chain transfer)

Termination rate: $v_t = k_t\ [\bullet P_n]^2$

Since $v_i = v_t$, then $v_p = k_p / (k_t)^{1/2}\ [M]\ (\Phi_i\ I_a)^{1/2}$

thus $v_p \sim I_0\ (1 - \exp\ (-2.303\ \varepsilon\ [PI]\ l))^{1/2}$

The assumptions made to estimate the propagation rate v_p, which is essentially the rate of the polymerization reaction, are:

• The light used is monochromatic and is absorbed by the photoinitiator exclusively.

• The absorption is small and homogeneous within the irradiated volume.

• As the polymerization proceeds, a stationary radical concentration is obtained.

• All polymer radicals exhibit the same reactivity toward propagation and termination [10].

2.3.5 Kinetics of cationic photopolymerization

Cationic polymerization is initiated either by strong Lewis acids such as BF_3 or PF_5 or by Brønsted acid such as H^+BF_4, H^+PF_6 or H^+SbF_6. Lewis acids are generated by

UV irradiation of aryldiazonium salts, whereas, upon UV irradiation, diaryliodonium, triarylsulfonium and triarylselenium salts produce strong Brønsted acids. The latter are preferred as initiating species in cationic polymerization [46].

Reaction steps in a photoinduced cationic polymerization are as follows:

Initiation:	H^+X^-	$\rightarrow H-M^+ + X^-$
Propagation:	$H-M^+ + nM$	$\rightarrow H-(M)_n-M^+$
Chain Transfer:	$H-(M)_nM^+ + ROH$	$\rightarrow H-(M)_n-M \rightarrow OR + H^+$
Termination:	$H-(M)_nM^+ + A^-$	$\rightarrow H-(M)_n-MA$

In the initiation step, the monomer M is initiated by intermediate protonation followed by the formation of a carbocation $H-M^+$. Propagation can be terminated by anionic or nucleophilic species A^-. If a hydroxy-functional compound (ROH) is present, chain transfer can occur via proton formation.

2.3.6 UV coating process

2.3.6.1 Introduction

The UV curing process is predominantly determined by the desired application of the coating. The intended end-product governs the substrate to be coated. This may be an abrasion resistant clear coat for ready-to-install parquet or an overprint varnish for paper cards, a colored base coat and a clear coat for plastic automotive parts or metal coils, as well as a flexible protective coat for window frames.

The function of the coating, for instance the coloration of the part, the protection against corrosion, scratching, and chemical attack or against weathering deterioration, determines the type and property requirements of the coating as well as the thickness required.

2.3.6.2 Coating application processes

The application of the UV coating to the substrate is usually done in automated processes. There are several application processes in operation, which are very well described in the literature [47]:

1. Roll coaters and curtain coaters, used for flat-panel production;

2. Airless or conventional spray guns, used for three-dimensional or shaped objects;

3. Vacuum coaters;

4. Electrostatic application.

The typical UV formulations are in a viscosity range (<4000 mPa s) to be used preferably in roll and curtain coating applications. The very low viscosities needed for spray coatings (less than 500 mPa s) are hard to obtain without the use of solvents or high amounts of diluents.

2.3.6.3 Uv curing equipment

Well over 100,000 high intensity ultraviolet curing units are in industrial use. Their main applications are surface curing of inks, coatings and adhesives. They typically operate in the 200–450 nm wavelength range, with lamp electrical power input as high as 240 W/cm (600 W/in.) [26].

The UV curing equipment consists essentially of the following three components:

1. The lamp (or bulb). The electrical energy supplied to the bulb is converted into UV energy inside it.

2. Lamp housing. The housing is designed to direct and deliver to the substrate or the part to be irradiated. The lamp housing reflects and focuses the ultraviolet energy generated by the lamp.

3. The power supply. The power supply delivers the energy needed to operate the UV lamp.

A typical UV curing unit might house one or more lamps. Most frequently, the material to be cured is passed by or under one or more lamps via a moving belt. The speed determines how long the surface is exposed to the light. The light generated by the lamp is reflected by a reflector that can either focus or defocus it, depending on the process.

2.3.7 Advantages and drawbacks of UV coatings

From the many advantages and disadvantages mentioned in the literature, some of the most important are listed below [25]:

Economical advantages

• Energy saving (commonly rapid cure at room temperature)

• High production speed

• Small space requirements

• Immediate post cure processing possible

Ecological advantages

• In general solvent free formulations (VOC reduction)

• Possibility of easy recycling (waste reduction)

• Energy saving

Performance advantages

• Low substrate heating

• High product durability

• Application versatility

• High scratch resistance and chemical resistance

• Exceptional abrasion, stain and solvent resistance

• Superior toughness

Drawbacks

• Material costs are higher than, e.g., alkyds, polyesters or epoxies

• 3D curing equipment development is in its infancy

• UV curing in the presence of UV stabilizers decelerated

• Oxygen inhibition at the surface (in many radical curing systems)

• Sensitivity to moisture (cationic curing system)

• Difficult through-cure of pigmented coatings (at thicknesses >5 μm)

Topics to eliminate weaknesses

• Improving adhesion to metal, plastics

• Minimizing skin irritation caused by some reactive diluents

• Reducing odor (of the formulations)

• Reducing extractables of cured coatings

• Improving photoinitiators (cost, migration, volatility)

• Direct food contact packaging approval

While the advantages and good performance characteristics of this technology are very obvious, the reasons for the limited penetration into large volume coating applications must lie in some substantial disadvantages. Major reasons are the limited availability of three-dimensional curing equipment, the very limited use of UV cured coatings in exterior applications, due to the existing paradigm, that UV curing would not be possible in the presence of UV exterior durability stabilizers, and higher material costs compared to conventional coatings.

2.3.8 UV curing applications

2.3.8.1 Introduction

UV curing hardware is available in a multitude of different sizes, designs, power, in-line, off-line, in combination with large coating or printing machines, together with alternative drying equipment, and stand-alone units. The selection of the type of UV curing equipment is then done with regard to the process, including the substrate, the coating, paint, adhesive or ink to be used and the configuration of the part to be irradiated. Substrates to be irradiated can be two-dimensional or three-dimensional, or the application can require only the irradiation of small areas (spot cure). The UV curing system can also be part of a robotic application.

UV curing is used for special coatings, paints, inks, adhesives, and in other special areas.

2.3.8.2 Functional and decorative UV coatings

Coatings are either clear or pigmented. Coatings for paper include clear coats for laminated paper on pressboard (wood-grain papers to simulate natural wood). High-gloss overprint varnishes for magazine covers, record jackets, and other consumer items are also often radiation-cured. Plastic coatings for interior and exterior

applications are also an important use segment. Important factors are cost, adhesion, weatherability, and availability of raw materials.

Electronics applications are important; photoresists (both wet and dry film), solder masks, potting compounds, and conformal coatings are products based on UV-curable materials. Optical fibers have been coated with a protective layer of UV-curable materials for a long time [48].

Coatings on flat, rigid substrates

UV-curable coatings are applied to a variety of flat rigid substrates, such as particle board, medium- and high-density fiberboard, wood veneers, polycarbonate, poly(methylmethacrylate), paper and metal sheets and foils. UV curing units are anessential part of the coating line, consisting typically of the following main components [49, 50]:

• Infeed

• Substrate preparation

• First coating station

• First UV curing unit

• Second coating station

• Second UV curing unit

• Last coating station

• Last UV curing unit

• Outfeed

UV Curing of coatings on flexible substrates

Coatings for flexible substrates are most often reactive systems that contain no solvents. Because they are usually highly viscous, they tend to produce a rough surface. Therefore, the selection of the proper application method and additives is crucial. The selection is determined by the following factors [51]:

• Coat weight (layer thickness)

• Coat viscosity and viscoelasticity

• Coat weight accuracy to ensure uniform cure characteristics

• Coating speed

• Substrate to be coated

2.3.8.3 UV curing of lacquers, varnishes and paints

The coatings include clear overprint varnishes, finish coatings for PVC, waxless flooring, finish coatings for paper and film applied as laminates in wood decoration, and transparent functional coatings with special characteristics such as high abrasion resistance, barrier properties, conductivity and chemical resistance. Coat weights of clear varnishes and lacquers may vary from 2–5 g/m^2 for typical overprint applications and from 10–100 g/m^2 for finish and functional coatings. Because of the relatively low coating weights, gravure and reverse roll coating methods are used in most cases [52].

2.3.8.4 Inks

Radiation-curable inks are applied to metal, paper, wood, and plastics. Lithographic (offset) and screen printing inks are the most important printing inks. Flexographic inks are already used on narrow web printing presses and are starting to find success in wide web applications. Presses have been modified to be able to print inks with a higher viscosity than conventional flexoinks. Intaglio inks (special inks used to avoid counterfeiting of items such as bank notes) are also employed and ink-jet printing with UV-curable materials is starting.

2.3.8.5 Adhesives

Adhesives are well established, mostly in lamination. Radiation-curable adhesives represent a small but growing segment of the overall radiation curing market because they represent an attractive alternative to solvent based, water-based and hot-melt adhesives. Structural adhesives, pressure-sensitive adhesives (PSA), laminating adhesives and transfer metallization adhesives can be radiation cured. Commercial adhesive products made on UV/EB equipment include pressure-sensitive tapes and labels, laminated foils and films, flocked materials for automotive and shoe applications, structural bonding adhesives and abrasive bonding systems. Technological and cost advantages of these adhesives is that they are single component materials that can be distributed with automatic dispensing equipment,

have long open time and low energy requirements, exhibit fast cure rates, and have the ability to precision bond and input to temperature-sensitive substrates at low heat [53].

2.4 UV Curable Systems in Printing and Graphic Arts

2.4.1 Introduction

UV curable systems used in graphic arts applications are divided into the categories of printing inks, containing pigments or dyes, and clear coat overprint varnishes (OPV). UV-curing inks and varnishes continue to grow in popularity and can still be regarded as new developments. This market in imaging, as inks, as well as overprint coatings/varnishes is by far the largest of all coatings applications [25].

The objective of printing is to create a visibly identifiable image that is consistent for a large number of impressions. In principle, this can be done with a printing plate; the various printing methods are named after the nature of the printing plate. Many techniques have been developed for this purpose. Flexography, lithography and gravure are the main printing techniques and these account for the vast majority of printing applications involving UV curing processes. Each of these printing methods has a number of variations.

Worldwide, graphic arts are a well established application for UV curing. Essentially, the processes used in the graphic arts include the generation of images to be reproduced onto the printing plate, silkscreen, etc., and the use of radiation curable inks and overprint varnishes. Many imaging processes rely on the exposure of materials to radiation to bring about the change in solubility in a solvent system (organic or aqueous), thus enabling exposed and unexposed areas to be differentiated. The differentiation between exposed and unexposed areas can lead to selective delamination, softening, tackiness (which may affect the adherence of toner powders) or a change in refractive index, which leads to holographic effects) [25].

2.4.2 Printing inks

Inks contain a colorant (dye or pigment), resin binders, carrying vehicles (solvent or water) and additives (catalysts, wetting agents, waxes). The printing ink market worldwide accounted for about 4% of the entire coating consumption, calculated to

about 1 million tons in the year 2000. In the US the value of shipped inks was about $ 5 billion in 2001, the most expensive components being the coloured pigments (about $ 800 million), whereof carbon black accounts for about 70%. The ink demand of end-use markets was largest for packaging (36%), commercial printing (33%) and publishing (23%) [54]. From a technology point of view, solvent-based inks have been popular in the past, but due to environmental concerns printers have been driven to water-based inks wherever possible. However, nowadays UV curable inks are desirable because of low VOC, fast cure, higher gloss and better chemical and rub resistance. UV-curable inks are mainly used in commercial screen, lithographic (offset) and letterpress/flexographic printing.

2.4.2.1 UV inks for screen-printing

Screen-printing is the largest printing application. With screen-printing, unlike other printing methods, all types of substrates, like paper, plastics, textiles, metals, leather, wood, ceramics or printed circuit boards, can be coated. Major applications of screen-printing are labels, signs, decals, optical disks (CD, DVD) and book covers. Typical products are display printing, industrial and container printing and printed circuit production [55].

2.4.2.2 Flexography

Flexographic printing is mainly used for flexible substrates, cardboards, paper, or labels. UV inks are experiencing high growth rates in flexographic printing applications [56]. Due to low viscous, 100% materials, exceptional image sharpness and excellent end use properties, like rub and chemical resistance can be achieved. UV flexo inks do not change consistency during processing in contrast to solvent-borne (evaporation) or water-based (pH changes) inks. Flexography is used mainly for package printing.

2.4.2.3 Lithographic or offset printing

Lithographic or offset printing is based on the use of hydrophilic oxidized aluminium plates containing the images brought about with the aid of a photolithographic process. The image areas are therefore hydrophobic and the hydrophilic areas are wetted with water in order to repel the hydrophobic (often oil-based) ink. During the

printing process the ink is offset (transferred) from the plate to a rubber cylinder and finally to the substrate. Offset is the largest printing application, however, UV-curable systems still have a very small share.

2.4.3 Over print varnish (OPV)

Varnishes and coatings comprise a major port ion of the market of UV curing products . Varnishing of printed material is carried out to provide protection and promote gloss. Ultra-violet roller coat varnishes almost achieve these criteria for gloss and lay, while the UV printing viscosity products although an order of magnitude lower in gloss are still superior to conventional oleoresinous or emulsion varnishes. A UV varnish may be required to coat any of the multitude of substrates in general use in the industry [57].

Radiation-cured overprint varnishes are clear coats applied, for example, on printed cartons (e.g., cosmetic boxes), magazines, catalogues or book covers, greeting cards, labels or CD, DVD jackets. The varnishes are usually applied inline after the lithographic/offset (cartons and covers) or flexographic printing (labels, flexible packaging) process in which interactions between ink and coating systems have to be carefully adjusted. Less often the coatings are applied in a separate coating step after printing.

The major features of overprint varnishes are depicted in Figure 2.22 [25].

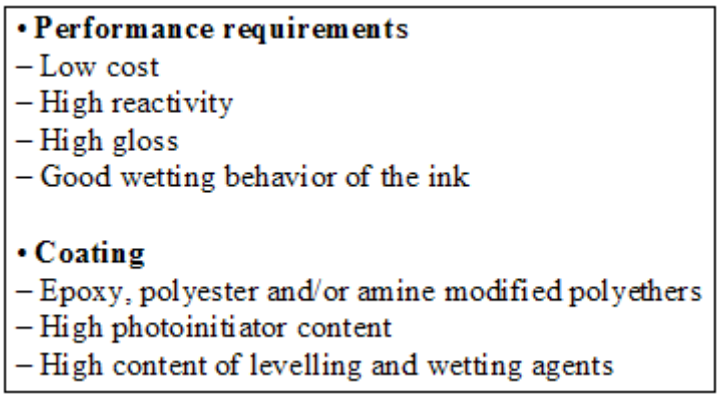


Figure 2.22: The major features of overprint varnishes

The performance requirements of high curing speed and low cost necessitate the employment of relatively cheap resins, and since applied in high concentrations, cheap photoinitiators.

2.4.4 Raw materials for radiation curable systems in printing inks

Radiation curing inks are basically formulated in the same way as any other ink –that is to say, they are composed of pigment, binders, diluents and additives necessary for specific applications. In these inks, the binders are generally acrylates of some sort. The diluents are also acrylates and non-volatiles. The additives in addition to the normal waxes and surfactants include photoinitiators and photoactivators in the case of UV inks.

2.4.4.1 Prepolymers

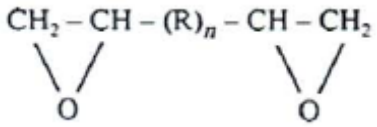
Activated carbon-carbon double bonds can be introduced into a resin structure via a number of readily unsaturated compounds. However, the rate of reactivity for an alkene group in a free-radical polymerization reaction is very sensitive to the nature of its neighboring groups. As far as the printing industry is concerned, it has been chiefly resins with acrylate functionality that have provided the necessary reactivity to bring about adequate cure at the throughput rates demanded by modern high speed presses. Table 2.1 lists the three main resin types that have provided the prepolymer.

Table 2.1 : Some acrylated prepolymers

Resin type	Typical properties
Epoxy acrylate Polyurethane acrylate Polyester acrylate	Inexpensive, fast curing Toughness, chemical resistance Low viscosity, good pigment wetting

Epoxy acrylates

Epoxy acrylates are prepared by the reaction of an epoxy group with acrylic acid. Generally the reaction produces medium to high viscosity fluids which have a fast cure rate and will act as the main vehicle of a lithographic ink. The most widespread type of resin used for inks is prepared by acrylating the diglycidyl ether of bisphenol A. Often, to ease handling during processing, this will be supplied diluted in one of the commonly used monomers to reduce viscosity. Many epoxy resins may be acrylated, the important reactive group being the hydroxyl groups(s). If we generalize an epoxy as:



Then each R contains one hydroxyl group, and in the general formula, there will be n hydroxyl groups. For the reaction, we must use n equivalents of acid, together with a small percentage of catalyst (e.g. triethylamine) and an appropriate inhibitor. These will be reacted together with heating until the acid value has reached the appropriate low level. Care must be exercised throughout to avoid gelatin, which can occur very rapidly.

A disadvantage of epoxy acrylate resins is their comparatively poor pigment -wetting ability. Consequently, UV inks based entirely on simple epoxy acrylate resin tend to have low gloss and poor lithographic performance. Improved pigment wetting, and at the same time enhanced substrate adhesion, may be obtained from resins with residual hydroxyl functions.

Notable features of such a structure arc the rotational flexibility imparted by the bisphenol A group, the chemical inertness of ether linkages and the hydroxyl sites which enhance adhesion and wetting while providing centers for further reaction if required. For example, to improve lithographic performance further, these residual hydroxyl functions are sometimes esterified with long-chain fatty acids.

Polyurethane acrylates

Inks and varnishes formulated on urethane resins are noteworthy for their toughness and chemical resistance. Urethane acrylates provide a class of resins for UV-curable products, which more or less retain these desirable characteristics. Products derived from resins based on aliphatic isocyanates have good color retention on exposure to light or on stoving. These resins, however, are rather expensive. The somewhat cheaper aromatic urethane acrylates suffer the drawback that they tend to yellow significantly on exposure to light or heat.

An urethane acrylate prepolymer can he prepared by reading isocyanate groups from an urethane resin with, for example, hydroxyl ethyl acrylate:

$$OCN - R - NCO + 2(HO - R') \rightarrow R'OCONHRNHCOR'$$

where R is the urethane backbone.

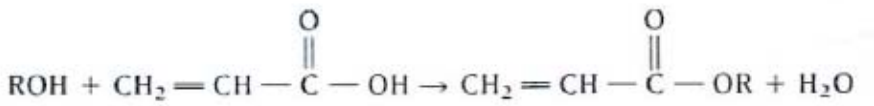
For the simplest case where R is an aromatic di-isocyanate, such as toluene diisocyanate (TOI). a lack of molecular flexibility leads to high viscosity resins. Generally, therefore, prior to acrylation, the isocyanate is chain extended by reaction with a polyol or alternatively with polyester or a polyether which itself has residual hydroxylic functionality. In this way complex mixed prepolymers often, with extensive branching, can be constructed.

Polyester acrylates and unsaturated polyesters

The wide range of comparatively low-cost polyesters that are available as precursors make these an attractive group of radiation-curable materials. Chemical and physical properties are very varied. General polyester prepolymers provide good pigment wetting and consequently make good inks with, if required, excellent lithographic performance. Their adhesion, particularly to non-porous substrates such as tinplate and plastic, is especially noteworthy.

The intrinsic ester linkages are more labile than are ethers thus when contrasted with epoxy acrylate the polyester acrylates tend to give products with inferior chemical resistance, particularly towards alkali. Furthermore, especially for the lower molecular weight polyester acrylates, reactivity can be poor and surface oxygen inhibition effects can be a serious problem. On the positive side, an advantage with many polyester acrylate prepolymers is that they have a low or relatively low viscosity. They may thus be used to replace part or all of a diluent monomer in a formulation.

Preparation is either by reaction of acrylic acid with residual hydroxyl groups from a polyester precursor or by reading residual acid groups from a polyester resin with a hydroxyl acrylate such as 2-hydroxy ethyl acrylate. For example :



where R is the polyester condensation product from a polyol and a polybasic acid and contains one or more residual hydroxyl or acid functions. However, in practice the esterification process is by no means simple.

The volatility and instability towards spontaneous polymerization inherent with acrylic acid and its derivatives limit permissible reaction temperatures to under 100^{o}C. To drive the esterification towards completion strong acids, for example methane sulphonic acid, are required. These have to be removed from the final product together with any excess acrylic acid.

To remove the water formed, azeotroping solvents such as benzene have to he introduced and subsequently removed.

Unsaturated polyesters are typically cheaper products, and have tended to be used in applications such as wood finishing. Some more specialized products are finding limited use in both inks and varnishes, however.

Acrylated polyols and polyethers

Resins which contain ether linkages that derive from polymerization of epoxides are customarily called epoxide resins by reference to their origins. Of considerable importance are the polyether acrylates derived by chain extension of simple polyol, prior to acrylation. Usually extension is limited to only a few ether units and these products are thus often termed oligomers.

These polyether acrylates and the products derived by direct acrylation of polyols are often comparative by low viscosity liquids. It is possible, particularly in a varnish formulation, for the vehicle system to be comprised almost entirely from such molecules.

2.4.4.2 Reactive diluents

Diluents are materials used to reduce the viscosity of formulation to levels suitable for the required method of printing. They may also he needed to solubilize a solid prepolymer and they certainly contribute to pigment wetting.

A diluent can be a non-reactive solvent which is either ultimately lost from the formulation by penetration and evaporation or else remains in the cured film as a plasticizer. In UV technology, however, diluents are more frequently species, which have acrylate functionality and are thus capable of copolymerizing with the main resin system to provide a 100% solid formulation. Potentially there are a large number of molecular species, which could function as reactive diluents. While these may vary in the number of acrylate groups they possess and can be complex

branched structures, they are usually distinct from resins in that they are discrete molecular unite. Hence the term 'monomers' is often applied to them.

In practice, the numbers of monomers that are acceptable for use by the printing industry are comparatively few. Many good viscosity-reducing acrylates are eliminated simply because they present a toxic hazard, but odour and volatility can also give problems.

Monofunctional monomers

Monofunctional monomers lack the ability to cross-link and, although good viscosity reducers, their excessive use may lead to poor film properties. An important use can be to impart flexibility to the print film. In this respect they may be thought of as reactive plasticizers. Two good examples in this respect are isodecyl acrylate (IDA) and phenoxy ethyl acrylate (PEEA).

In the coatings industry generally, 2-hydroxy ethyl acrylate (2EHA) is very widely used but like many of the acrylated low molecular weight alcohols, toxicity, volatility and odour restrict its use in printing applications.

Difunctional acrylates

Most of the popular difunctional monomers are derived from simple diols. In this class may be included the low molecular weight species derived by acrylating the product of bisphenol A condensation with ethylene oxide. The viscosity of these molecules is not particularly low but this is compensated for by their good pigment wetting and ink making properties.

Table 2.2 lists a selection of the more important of the available difunctional acrylate monomers. Manufacture of this type of product is usually by reaction of a dial with acrylic acid.

Trifunctional acrylates

The three most important polyols that have provided the industry with useful trifunctional monomers after acrylation are penta-erythritol, trimethylol propane and glycerol.

Table 2.2 : Difunctional acrylate diluents

Abbreviation	Chemical Name	Viscosity at 25°C (cp)
BDDA	1,4-butane diol diacrylate	6
HDDA	1,6-hexane diol diacrylate	7
NPGDA	Neopentyl glycol diacrylate	7
DEGDA	Diethylene glycol diacrylate	8
TEGDA	Triethylene glycol diacrylate	25
PEGDA (n)	Polyethylene glycol diacrylate	10-30
TPGDA	Tripropylene glycol diacrylate	16
DDA	2,2-dionol diacrylate	ca. 1000
ABPE2	Bisphenol A diacrylate	1000-1500

High functionality monomers

Until recently very few acrylate monomers with functionality four or more have found favour in the ink industry. However, a number of companies have recently introduced tetra-acrylates variously known as PPTTA or ATTA, of which the full structure has not yet been disclosed. Hexa-functional acrylates are now readily available giving fast cure rates.

2.4.4.3 Photoinitiators

In UV curing inks these are chemicals which become excited by UV radiations, forming free radicals, which in turn react with the vehicle of the ink or varnish to begin polymerization. The term is also used to include proton donors such as amines. Benzophenone is one of the cheapest, most widely used photoinitiators. It requires a proton donor, such as amine, to be present in order to yield radicals easily. In addition, a wide range of amines, and acrylated amines are available as proton donors for UV systems.

2.5 Phosphorus Flame Retardance in Polymers

2.5.1 Flame retardancy in polymers

For many plastic materials, the most feasible method of improving their fire performance is the incorporation of commercially available retardants. In previous years, these retardants were considered primarily fire retardants; many are now viewed as smoke and smolder retardants because smoke and smoldering are fire response characteristics of concern in some applications.

Pyrolysis and combustion of polymers occur in several stages. The polymeric substrate heated by an external heat source is pyrolysed with the generation of combustible fuel. Usually, only a part of this fuel is fully combusted in the flame by combining with the stoichiometric amount of atmospheric oxygen. The other part remains and can be combusted by drastic means, e.g. in the presence of a catalyst and by an excess of oxygen.

A part of the released heat is fed back to the substrate and causes its continued pyrolysis, perpetuating the combustion cycle. Another part is lost to the environment. The energy needed to heat the polymer to the pyrolysis temperature and to decompose and gasify or volatilise the combustibles and the amount and character of the gaseous products determines the flammability of the substrate. A flame retardant acting via a condensedphase chemical mechanism alters the pyrolytic path of the substrate and reduces substantially the amount of gaseous combustibles, usually by favouring the formation of carbonaceous char and water [58]. In this case the heat released in the combustion decreases with an increase in the amount of the flame-retarding agent.

Additive flame-retardant systems are generally composed of both organic and inorganic materials acting synergistically to provide an optimum balance of flame retardancy, physical properties and cost. Additive retardants are generally incorporated by compounding and are useful in a variety of polymer systems. These materials are generally used for thermoplastic resins , although there are exceptions. With few exceptions, additive resins are used to fire retard flexible polyurethane foams**.** Halogenated organic compounds, such as PVC, or decabromodiphenyl oxide (DBDPO) in combination with antimony oxide represent this type of system. Other compounds of this type include polychloroprene, chlorinated polyethylene, and chlorosulfonated polyethylene, chlorinated paraffins, tris(dichloropropy1) phosphate, methyl pentachlorostearate, and various chlorinated phosphates for polyurethane foams and topical fabric treatment; cycloaliphatic chlorine-containing flame retardants (with higher thermal stability) for thermoplastics like polypropylene and nylon; and chlorendic anhydride, which is used as an intermediate in making flame retardant polyester and resin**.**

The general approaches involved in the use of reactive type fire retardants are the following:

i. Modification of the polymer to favor the decomposition and combustion reactions producing gases which are non-combustible, or heavy enough to interfere with normal interchange of combustion gases and combustion air. Phosphorus is introduced into polyurethane polymers in the form of phosphonate, phosphate, and phosphite polyols. Halogens are introduced into polyester polymers in the form of halogenated anhydrides such as chlorendic anhydride and tetrabromophthalic anhydride, into epoxy polymers in the form of halogenated compounds such as tetrabromobisphenol-A, and into polyolefins in the form of chlorinated paraffins and olefins.

ii. Modification of the polymer to favor decomposition and combustion reactions producing reduced heat of combustion. Phosphorus compounds appear effective in this approach.

iii. Modification of the polymer to increase the amount of solid residue, to maintain structural integrity and to impede access of oxygen and heat. Phosphorus compounds appear effective in this approach. Char formation in polyurethanes is improved by substituting polymeric polyaryl isocyanates for polylene diisocyanate, and by employing sucrose-based polyethers.

2.5.2 Phosphorus-containing flame retardants

Flame inhibition, heat loss due to melt flow, surface obstruction by phosphorus-containing acids, acid-catalysed char accumulation, char enhancement and protection of char from oxidation have all been noted in particular polymer systems containing phosphorus-based flame retardants [59] although the relative contribution of each mode of action depends on the polymer system and the fire exposure conditions. It is quite likely that in many cases, more than one mode of action is involved.

There is very convincing evidence, especially in oxygen-containing polymers such as cellulose and rigid polyurethane foam, that phosphorus compounds can increase the char yield. Formation of char means that less material is actually burned. Secondly, char formation is often accompanied by water release, which dilutes the combustible vapours.Moreover, the char can often protect the underlying polymer and the char-forming reactions are sometimes endothermic.

Another mode of action in which phosphorus is important as a char former is in intumescent fire-retardant paints and mastics. These typically have a phosphorus compound such as ammonium polyphosphate and a char-forming polyol such as pentaerythritol, along with a blowing agent such as melamine, and, of course, a binder [60]

In poly(ethylene terephthalate) [61-63] and poly(methyl methacrylate) [64-67], various phosphorus flame retardants cause an increase in the amount of residue and a retardation of the release of volatile fuel.This is probably the result of acid-catalysed cross-linking, perhaps by way of anhydride linkages.

Phosphorus can also inhibit smouldering, also known as glowing combustion of the char [68,70] the mode of action has long been postulated to involve some sort of polyphosphoric acid coating which is possibly a physical barrier action; besides this a deactivation of oxidation-active centres on the carbon can be demonstrated [70-72]. It has been shown that incorporation of phosphorus even in amounts as small as 0.1% can inhibit oxidation of graphitic carbon by free oxygen.

Hydrophilic phosphorus acid groups and other P=O structures can bond to oxidation-prone sites (the ‘armchair’ sites) on the surface. Research at Alma-Ata recently showed that a phosphorus flame retardant can reduce the permeability of char, improving its barrier action [73]. In some cases, phosphorus compounds can act under fire-exposure conditions by generating acids which catalyse thermal breakdown of the polymer melt [74] reducing melt viscosity and encouraging the flow or drip of the molten polymer from the fire zone.

3. EXPERIMENTAL PART

3.1 Materials

For the synthesis of epoxy acrylate resin, Bisphenol A type epoxy resin (Elkay Chemicals), Hydroquinone, Triethylamine (Acros Chemicals), Acrylic acid were used.

For the synthesis of urethane acrylate, Isophorone diisocyanate (IPDI), Propylene glycol (PPG), Hydroxyethylmethacrlate (HEMA), Dibutyltindilaurate (DBTL), Hydroquinone were used.

For the synthesis of bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO), Magnesium (Riedel-de-Haen), Tetrahydrofuran (THF) (J.T.Baker), p-Bromofluorobenzene (Acros), Dichlorophenyl phosphine oxide (Merck), Sodium carbonate (Merck) were used.

For the synthesis of Synthesis of bis(4-hydroxyphenyl)phenyl phosphine oxide (BOHPPO), Potassium Hydroxide (Merck), Dimethyl sulphoxide (Lab Scan) were used.

For the synthesis of bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide (BOHEPPO), Ethylene carbonate (Riedel-de Haen), Sodium carbonate (Merck) were used.

For the synthesis of Bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide polyester (BOHEPPO PE), Adipic acid, p-toluenesulfonic acid were used.

For the synthesis of bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide polyester containing polyurethane acrylate (BOHEPPO PE UA), Isophorone diisocyanate (IPDI), Hydroxyethylmethacrlate (HEMA), Dibutyltindilaurate (DBTL), Hydroquinone were used.

For the UV curing formulation, Dipropyleneglycoldiacrylate (DPGDA, Cytec Chemicals), 1,6-hexanedioldiacrylate (HDDA, from Sartomer Chemicals),

Trimethylolpropane triacrylate (TMPTA) and Irgacure 184 (from Ciba Chemicals) were used. As commercial resins, Ebecryl 3703 (Cytec Chemicals), Photomer 6217 (Cognis), Ebecryl 525 (Cytec Chemicals) were used.

Epoxy Resin is bisphenol A diglycidyl ether resin, was used as epoxy resin. Epoxy equivalent weight is 205 g/Eq. Density of epoxy resin is 1,12-1,15 g/ml. Viscosity, according to Brookfield, 600-800 cps at 25^0C.

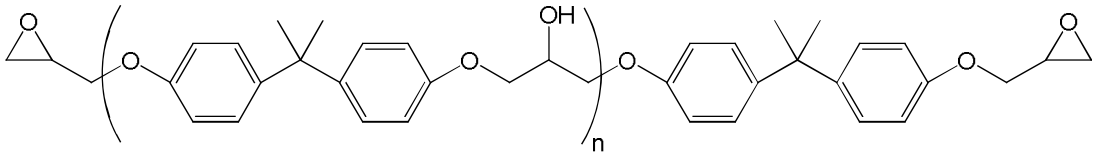


Figure 3.1 : Bisphenol A diglycidyl ether resin

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

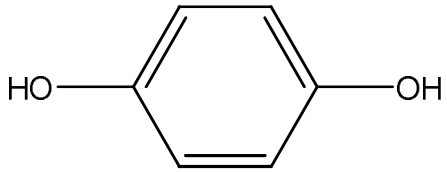


Figure 3.2 : Hydroquinone

Acrylic Acid is the simplest unsaturated carboxylic acid, consisting of a vinyl group connected directly to a carboxylic acid terminus. It is a colorless liquid. It was used for epoxy acrylate resin synthesis. Its density is 1,051 g/ml.

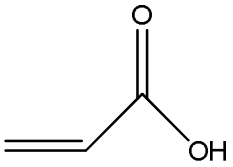


Figure 3.3 : Acrylic acid

Urethane Acrylate (UA) was used in the film formulations.

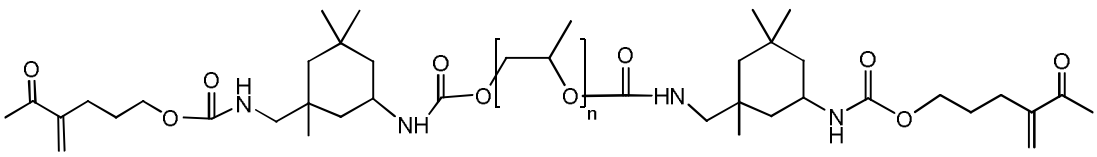


Figure 3.4 : Urethane Acrylate

TMPTA (Trimetyhlolpropane triacrylate) is a trifunctional monomer. It has good lithortaphic behaviour, a high reactivity and a reasonable viscosity. It was used as a crosslinking agent in photopolymerization system.

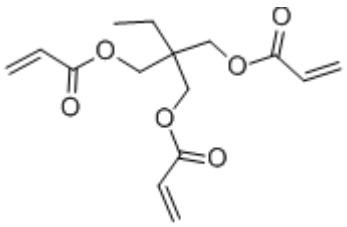


Figure 3.5 : Trimetyhlolpropane triacrylate

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

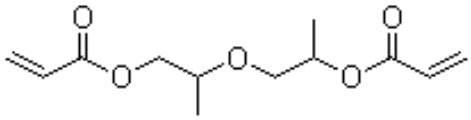


Figure 3.6 : Dipropylene glycol diacrylate

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

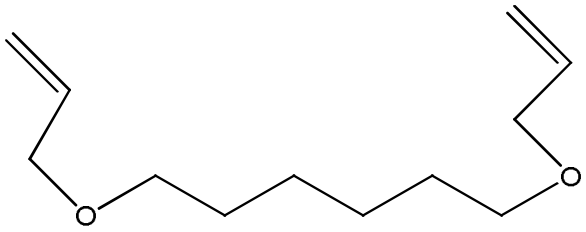


Figure 3.7 : HDDA

Ebecryl 3703® (Cytec Chemicals) is a modified Bisphenol A epoxy diacrylate, which is used in film formulations as reactive resin.

Photomer 6217® (Cognis) is an aliphatic urethane diacrylate, which is used in film formulations as reactive resin.

Ebecryl 525® (Cytec Chemicals) is a modified polyester resin diluted with %40 of TPGDA, which is used in film formulations as reactive resin.

IRGACURE® 184 (1-hydroxy-cyclohexyl-phenyl-ketone) is a highly efficient non-yellowing photoinitiator which is used to initiate the photopolymerisation of chemically unsaturated prepolymers or acrylates in combination with mono- or multifunctional vinyl monomers.

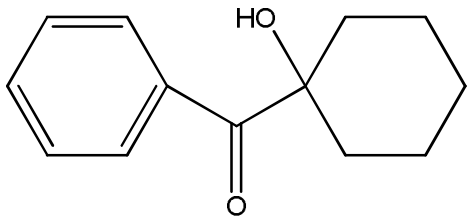


Figure 3.8 : Irgacure® 184

3.2 Equipments

3.2.1 Infrared Analysis (IR)

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

3.2.2 Nuclear Magnetic Resonance (NMR)

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

3.2.3 UV Spectroscopy Analysis

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

3.2.4 Thermogravimetrical Analysis (TGA)

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

3.2.5 Contact Angle Meter

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

3.2.6 Gloss Meter

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

3.2.7 Pendulum Hardness Tester

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

3.2.8 Tensile Loading Machine

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

3.3 Synthesis

3.3.1 Synthesis of epoxy acrylate

100 g epoxy resin (epoxy equivalent value 195-215 g/mol), hydroquinone was placed in a 250 mL three-necked round bottom flask equipped with nitrogen inlet, thermometer, $CaCl_2$ tube and condenser. The mixture was stirred at room temperature for 30 min. Then the system is placed in an oil bath and the heat was setted to 50^{o}C. Than at 50^{o}C 2.07 mL of triethylamine is added to the flask and was left stirring and the heat is setted to 60^{o}C. Than 33.45 mL acrylic acid was added to mixture as dropwise at 60^{o}C and the system was stirred until the addition was completed. Than the mixture was heated until the system is reached to 80^{o}C. The system was left stirring for approximately 22 h to have an acid value between 5-10. The acid value was controlled by titration of 0,1N KOH solution with phenolphthalein indicator. At the end of the reaction. The product was clear-yellow, viscous liquid and checked by infrared spectroscopy. The final product was vacuum dried at ambient temperature.

3.3.2 Synthesis of polyurethane acrylate

In a three-necked round bottom flask equipped with nitrogen inlet, thermometer, $CaCl_2$ tube and condenser was added 1 mol of polypropylene glycol and 10 mL acetone. Then 2 mol of isophorone diisocyanate (IPDI) dissolved in 10mL acetone was dropped into the flask at room temperature for 30 min. The dibutyltinlaurate was

added as catalyst and the temperature was left increasing up to 55^{o}C. The reaction was continued till the NCO content reached the theoretical value as determined by dibutylamine titration. Then 2 mol of hydroxyethyl methacrylate (HEMA) dissolved in 10mL acetone was added as drop wise at room temperature for 30 min and it as left mixing. After having dropped all the dropping funnel content the mixture was increased to 45^{o}C and it was left stirring. The flask was maintained at this temperature until the NCO peak at 2270 cm^{-1} disappeared totally in the FTIR spectra. The peak disappearance was controlled by samples taken from the reaction medium every 0.5h. The final product was vacuum dried at ambient temperature.

3.3.3 Synthesis of bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO)

Bis(4-fluorophenyl)phenyl phosphine oxide (BFPPO) was prepared by a variation of known Grignard techniques. A flame dried 2l 3-neck round bottom flask fitted with an overhead mechanical stirrer, an addition funnel and a nitrogen inlet were added 12.2 g magnesium and 400 ml dry THF. This solution was cooled with an ice water bath. To this stirred solution was added dropwise at or below 5 ^{0}C 88 g (54,7 ml) p-bromofluorobenzene over 2 hours. This mixture was stirred at room temperature overnight to give a gray slightly cloudy solution. Next, 36.6 ml dichlorophenyl phosphine oxide was added dropwise at 5 ^{0}C over 2 hours and this solution was allowed to stir at room temperature overnight to give a yellow clear solution. Enough 10% aqueous sulfuric acid was added to make the solution acidic and water was added, yielding a homogeneous golden yellow mixture. Ether was added in order to separate the solution into organic and aqueous phases. The aqueous layer was washed well with ether and all organic layers were combined. This organic solution was washed well with 10% sodium bicarbonate, followed by water washings. Then sodium sulphate was added to stir at room temperature overnight to clearing the cloudy ether phase. After filtering from the blue banded filter paper, THF and ether was distilled by rotary evaporator. Proportion of (30/70) of THF/hexane solution was used for crystallization. The white crystals were collected by vacuum filtration [75].

3.3.4 Synthesis of bis(4-hydroxyphenyl)phenyl phosphine oxide (BOHPPO)

BOHPPO was synthesized by hydrolyzing BFPPO using potassium hydroxide in DMSO. For example, 10 g BFPPO and 40 ml of DMSO were added to a 250 ml 3-neck flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and a

condenser. To the solution was added a 15 N (10.67 ml) solution of 8.96g of potassium hydroxide in water. The solution was then raised to reflux (approximately 135 ^{0}C) and allowed to react for 8 hours. The solution was acidified well with 10% HCl and DMSO removed using a rotovap to afford a pale yellow solid. Water was then added to solid to remove remaining salt. The product was filtered, dried in vacuum oven at 150 ^{0}C overnight, and then purified using fractional recrystallization from 1:5 v/v ratio of methanol/water [76].

3.3.5 Synthesis of bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide (BOHEPPO)

A spherical flask (250 ml), equipped with a reflux condenser, stirrer, thermometer, and nitrogen inlet, was charged with 1.4 g BOHPPO, 7.04 g ethylene carbonate, and 0,042g sodium carbonate as catalyst. The mixture was heated to 165-170 ^{0}C under nitrogen for 2 h. The crude product was washed with water several times to remove unreacted ethylene carbonate. A light brown viscose liquid was obtained [77].

3.3.6 Synthesis of bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide polyester (BOHEPPO PE)

10 g BOHEPPO, 2.7 g diethylene glycol and 3.7 g adipic acid with *p*-toluenesulfonic acid was placed in a 250 mL three-necked round bottom flask equipped with nitrogen inlet, thermometer, $CaCl_2$ tube and condenser. The mixture was purged with nitrogen. The temperature of the system was gradually raised to 150 ^{o}C. And the system was kept 3h at 150 ^{o}C and left stirring. The water formed during the reaction was collected via dean stark. At the end of the reaction the product was clear-yellow, viscous liquid. The final product was vacuum dried at ambient temperature and checked by IR and ^{1}H-NMR.

3.3.7 Synthesis of bis[(4-β-hydroxyethoxy)phenyl]phenyl phosphine oxide polyester containing urethane acrylate (BOHEPPO PE UA)

In a three-necked round bottom flask equipped with nitrogen inlet, thermometer, $CaCl_2$ tube and condenser was added 1 mol of BOHEPPO PE and 10 mL acetone. Then 2 mol of isophorone diisocyanate (IPDI) dissolved in 10mL acetone was dropped into the flask at room temperature for 30 min. The dibutyltinlaurate was

added as catalyst and the temperature was left increasing up to 55°C. Then 2 mol of hydroxyethyl methacrylate (HEMA) dissolved in 10mL acetone was added as drop wise at room temperature for 30 min and it as left mixing. After having dropped all the dropping funnel content the mixture was increased to 45°C and it was left stirring. The flask was maintained at this temperature until the NCO peak at 2270 cm^{-1} disappeared totally in the FTIR spectra. The peak disappearance was controlled by samples taken from the reaction medium every 0.5h. The final product was vacuum dried at ambient temperature.

3.4 Preparation of Formulations

Twelve different formulations were prepared for UV curable paper coating. Also free films were prepared by these formulations for further tests.

The components of these formulations based on UV curing are; reactive resins, reactive diluents and photoinitiators.

Formulations contain about 60 to 80% of resins, about 15 to 35 of reactive diluents and 5% of photoinitiator. Different ratios are shown in Table 3.1.

Reactive resins containing a plurality of polymerizable double bonds like epoxy acrylate, urethane acrylate, unsaturated polyester urethane acrylate, modified polyester and BOHEPPO PE UA were used.

Table 3.1: Component ratios of formulations

(wt.%) / Sample	Resin	Reactive Diluent	Photoinitiator
F1	80	15	5
F2	70	25	5
F3	60	35	5
F4	60	35	5
F5	60	35	5
F6	60	35	5
F7	60	35	5
F8	60	35	5
F9	60	35	5
F10	60	35	5
F11	60	35	5
F12	60	35	5

Reactive diluents, like monofunctional or difunctional or multifunctional acrylate monomers, are responsible for the reduction or adjustment of the viscosity of the formulation and participate to the crosslinking. In these formulations difunctional (HDDA, TPGDA) and trifunctional (TMPTA), acrylate monomers were used.

Table 3.2: Formulations containing unsaturated polyester urethane acrylate

Sample / (wt.%)	F1	F2	F3	F4	F5	F6	F7
Epoxy Acrylate	40	10	15	10	5	15	5
Polyurethane Acrylate	10	35	35	35	45	45	45
Unsaturated Polyester Acrylate	30	25	10	15	10	-	10
TMPTA	10	10	15	15	10	15	15
HDDA	5	15	20	20	10	20	20
DPGDA	-	-	-	-	15	-	-
Irgacure® 184	5	5	5	5	5	5	5

A general surface cure photoinitiator, which providing non-yellowing, was used in each formulation.

Samples between F1 to F7, were prepared by epoxy acrylate, urethane acrylate which syntheses were mentioned in section 3.3 and unsaturated polyester urethane acrylate in different ratios as shown in Table 3.2.

Sample F8 was prepared with commercial oligomers, Ebecryl® 3703, Photomer® 6217 and Ebecryl® 525 as shown in Table 3.3.

Sample F9 contains epoxy acrylate, urethane acrylate which syntheses were mentioned in section 3.3 and Ebecryl® 525 as modified polyester (Table 3.3).

Table 3.3: Formulations containing commercial oligomers

Sample / (wt.%)	F8	F9
Epoxy Acrylate	-	5
Polyurethane Acrylate	-	45
Ebecryl® 3703	5	-
Photomer® 6217	45	-
Ebecryl® 525	10	10
TMPTA	15	15
HDDA	20	20
Irgacure® 184	5	5

Table 3.4: Formulations containing BOHEPPO PE UA

Sample / (wt.%)	F10	F11	F12
Epoxy Acrylate	5.5	5	4.5
Polyurethane Acrylate	49.5	45	40.5
BOHEPPO PE UA	5	10	15
TMPTA	15	15	15
HDDA	20	20	20
Irgacure® 184	5	5	5

Samples between F10 to F12 contain epoxy acrylate, urethane acrylate and BOHEPPO PE UA which synthesis was mentioned in section 3.3 (Table 3.4)

3.4.1 Preparation of test samples

3.4.1.1 Coated papers

Solutions were prepared according formulations to Table 3.2, Table 3.3 and Table 3.4. After that, solutions were kept under vacuum approximately 30 minutes to remove bubbles. 1g of solution for each paper was prepared. The papers were put on smooth surface and coated with liquid solution by pulling a glass rod from one side to another. Liquid solutions were cured under EMA UV machine for 5 pass and kept waiting for a couple of days before further tests. Than pendulum hardness, contact angle, gloss test were applied on these coated papers.

3.4.1.2 Free films

Free film formulations were prepared according to the Table 3.2, Table 3.3 and Table 3.4. Solutions were kept under vacuum approximately 30 minutes to remove bubbles. 2g of solution for each film was prepared. Then, to prepare free films, the solutions were spilled between the PET films and to spread the solution the PET films were put between the plexiglass plates. And the solutions were kept waiting until getting a constant thickness. Liquid solutions were cured under EMA UV machine for 5 pass and kept waiting for a couple of days before further tests. Then, strain-stress test, gel content test, solvent resistance, and thermal analysis were applied on these free films.

3.5 Analyses

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

3.5.1 Infrared Analysis

Infrared spectroscopy (IR) is used in the areas of determination of molecular structure, identification of chemical species, quantitative/qualitative determination of chemical species, and in a host of other applications.

This technique is used in the investigation of matter in the solid, liquid, and gaseous states. The application of IR is well known in the fields of chemistry, physics, materials science, etc. If a molecule is placed in an electromagnetic field (e.g., light), a transfer of energy from the field to the molecule will occur only when Bohr's frequency condition is satisfied.

$E = hv$

where,

h = Planck's constant

v = frequency of light

In the case of a diatomic molecule, it can be proven from mechanical considerations that the vibrations of the two nuclei in a diatomic molecule are equivalent to the motion of a single particle of mass, μ, whose displacement from its equilibrium position is equal to the change of the internuclear distance. The term μ is called the *reduced mass* and is given by:

$1/\mu = 1/m_1 + 1/m_2$

where, $m1$ and $m2$ are masses of the two nuclei.

The infrared vibrational spectrum of a molecule consists of a series of bands, each of which results from a transition between pairs of vibrational levels associated with the ground electronic state. With the help of quantum mechanics, the probability of a vibrational transition of a molecule can be obtained. The variation of the dipole moment vector can be expanded in a series in terms of the normal coordinates [78].

3.5.2 Nuclear Magnetic Resonance Analysis

NMR observes radio frequency signals from atomic nuclei occupying excited spin states, and understanding the observations is best accomplished though a combination of the quantum mechanical and classical descriptions of the phenomena.

NMR active nuclei are considered to have a quantized property called spin, which can usefully be thought of as being caused by physical spinning of the nucleus. The angular momentum, J, of such a nucleus is given by:

$J = h\,[I(I + 1)]^{1/2}$

where h is Planck's constant/2π and I is the spin quantum number which can be either an integer or half-integer. Nuclei with even mass number and even charge (e.g., ^{12}C, ^{16}O) have zero spin and are of no interest to NMR spectroscopy. Nuclei with odd mass numbers (e.g., ^{17}O, ^{27}Al, ^{29}Si) have half-integer spins and are of most interest here. Nuclei with even mass numbers and odd charge (e.g., ^{2}H, ^{14}N) have integer spins and can be more difficult to examine, but can also be of considerable importance. Most nuclei have spins between 0 and 9/2. The magnetic moment of a nucleus is a fundamental property.

Each nucleus has $2I + 1$ spin energy levels which take on the values I, I - 1, I - 2, ..., - I. In the absence of a magnetic field, these energy levels are degenerate (have the same energy), but when a magnetic field is present this degeneracy is lifted. The chemical shift corresponding to the isotropic shielding is called the isotropic chemical shift, δi, and has units of ppm. More negative or less positive chemical shifts correspond to larger shieldings. In many cases, the isotropic chemical shift is the most useful NMR parameter for structural investigations [78].

3.5.3 Thermogravimetric Analysis

TGA is widely used to evaluate the thermal stability and thermal degradation behaviour of polymers [79]. TGA measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties [80].

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 [81].

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 800°C under N_2 (flow rate: 90 mL/min) at an applied heating rate of 20°C /min. During the heating period, the weight loss and temperature difference were recorded as a function of temperature. The test results are shown in the Table 4.1.

3.5.4 Gel Content Measurement

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

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

Where m_1 is the weight of the cured film sample; m_2 is the residual weight of the cured film sample. Solvents used in this test and results are shown in the Table 4.2.

3.5.5 Solvent Resistance

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

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

Solvents used in this test and results are shown between Table 4.3 to Table 4.14.

3.5.6 Contact Angle Measurement

The contact angle is an important parameter in surface science. It is a common measure of the hydrophobicity of a solid surface In the past several decades, numerous techniques have been used to measure contact angle which were inspired by the idea of using the equation first derived by Thomas Young in 1805. Young's equation governs the equilibrium of the three interfacial tensions and the Young contact angle of a liquid drop on a solid. The derivation of Young's equation assumes that the solid surface is smooth, homogeneous and rigid; it should also be chemically and physically inert with respect to the liquids to be employed. Ideally, according to Young's equation, a unique contact angle is expected for a given system a liquid drop on a solid surface. In a real system, however, a range of contact angles is usually obtained instead. The upper limit of the range is the advancing contact angle which is the contact angle found at the advancing edge of a liquid drop. The lower limit is the receding contact angle which is the contact angle found at the receding edge. The difference between the advancing and receding contact angles is

known as the contact angle hysteresis. [82] θ is the Young contact angle, i.e. a contact angle which can be inserted into Young's equation. (Figure 3.10).

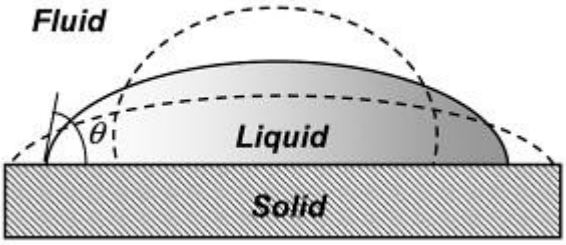


Figure 3.9 : Scheme of a sessile-drop contact angle system

The water contact angle of films prepared in are listed in Table 4.15.

3.5.7 Gloss Test

Specular gloss meters are widely used, but correspondence between meter reading and visual comparisons is limited. Such instruments give significantly different readings with differences in intensity of reflected light, but observers are relatively insensitive to such differences. Furthermore, the aperture of the slit in a gloss meter about 2^{o}, whereas the limit of resolution of a human eye is about 0.0005^{o} of arc [83]. The most widely used gloss meter, also called reflectometers, are simplified goniophotometers in which one measures a response only at the secular angle. Those most commonly used in the coatings industry can make measurements when the angles of incidence and viewing are 20^{o}, 60^{o}, and 85^{o}. A schematic drawing is shown in Figure 3.11.

The first step for using a gloss meter is to calibrate the instrument with two standards: one with high gloss and e other a lower gloss. If the second standard does not give the standard reading after the instrument is set with the first standard, something is wrong; most commonly, one or both of the standards is dirty or scratched. Other possible problems include panel misalignment, deterioration of the light source, or a malfunction of the photometer. One must use the standard that has been calibrated at the angle selected. Black and white standards are available [84]. The water contact angle of films prepared in our experiments are listed in Table 4.16.

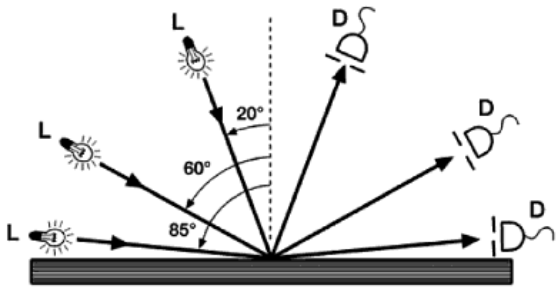


Figure 3.10 : Conventional glossmeter. L, lamp; and D, Detector

3.5.8 Pendulum Hardness Test

Standard hardness tests relate oscillation damping to surface hardness. The Konig test for hard coatings measures the time taken for the amplitude to decrease from 6° to 3°. It uses the damping properties of organic surfaces (e.g., paints, coatings, plastic materials, films of all kinds, and paper) to determine the hardness. In its operation, the oscillations of a standard pendulum supported on the test surface by balls are dampened more strongly on softer surfaces. The degree of dampening is measured by the time in seconds taken for the amplitude of the pendulum to diminish from the initial to the final value [85]. It is described in the ISO Recommendation 1522 as follows: [86]

The pendulum rests on two stainless steel balls, 5 ± 0.005 mm diameter, of hardness HRC 63 ± 3, 30 ± 0.2 mm apart, and is counterpoised (to adjust the naural frequency of oscillation) by means of a weight sliding on a vertical rod attached to a cross bar. The period of oscillation should be 1.4 ± 0.2 s on a polished plate glass panel; the time for damping from a 6^o displacement to a 3^o displacement, o the same substrate, should be 250 ± 10 s. The total weiht of the pendulum should be 200 ± 0.2g.

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

3.5.9 Pencil Hardness Test

ASTM Test Method for Film Hardness Test (D3363) is practical for laboratory use, for use on a production line, or in the field to assess quantitatively the rigidity or firmness (elastic modulus) of organic coatings applied to rigid substrates such as metal or plastic. Hardness values may define requirements for particular coating applications or may be used to evaluate state of cure or aging of a coating.

In this test, pencil leads of increasing hardess values are forced against a coated surface in a precisely defined manner until one lead marks the surface. Surface hardness is definedby the hardest pencil grade which fails to mark the organic coating surface.

Pencils are available in different grades of hardness, ranging form the softest, and 6B, to the hardest. 6H, although harnesses greater than 6H have been available. Pencil leads are blends of graphite, clay, and binders. They range in hardness from softest to hardest as follows [87]:

6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H and 6H.

The results are shown in Table 4.18.

3.5.10 Tensile Test

The tensile test serves as the basis for determining several important mechanical properties of materials. In this test, the yield strength, tensile strength, elongation, and reduction in area of a material specimen are determined. In addition, the modulus of elasticity, modulus of resilience, and modulus of toughness of a material are found from the stress–strain curve measured during the tensile test. In the tensile test the specimen is loaded in uniaxial tension until the specimen fractures. Because of the difficulty in determining the elastic limit, it is commonly replaced by the proportional limit, which is the stress at which the stress–strain curve is out of linearity. The modulus of elasticity, or Young's modulus, E, a measure of the stiffness of the material, is the slope of the curve below the proportional limit. The increase in load that occurs in some materials after the yield strength is reached is known as strain hardening or work hardening. Poisson's ratio v is the absolute value of the ratio of the transverse strain to the axial strain of a specimen under uniformly distributed axial stress below the elastic limit. The specimen for a Poisson's ratio tensile test is of rectangular cross section.

The tensile strength of the material is calculated by dividing the maximum applied load by the initial undeformed cross-sectional area of the specimen. According to their ability to undergo plastic deformation under loading, materials are identified as being ductile or brittle. In a brittle material, fracture can occur suddenly because the yield strength and tensile strength are practically the same. The elongation and

reduction of area give an indication of the ductility of a material specimen, and the modulus of toughness shows the energy-dissipating capacities of the material, but both ductility and capacity for energy absorption are influenced by such factors as stress concentration, specimen size, temperature, and strain rate. A normally ductile material such as mild steel will behave in a brittle manner under conditions of low temperature, high strain rate, and severe notching. On the other hand, normally brittle materials will behave ductile under high hydrostatic pressures and temperatures. Therefore, assessment of the ductility and energy-absorbing capacity of a material must be made by taking into consideration the service conditions of the final product [88].

The results are shown in Table 4.19.

4. RESULTS AND DISCUSSION

This thesis will concern of the preparation of novel polyester-based urethane acrylate containing phosphorus compound. Then, this component is used in UV curable formulations for paper coating. And the coated paper is characterized by various analysis such as contact angle, hardness, gloss, and stress-strain test. In addition, the thermal behavior of the coating is investigated.

For this purpose, several formulations were prepared in different ratios. Than coated paper properties were compared with the non-coated blank paper.

4.1 Synthesis of Epoxy Acrylate

Epoxy acrylate resin was synthesized according to procedure (Figure 4.1) mentioned in section 3.3.1. A ring opening reaction was occurred by the reaction of epoxy oligomers with acrylic acid to yield hydroxyl containing epoxy acrylates. Completion of reaction was checked by FT-IR spectrum.

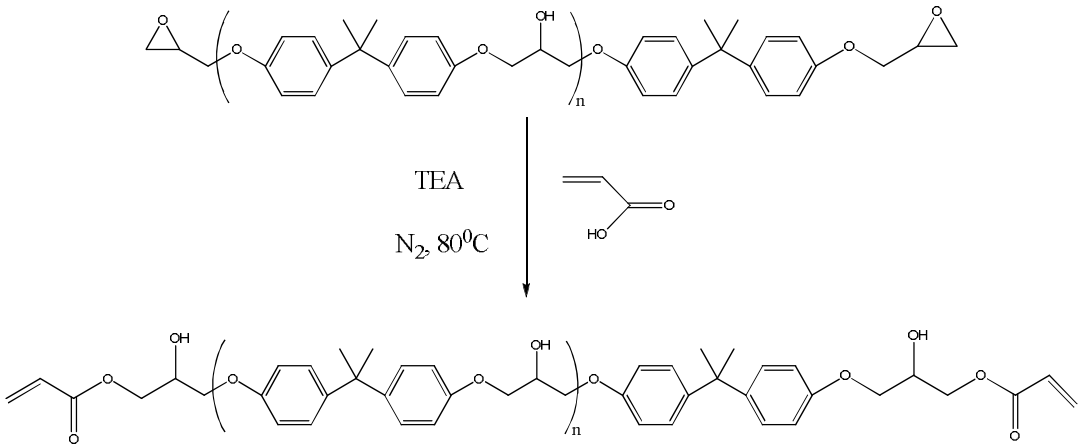


Figure 4.1 : Synthesis of epoxy acrylate

The FT-IR spectrum analysis of epoxy resin in Figure 4.2 contains characteristic epoxy group at 915 cm^{-1}. As a result of the ring opening of epoxy group, we can clearly see high decrease of this characteristic epoxy group, in epoxy acrylate FT-IR spectrum showed in Figure 4.3.

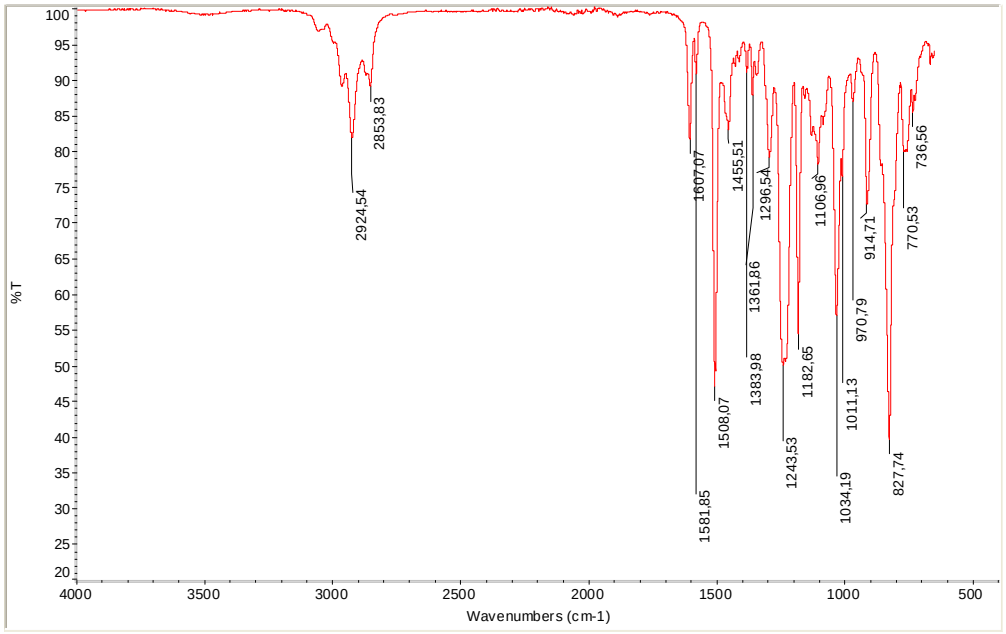


Figure 4.2 : IR Spectra of epoxy resin

Also at the end of epoxy acrylate reaction FT-IR spectrum analysis of epoxy acrylate in Figure 4.3 contains characteristic broad band –OH at 3437 cm-^{1}, -C=O at 1723 cm-^{1}, -C=C at 1606 cm-^{1} and -CH at 2927 cm-^{1}. The increasing values of –OH, -C=C and –C=O groups show the formation of epoxy acrylate.

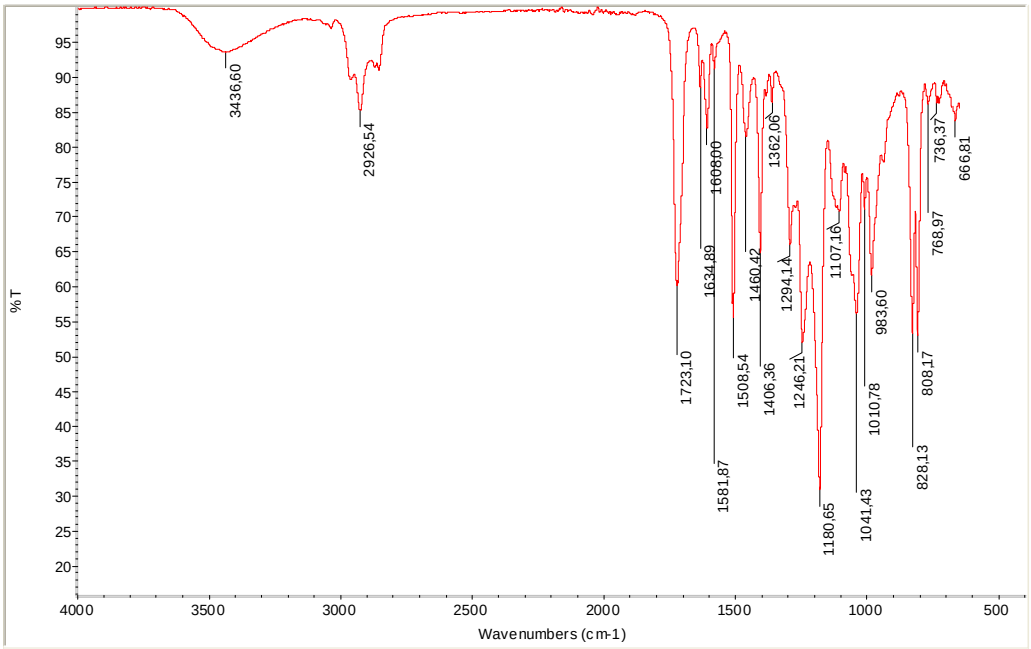


Figure 4.3 : IR Spectra of epoxy acrylate

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

^{1}H-NMR spectrum of epoxy acrylate was taken in $CDCL_3$ as shown in Figure 4.4. The structure of epoxy acrylate is proved by the spectrum. 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 3.48 ppm. And the epoxy aromatic ring have signals at 6.78-6.81, 7.10-7.25.

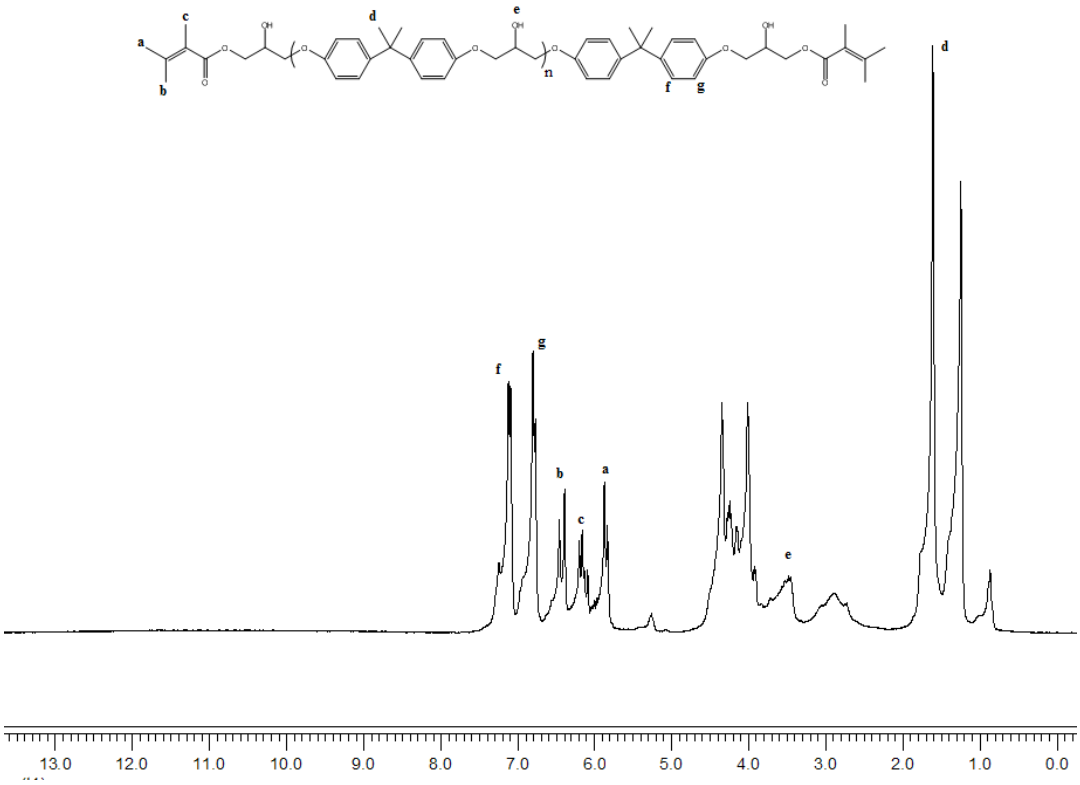


Figure 4.4 : ^{1}H-NMR Spectrum of epoxy acrylate

4.2 Synthesis of Urethane Acrylate

Urethane acrylate was synthesized according to the procedure Figure 4.5 as mentioned in section 3.3.2. Isophorone diisocyanate was reacted with polypropyleneglycol and 2 hydroxyethylmethacrylate to yield urethane acrylate. Completion of reaction was checked by FT-IR as shown in Figure 4.6.

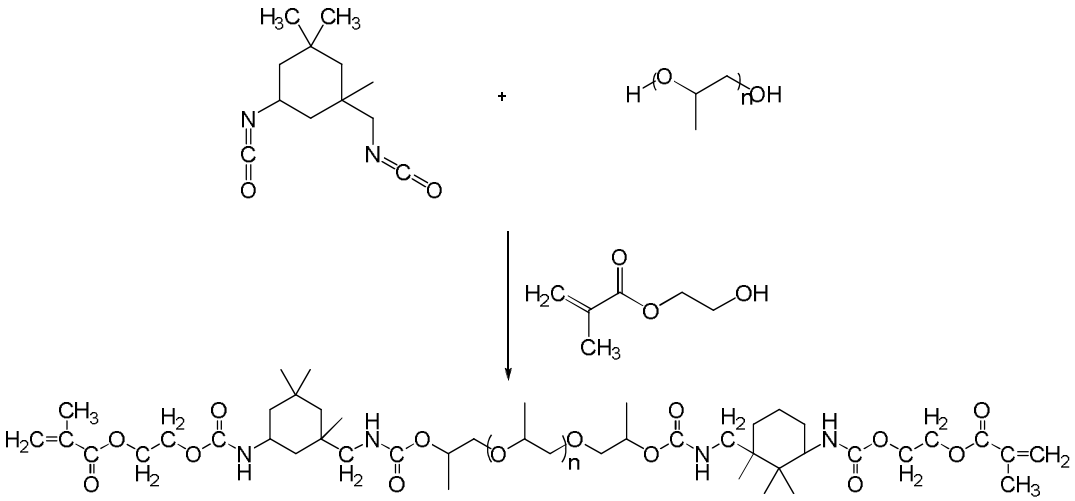


Figure 4.5 : Synthesis of Urethane Acrylate

The IR spectrum in Figure 4.6 contains characteristic peaks of N-H at 3352 cm^{-1}, and C=O at 1712cm^{-1}, -C-N- stretching bands at 1544 cm^{-1}, C-H aliphatic stretching band at 2872 cm^{-1} are also observed. The reaction resulting by urethane acrylate formation is also proved by the disappearance of the absorption bands of the NCO group at 2265 cm^{-1} of IPDI. The absorption band at 1099 cm^{-1} demonstrate C-O-C group. There are phenyl absorption bands at 1527 cm^{-1}.

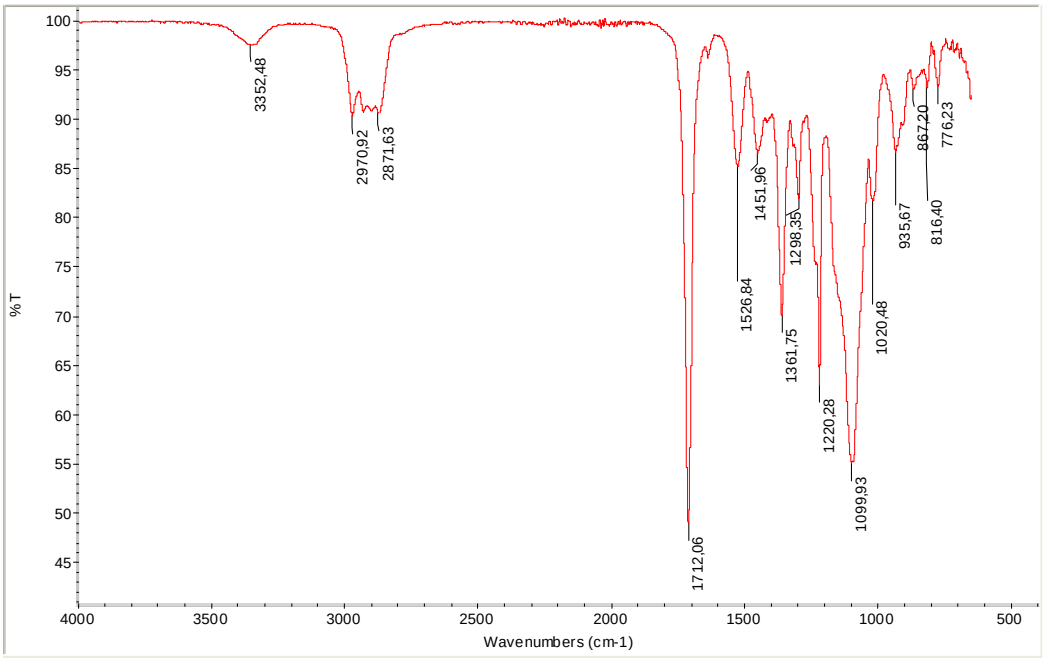


Figure 4.6 : The IR spectrum of urethane acrylate

4.3 Synthesis of Bis(4-fluorophenyl)phenyl Phosphine Oxide (BFPPO)

In this part, BFPPO was synthesized according to the procedure [75] in Figure 4.7. The structure of product was confirmed by FT-IR spectrum.

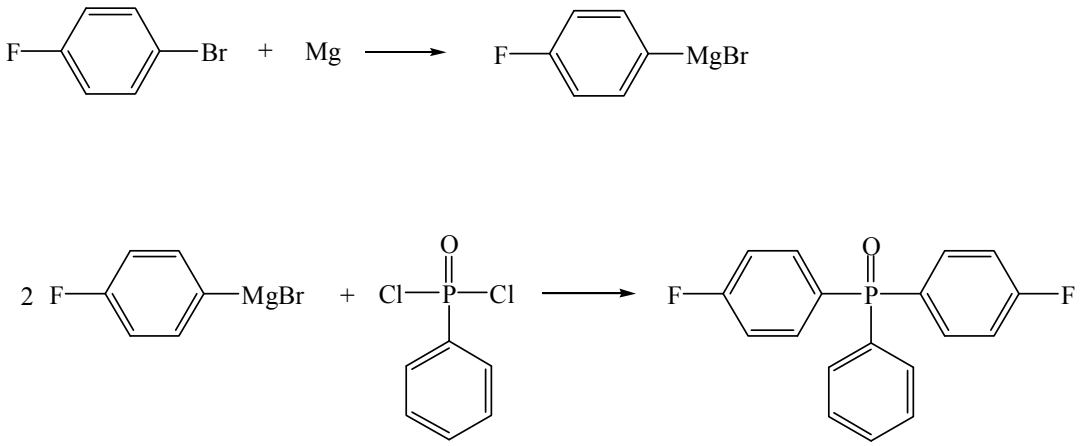


Figure 4.7 : Synthesis scheme of BFPPO

The FT-IR spectrum of BFPPO in Figure 4.8 contains the characteristic broad band P=O at 1397 cm^{-1}, P-Ph at 1437 cm^{-1}, C-F at 1219 cm^{-1}, -CH at 3063 cm^{-1}, and C=C at 1437-1588 cm^{-1}.

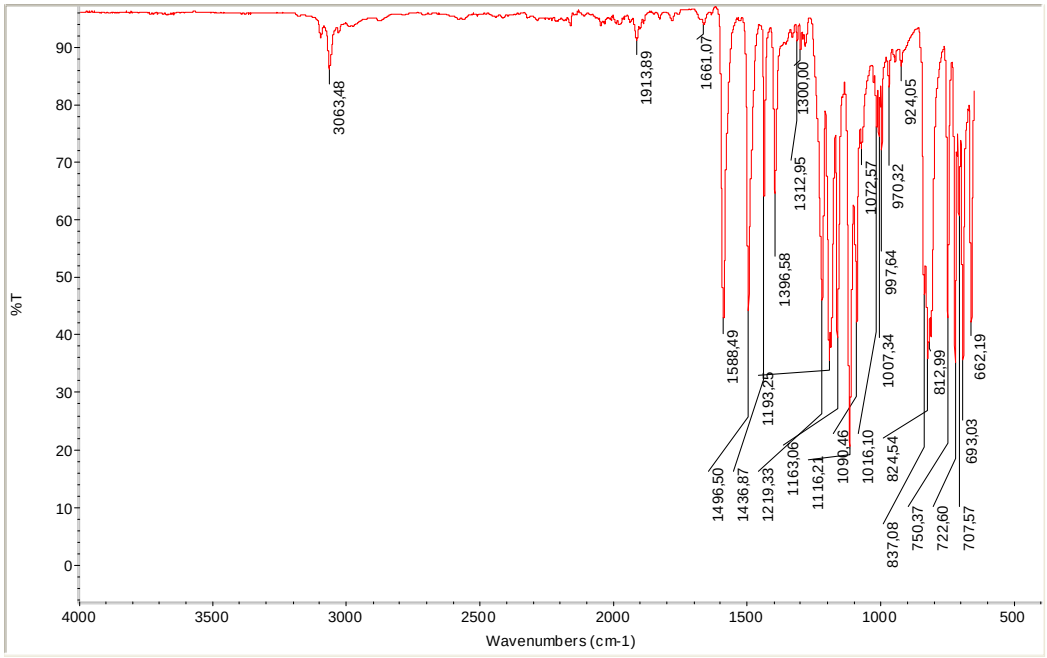


Figure 4.8 : FT-IR spectra of BFPPO

4.4 Synthesis of Bis(4-hydroxyphenyl)phenyl Phosphine Oxide (BOHPPO)

In this part, BFPPO was synthesized according to the procedure [76] in Figure 4.9.

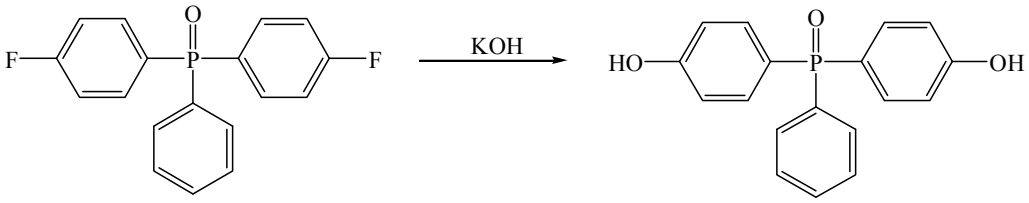


Figure 4.9 : Synthesis scheme of BOHPPO

The chemical structures of the resulting material (BOHPPO) was characterized by FT-IR (Figure 4.10). The characteristic absorption peak of the functional group Ph-OH 3062 cm^{-1} was detected for BOHPPO. Peaks at 1280 cm^{-1} -P=O, 1436 cm^{-1} -P-Ph, 1118 cm^{-1} C-O, and 1581-1600 cm^{-1} C=C proved the existence of phenyl phosphine oxide and hydroxy structure.

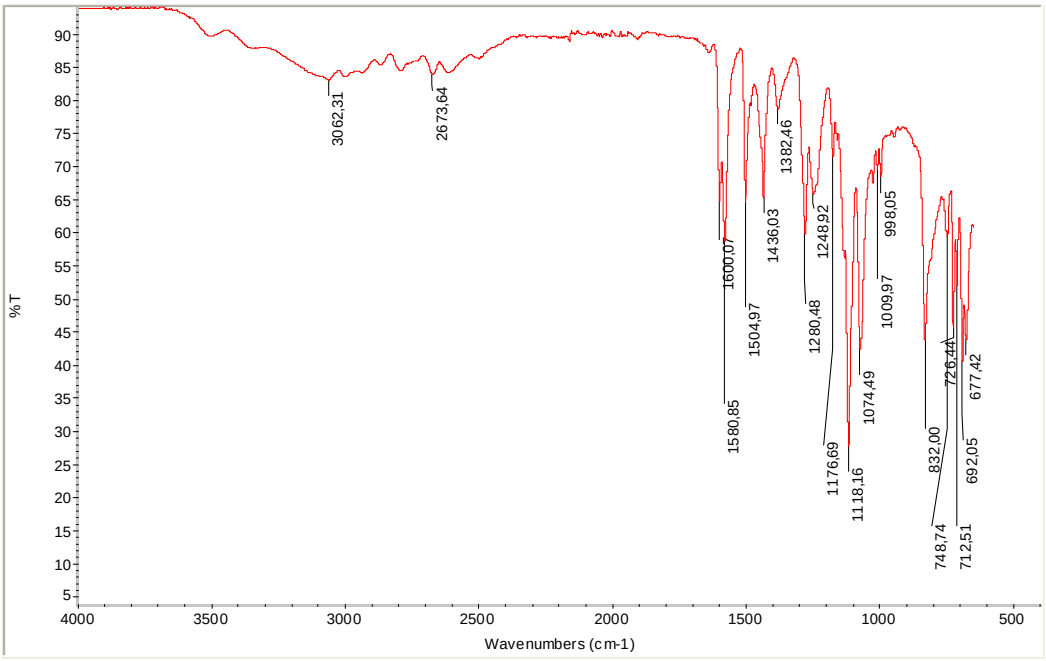


Figure 4.10 : FT-IR Spectra of BOHPPO

4.5 Synthesis of Bis[(4-β-hydroxyethoxy)phenyl]phenyl Phosphine Oxide (BOHEPPO)

In this part, BFPPO was synthesized according to the procedure [77] in Figure 4.11.

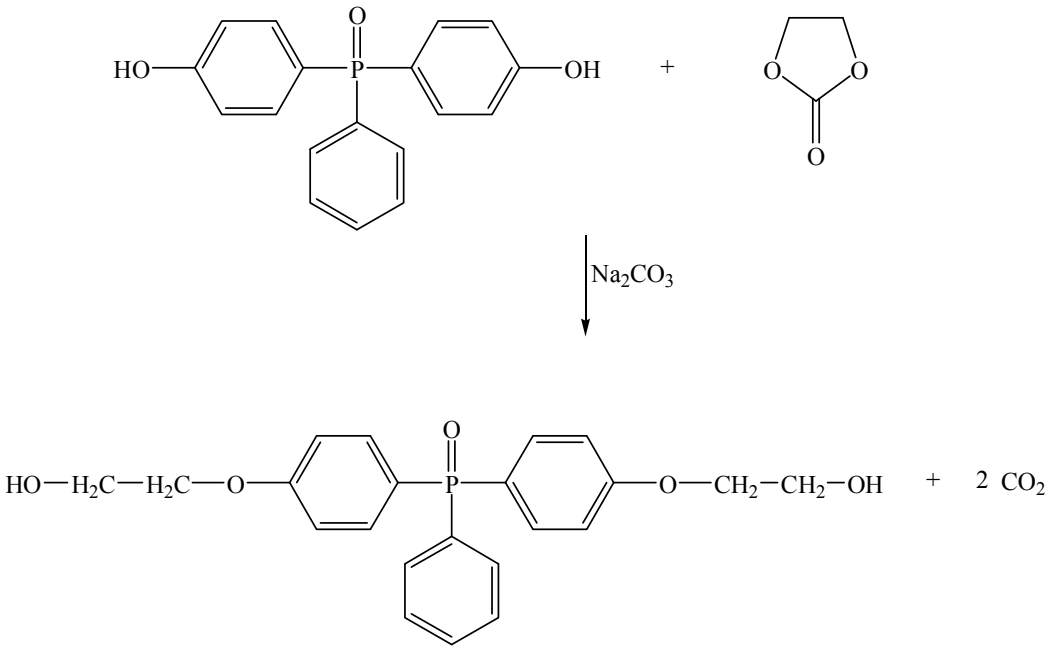


Figure 4.11 : Synthesis scheme of BOHEPPO

The structure of BOHEPPO was confirmed by IR and ^{1}H-NMR. Figure 4.12 presents the FT-IR spectra of BOHEPPO.

In the IR spectra, absorptions due to hydroxyl groups -CH_2-OH was observed at 3308 cm^{-1}, -C-O at 1160-1045 cm^{-1}, -CH at 2930 cm^{-1}, C=C at 1595-1500 cm^{-1} and an absorption based on triphenylphosphine was observed at 1437 cm^{-1}.

Figure 4.13 shows 1H-NMR spectra of BHEPPO. The peak at 3,92 ppm was due to CH_2 protons near to hydroxyl group and 4,05 ppm was due to CH_2 protons near to etheric oxygen atom. The hydroxyl groups were observed at 3,06 ppm. The aromatic protons of BHEPPO near to etheric oxygen atom appeared at δ = 6,6-7 ppm, and the other aromatic protons bonded to phosphine oxide group appeared at δ= 7-7,7 ppm.

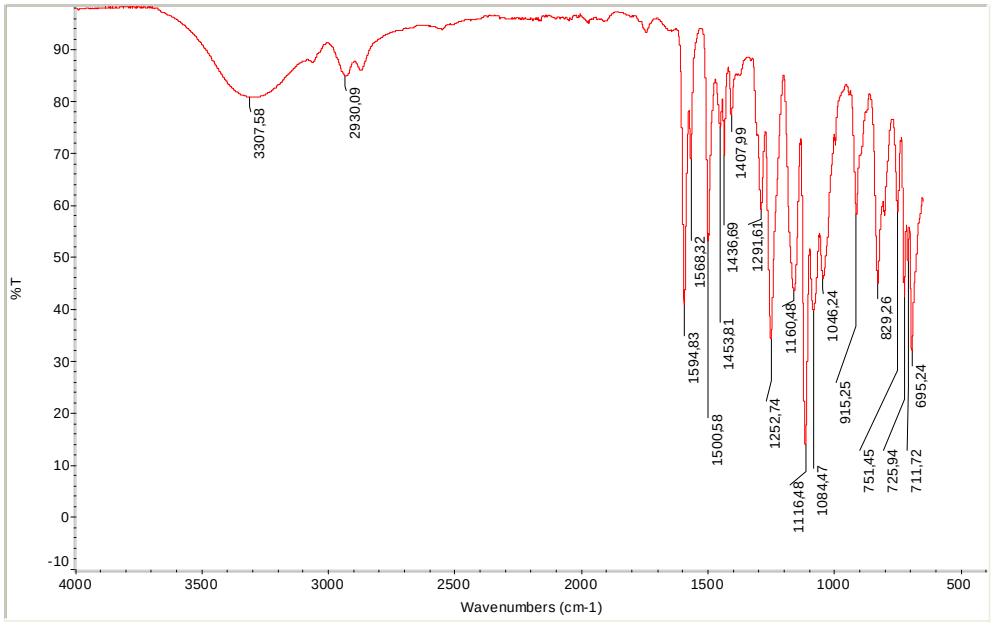


Figure 4.12 : FT-IR spectra of BOHEPPO

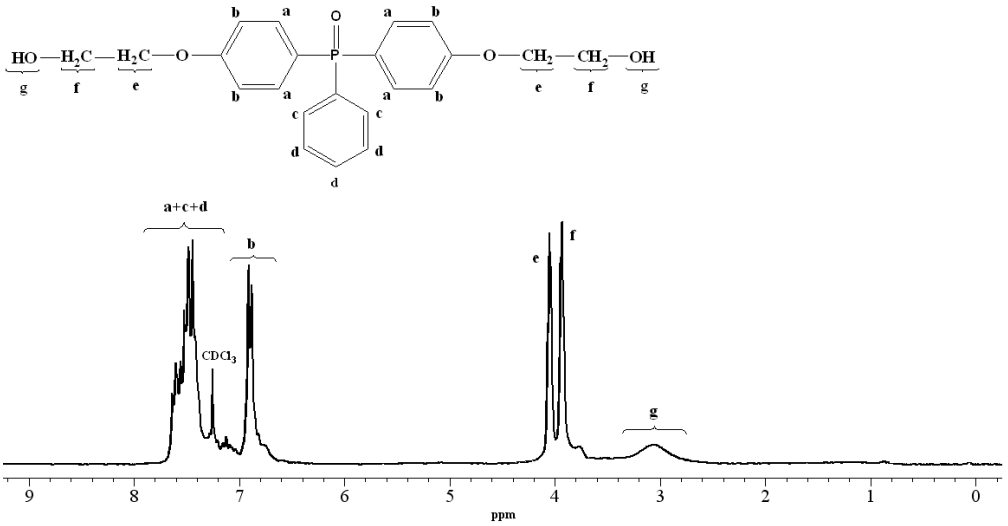


Figure 4.13 : ^{1}H-NMR Spectrum of BOHEPPO

4.6 Synthesis of Bis[(4-β-hydroxyethoxy)phenyl]phenyl Phosphine Oxide Polyester (BOHEPPO PE)

In this part BOHEPPO PE was synthesized by condensation esterification of BOHEPPO with adipic acid according to procedure mentioned in section 3.3.6 (Figure 4.14). The structure of polyester was confirmed by FT-IR and ^{1}H-NMR.

Figure 4.15 presents the FT-IR spectra. In the IR spectra, absorptions due to hydroxyl groups was observed at 3334 cm^{-1}, -C-O at 1166 cm^{-1}, -CH at 2942 cm^{-1} and –C=O at 1729 cm^{-1}.

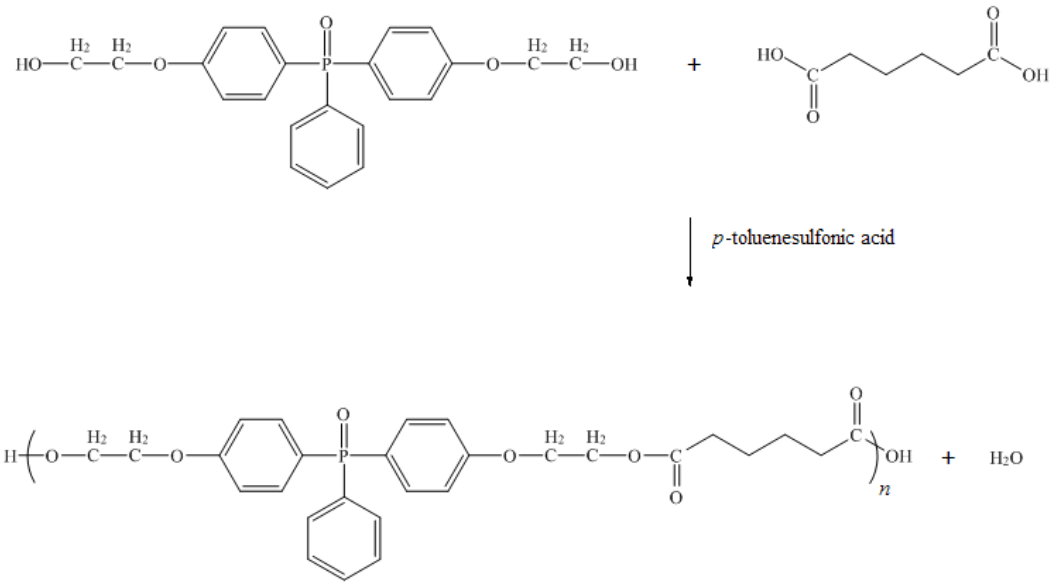


Figure 4.14 : Synthesis scheme of BOHEPPO PE

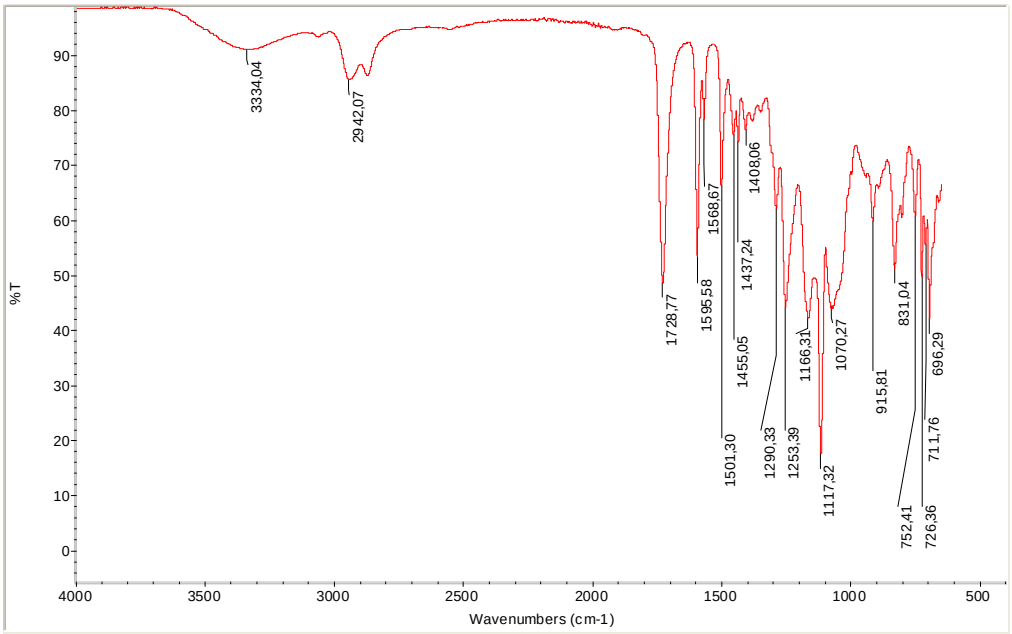


Figure 4.15 : FT-IR spectra of BOHEPPO PE

The compound was further characterized by ^{1}H-NMR, as shown in Figure 4.16, measured with $CDCl_3$ as an external reference. Absorptions of characteristic aromatic protons were found at 6.97-7.60 ppm, methylene protons attached to ester units at 3.6-4.4 ppm and hydroxyl proton of polyester at 4.84 ppm which prove the esterification reaction.

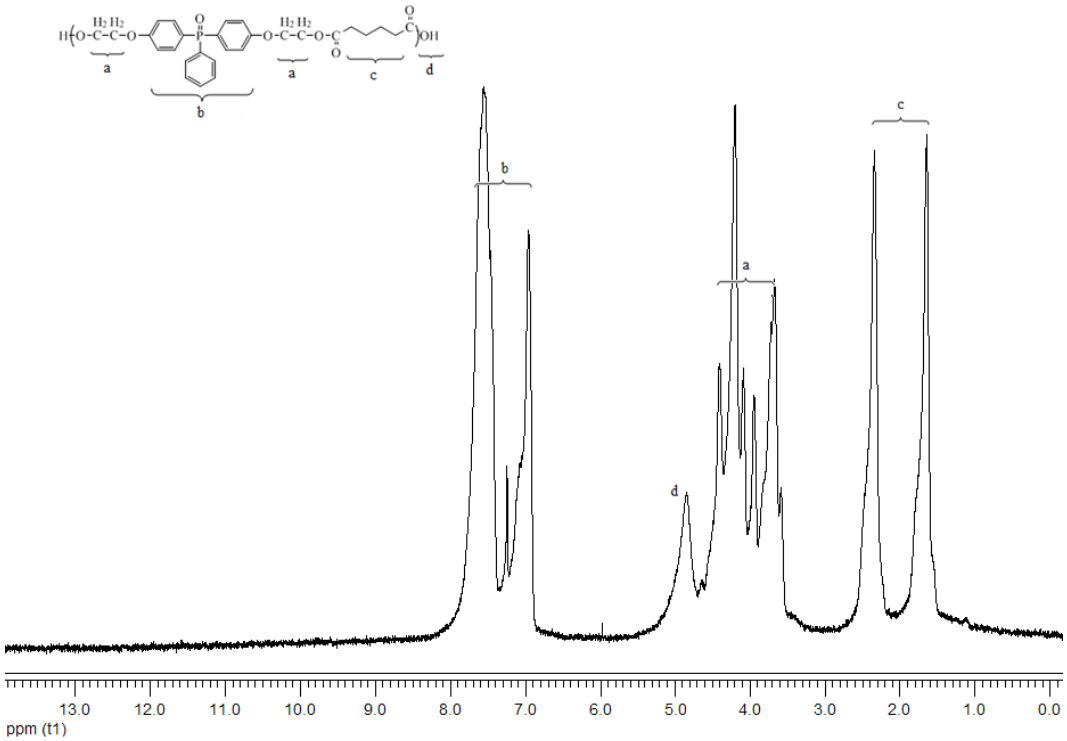


Figure 4.16 : ^{1}H-NMR Spectrum of BOHEPPO PE

4.7 Synthesis of Bis[(4-β-hydroxyethoxy)phenyl]phenyl Phosphine Oxide Polyester Containing Polyurethane Acrylate (BOHEPPO PE UA)

In this part the polyester based polyurethane acrylate, BOHEPPO PE UA, was synthesized according to the procedure mentioned in section 3.3.7 (Figure 4.17). Isophorone diisocyanate was reacted with BOHEPPO polyester polyol and 2 hydroxyethylmethacrylate to yield urethane acrylate. Completion of reaction was checked by FT-IR and ^{1}H-NMR as shown respectively in Figure 4.18 and Figure 4.19.

The IR spectrum in Figure 4.18 contains characteristic peaks of N-H (3355 cm^{-1}), and C=O (1713 cm^{-1}), -C-N- stretching bands (1568 cm^{-1}), C-H aliphatic stretching

band (2925 cm^{-1}) are also observed. The disappearance of the absorption bands of the NCO group (2270 cm^{-1}) of IPDI, which exists before reaction, also proves the synthesis of the urethane acrylate.

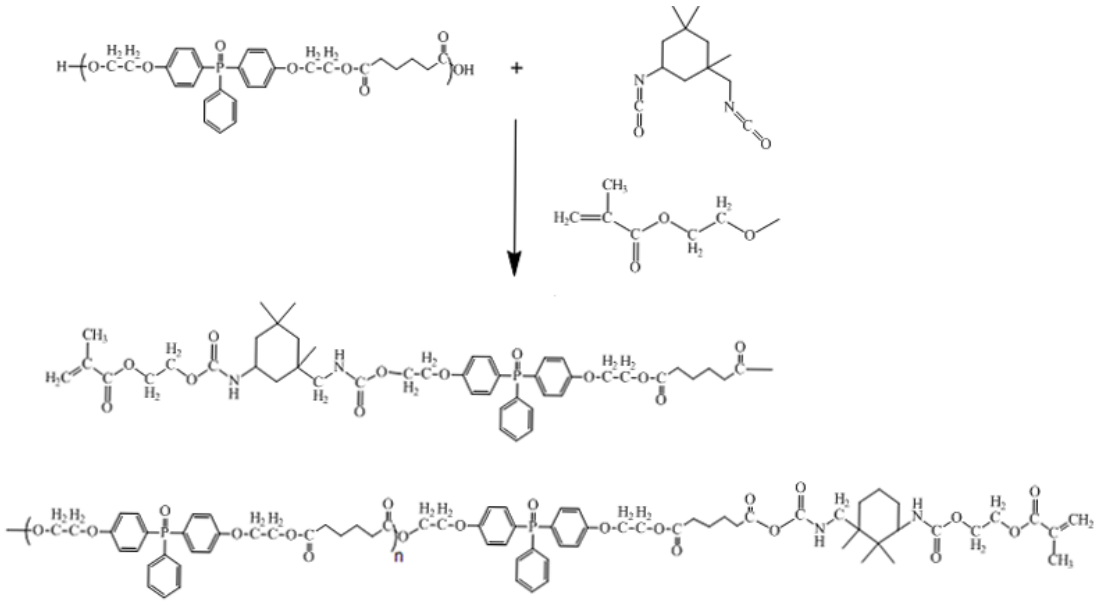


Figure 4.17 : Synthesis scheme of BOHEPPO PE UA

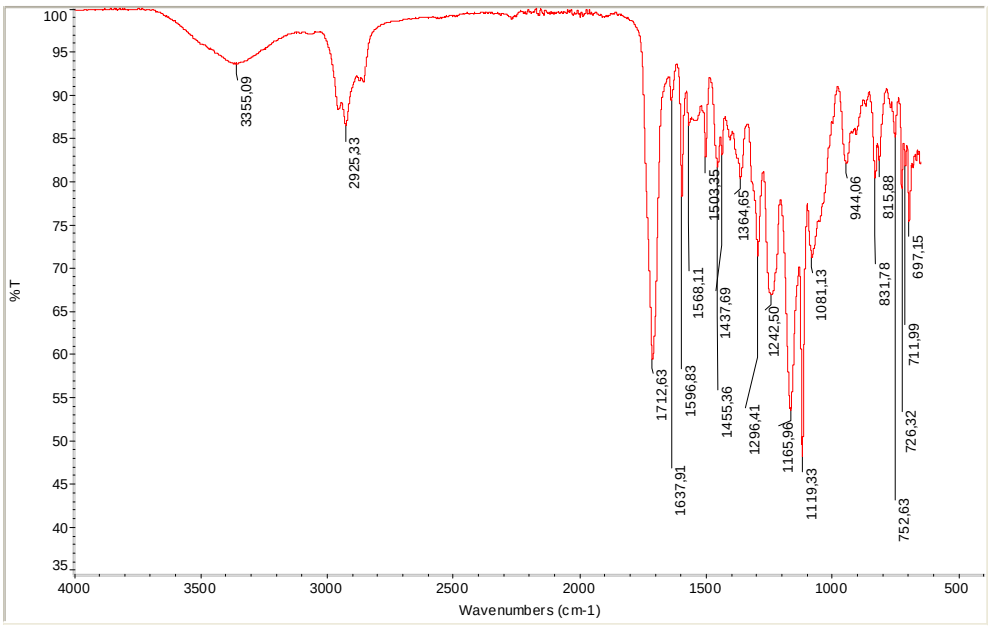


Figure 4.18 : FT-IR spectra of BOHEPPO PE UA

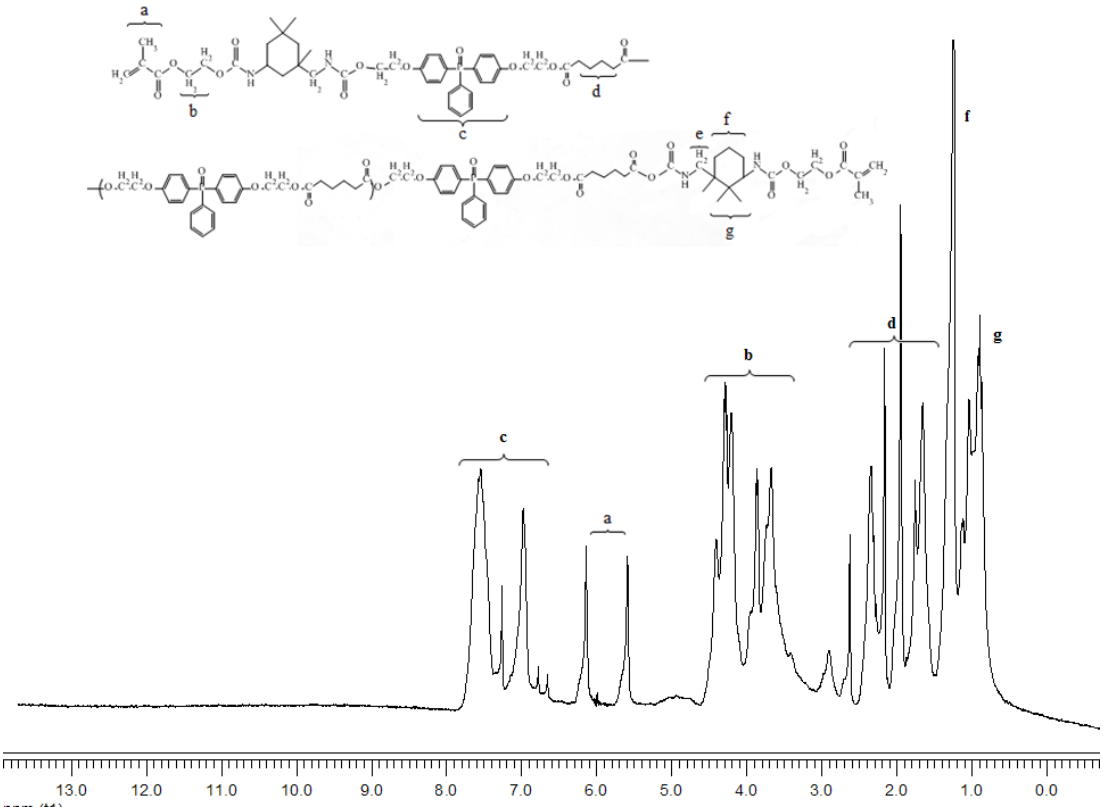


Figure 4.19 : ^{1}H-NMR Spectrum of BOHEPPO PE UA

4.8 Film Formation

Films were prepared according to procedure mentioned in section 3.4. Free films and coated papers were obtained by UV curing. In addition, samples are tested by methods mentioned in section 3.5.

4.8.1 Thermogravimetric Analysis

TGA analysis were carried out in a nitrogen atmosphere at a heating rate of 20°C/min between 30°C and 800°C for analyzing thermal stabilities of the films**.** Figure 4.20 shows TGA curves for free films of different formulations. The thermogram results are showed in Table 4.1.

All samples exhibited 5% weight loss at around 310 ^{0}C. 5% weight loss temperature values of F10, F11, F12 ,containing respectively %5, %10, %15 phosphorus material (BOHEPPO PE UA), are decreasing by increasing phosphorus values. It can be assumed that -P=O bonds have poorer stability than C-C which decrease the thermal stability.

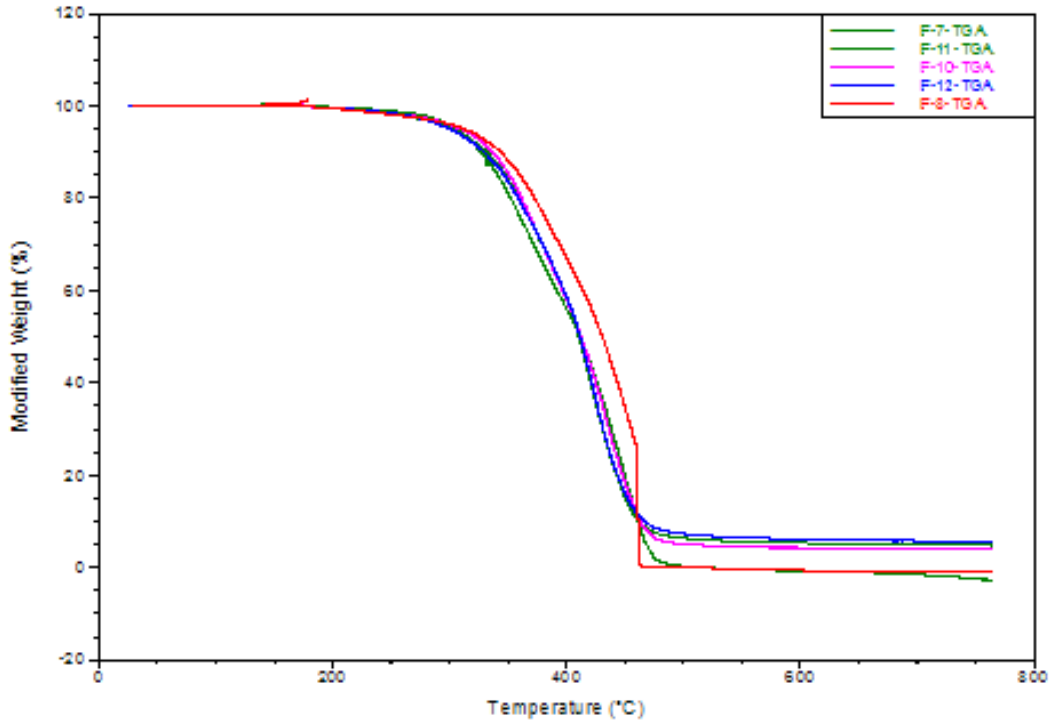


Figure 4.20 : TGA thermogram of samples F7, F8, F10, F11, F12

Table 4.1: TGA analysis values of cured free films

Sample Code	5% Weight Loss Temperature (°C)	50% Weight Loss Temperature (°C)	Char Yield (%)
F7	306	412	0
F8	313	431	0
F10	310	413	4
F11	302	410	5
F12	300	412	6

The samples containing phosphorus material (BOHEPPO PE UA) have higher char values. And the increasing BOHEPPO PE UA ratio caused an increase in char yield It can be assumed that phosphorus content increase flame resistant of coating. The residual content increase and act as physical barrier which prevent further combustion.

4.8.2 Gel Content Measurement

Gel content test was applied to free films cured by UV radiation. It was applied to measure the polymerization degree of the system. This procedure was preceded as mentioned in section 3.5.4 and gel content values are listed in Table 4.2.

Table 4.2: Gel content of cured free films

Sample Code	Gel Content (wt %)
F1	98
F2	97
F3	96
F4	98
F5	96
F6	97
F7	99
F8	97
F9	96
F10	95
F11	93
F12	92

This results show us that unreacted part of cured materials are mostly under wt. 5%. It may be attributed that gel content values of the films increase because of high polymerization degree due to crosslinking. In addition phosphorus containing formulations have more unreacted monomers. The reason can be the difficulty of crosslinking of phosphorus containing structure because of the steric hindrance of phenyl groups.

4.8.3 Solvent Resistance

Solvent resistance test was applied to cured free films according to section 3.5.5. The solvents and the results were listed in tables between Table 3.3 to Table 3.14.

Table 4.3: Solvent resistance of F1

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

F1 which contains high epoxy acrylate ratio gives the best solvent resistance values because of the good chemical resistance property of the epoxy acrylate. Also F1 has less reactive diluent ratio than the other formulations.

Table 4.4: Solvent resistance of F2

Solvents	Weight loss (%)	Appearance
Xylene	1	Good
Methanol	4	Good
Chloroform	< 1	Good
10% CH_3COOH	−	Good
10% HCl	−	Good
10% NaOH	< 1	Good

F2 has less epoxy acrylate and less reactive diluent than F1 which makes F2 less solvent resistant. But the results show that F2 has better solvent resistance than the other formulations except F1.

Table 4.5: Solvent resistance of F3

Solvents	Weight loss (%)	Appearance
Xylene	1	Good
Methanol	5	Good
Chloroform	< 1	Good
10% CH_3COOH	−	Good
10% HCl	1	Good
10% NaOH	1	Good

Table 4.6: Solvent resistance of F4

Solvents	Weight loss (%)	Appearance
Xylene	2	Good
Methanol	3	Good
Chloroform	< 1	Good
10% CH_3COOH	< 1	Good
10% HCl	−	Good
10% NaOH	< 1	Good

F3 and F4 have the same ratio of reactif diluent. And their resin ratio values are similar. Then, they have similar solvent resistance results. There isn't any broken part in these materals. And in addition they still have good appearances after the test.

Table 4.7: Solvent resistance of F5

Solvents	Weight loss (%)	Appearance
Xylene	6	Good
Methanol	6	Good
Chloroform	1	Good
10% CH_3COOH	−	Good
10% HCl	< 1	Good
10% NaOH	−	Good

F6 doesn't contain polyester group in its formulation. After testing in chloroform solvent the material had broken. It can be said that polyester based urethane acrylate improves also solvent resistance of the material.

Table 4.8: Solvent resistance of F6

Solvents	Weight loss (%)	Appearance
Xylene	3	Good
Methanol	6	Good
Chloroform	< 1	Broken
10% CH_3COOH	−	Good
10% HCl	3	Good
10% NaOH	3	Good

Table 4.9: Solvent resistance of F7

Solvents	Weight loss (%)	Appearance
Xylene	3	Good
Methanol	3	Good
Chloroform	−	Good
10% CH_3COOH	−	Good
10% HCl	1	Good
10% NaOH	1	Good

F7 has high urathane acrylate ratio. And it have a good appearance and good solvent resistance results comparing the other formulations containing 60% resin.

Table 4.10: Solvent resistance of F8

Solvents	Weight loss (%)	Appearance
Xylene	−	Good
Methanol	5	Good
Chloroform	−	Good
10% CH_3COOH	−	Good
10% HCl	1	Good
10% NaOH	−	Good

F8 which contains commercial resins gives good results and appearance after being testing.

Table 4.11: Solvent resistance of F9

Solvents	Weight loss (%)	Appearance
Xylene	3	Good
Methanol	<1	Good
Chloroform	−	Good
10% CH_3COOH	−	Good
10% HCl	1	Good
10% NaOH	−	Good

Formulations between F10 and F12 contain phophorus urethane acrylate component. F10 and F11 were broken in chloroform solvents. And the solvent resistance test results are lower than non phosphorus containing formulations.

Table 4.12: Solvent resistance of F10

Solvents	Weight loss (%)	Appearance
Xylene	−	Good
Methanol	5	Good
Chloroform	5	Broken
10% CH_3COOH	−	Good
10% HCl	1	Good
10% NaOH	<1	Good

Table 4.13: Solvent resistance of F11

Solvents	Weight loss (%)	Appearance
Xylene	4	Good
Methanol	8	Good
Chloroform	10	Broken
10% CH_3COOH	−	Good
10% HCl	−	Good
10% NaOH	<1	Good

Table 4.14: Solvent resistance of F12

Solvents	Weight loss (%)	Appearance
Xylene	4	Good
Methanol	8	Good
Chloroform	8	Good
10% CH_3COOH	3	Good
10% HCl	−	Good
10% NaOH	−	Good

4.8.4 Contact Angle Measurement

Contact angle measurement was applied to the coated papers. This test measures the contact angle of water on the cured films by direct reflection of the surface wettability. The contact angle value of a liquid on a film is a direct reflection of the surface wettability. Contact angles of water were measured on coated papers. For each measurement one drop of water was tested on the surfaces and results are shown in Table 4.15.

According to the results every coated papers has a hydrophobic effect in comparison with the paper non-coated. In addition, phosphorus containing sample have high contact angle values. This is an expected behavior assuming that phosphorus component comes from BOHEPPO PE UA makes the surface more hydrophobic. Increasing phosphorus content the contact angle values shift to higher values.

Table 4.15: Contact angle test results

Sample Code	Water Contact Angle (°)
Blank	67
F1	69
F2	73
F3	71
F4	77
F5	75
F6	73
F7	78
F8	69
F9	69
F10	75
F11	76
F12	81

4.8.5 Gloss test

Gloss test applied to the coated papers were measured at the angles of 20^0, 60^0 and 85^0. The test materials were prepared by coating paper as mentioned in section 3.5.7. The test results are given in table 4.16.

Table 4.16: Gloss test values of coated papers

Sample Code	Gloss		
	20	60	85
F1	85	96	97
F2	83	91	97
F3	82	93	98
F4	72	88	96
F5	71	86	96
F6	86	92	97
F7	75	87	96
F8	73	93	96
F9	85	92	98
F10	72	88	95
F11	73	89	95
F12	72	89	96

Every sample containing high epoxy acrylate ratio increase the gloss value of the coated paper. In addition, unsaturated polyester containing formulations make the gloss values less than the other sample. It can be assumed that gloss values were decreased according to the double bonds of unsaturated polyester, which give a clear yellow color to the sample. According to the wellness of the other mechanical

behavior of these samples can be used in pigmented or matt varnishes on request. In addition, phosphorus components give a good gloss behavior to the papers. Different phosphorus ratios give a slightly change on gloss values

4.8.6 Pendulum Hardness Test

König pendulum hardness test is applied after all formulations coated papers surfaces. The results are shown in Table 4.17.

Table 4.17: Pendulum hardness results (oscillation)

Sample Code	Pendulum Hardness
F1	64
F2	42
F3	31
F4	35
F5	38
F6	41
F7	35
F8	29
F9	33
F10	32
F11	36
F12	37
Blank	23

The pendulum hardness test is based on the principle that the amplitude of the pendulum's oscillation will decrease more quickly when supported on a softer surface. The hardness of any given coating is given by the number of oscillations made by the pendulum. The Konig test is for hard coatings. And the hardness of the coating is related to the abrasion and scratch resistance. Also crosslinking degree and chain flexibility are affecting hardness value of materials. Blank paper pendulum hardness value is 23. The results the results given in table 4.17 shows that as the epoxy acrylate content increase, the hardness values of the films increase due to the rigidity of the epoxy chain. Also increasing phosphorus ratio the hardness value of the paper is increasing.

4.8.7 Pencil Hardness

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

The results show that samples containing phosphorus compounds has a good surface hardness which are close to the pendulum hardness results. The results depends on photocrosslinking degree as well as chemical structure of coatings. Then It can be said that the hardness of these materials is a result of the crosslinking materials.

Table 4.18: Pencil hardness results

Sample	Pencil Hardness
F1	>5H
F2	>3H
F3	>3H
F4	>3H
F5	>4H
F6	>4H
F7	>5H
F8	>4H
F9	>3H
F10	>4H
F11	>5H
F12	>5H

4.8.8 Tensile Test

Stress-strain test was applied to the free films prepared at dimensions shown in Figure 4.21. And the stress-strain values of this mechanical test are given in Table 4.19.

The tensile test serves as the basis for determining several important mechanical properties of materials. In this test, the yield strength, tensile strength, elongation,

and reduction in area of a material specimen are determined. In addition, the modulus of elasticity, modulus of resilience, and modulus of toughness of a material are found from the stress–strain curve measured during the tensile test. An elastic modulus, or modulus of elasticity, is the mathematical description of an object or substance's tendency to be deformed elastically.

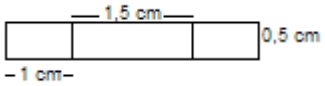


Figure 4.21 : Standard dimensions of the sample

Table 4.19: Stress-Strain Analysis Results

Sample Code	Modulus (N/mm^2)	Tensile Strength (MPa)	Elongation at Break (%)
F2	465	27	9
F3	366	22	10
F4	357	23	10
F5	244	12	7
F6	340	13	6
F7	426	23	11
F8	627	29	7
F9	290	13	7
F10	232	15	11
F11	235	16	10
F12	240	13	9

The resulting stress-strain curves show that these crosslinked materials are lightly elastic and rather brittle. These materials deform only to a small extent at relatively high loads.

Modulus value is a measure of the stiffness of material, then the results show that phosphorus containing materials are less stiffer than the other samples while their elongation values, which demonstrate the flexibility, are similar to them.

Because of its higher ratio of resin content, sample F3 has a greater modulus value than the other samples.

Sample F6 which doesn’t contain polyester urethane acrylate component in its formulation. It has the lower elongation value. This can be estimated that, the presence of polyester urethane acrylate provide flexibility to the materials.

5. CONCLUSION

The aim of this study was to synthesis a new UV curable polymeric compound containing phosphorus to use as a paper coating material and to improve paper mechanical and thermal properties. For this purpose phosphorus containing polyester was synthesized and used as polyol in urethane acrylate reaction. The resulting material used in UV curable coating formulations.

Formulation with high urethane acrylate ratios gives better mechanical properties as flexibility and abrasion resistance as expected from polyester based urethane acrylate. In addition it is clearly seen by the results that phosphorus containing acrylates were increased the char yield which plays an important role in improving flame retardency. Furthermore, they exhibit good gloss and contact angle values comparing to the non-phosphorus materials. Then, instead of using flame retardant additives which can be disadvantageous for UV curing system and the cured film, using curable flame retardant material will enable the curing system. This work shows that incorporated phosphorus compound gives also good mechanical properties beside the thermal feature.

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