

**BORON CONTAINING EPOXY ACRYLATE COATINGS**

**M.Sc. THESIS**

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**BOR İÇEREN EPOKSİ AKRİLAT KAPLAMALAR**

**YÜKSEK LİSANS TEZİ**

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*To my family,*



## **FOREWORD**

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## ABBREVIATIONS

<b>BFPPO</b>	: Bis(4-fluorophenyl)phenylphosphine oxide
<b>BOHPPO</b>	: Bis(4-hydroxyphenyl)phenyl phosphine oxide
<b>BOHEPPO</b>	: [(4- $\beta$ -hydroxyethoxy)phenyl]phenyl phosphine oxide
<b>BM-M</b>	: Boron methacrylate monomer
<b>BM-O</b>	: Boron methacrylate oligomer
<b>HEMA</b>	: 2-Hydroxy ethyl methacrylate
<b>NMR</b>	: Nuclear Magnetic Resonance
<b>TGA</b>	: Thermal Gravimetric Analysis
<b>FT-IR</b>	: Fourier Transform Infrared
<b>DPGDA</b>	: Dipropyleneglycoldiacrylate
<b>HDDA</b>	: 1,6-hexanedioldiacrylate
<b>MeHQ</b>	: Methylhydroquinone
<b>APPO</b>	: Acrylated phenyl phosphine oxide



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## **BORON CONTAINING EPOXY ACRYLATE COATINGS**

### **SUMMARY**

UV-Curable coating applications have gained wide interest due to their advantages such as lower energy consumption, less environmental pollution, lower process costs, high chemical stability, and very rapid curing even at ambient temperatures. UV-Curable coatings are continually being developed by many leading suppliers in efforts to reduce any detrimental effects to the environment and to meet the high standards required by industry. Especially, in the UV-curing industry, epoxy and epoxy acrylate derivatives have been widely used as coatings, structural adhesives, and advanced composite matrices. What distinguishes epoxy resins from the other polymers is their excellent chemical and solvent resistance, good thermal and adhesion properties, and versatility in cross-linking. For this reason, enhanced hardness and superior thermal stability are also frequently required.

In the area of flame resist polymers, boron containing polymers have been pointed out in recent developments. The flame-retardant action of the boron-containing compounds on polymeric materials is chemical as well as physical. It was found that these inorganic boron compounds promote char formation in the burning process.

Organic-inorganic hybrid materials suitable for the development of sol-gel coatings were prepared with tetraethylortho silicate and methacryloxypropyltrimethoxy silane. The hybrid materials can be formed by hydrolysis and condensation of the reactants.

In this study, polymerizable boron methacrylate monomer and boron methacrylate oligomer was prepared and a series of UV-curable boron containing epoxy acrylate coatings were set up. UV-cured organic-inorganic hybrid materials can be prepared through a combination of hydrolysis and condensation reactions of the inorganic part and photopolymerization of the organic moieties in order to obtain glass-like materials. The flame retardant performance of boron element was investigated with thermal gravimetric analysis. Also, the incorporation of phosphorus into polymer is expected to introduce flame retardancy, thermal stability to the material. Furthermore, coating performances were examined with various tests, such as pencil hardness, contact angle, gel content, tensile test, solvent resistance.





## BOR İÇEREN EPOKSİ AKRİLAT KAPLAMALAR

### ÖZET

Epoksi reçineler plastikler ve yapıştırıcılar üretiminde kullanılan termoset polimerlerdir ve kürlleme bileşikleriyle karıştırıldığında çapraz bağlı yapılara dönüşürler. Fiziksel hali düşük viskoziteli sıvıdan erime noktası yüksek katılara kadar değişen ürünler vardır. Çeşitli sertleştiricilerle kontrol altında çapraz bağlı yapılar oluşturulabildiğinden istenilen fiziksel özelliklerde ürünler elde edilebilir; bu nedenle temel endüstri tarafından oldukça sık kullanılan bir reçine grubudur. Epoksi reçineler çeşitlidir; en çok üretilen tür Bisfenol A bazlı epoksi reçinelerdir; bunlar epiklorohidrin ve bisfenol A bileşiklerinden üretilir. Epoksi reçineler düşük ve yüksek sıcaklıklara dayanıklıdır, darbeyi absorblayacak esnekliktedir, elektrik direnci ve kimyasal maddelere karşı dirençleri yüksektir, yapıştırıcı özelliği yüksektir. Epoksiler değerli kaplama maddeleridir, elektrik ve elektronik parçaların kaplanması için kullanılır. Epoksi yapıştırıcılar metaller, konstrüksiyon malzemeleri ve diğer sentetik reçinelerin üzerine uygulanabilir. Bazı endüstriyel uygulamalarda perçin ve kaynak maddesi olarak, yiyecek ve içecek kaplarının iç kısımlarını kaplamada ve tekne, yat v.s.de dış kotuyucu kaplama malzemesi olarak kullanılabilir.

UV ışınları ile sertleştirilen kaplama malzemeleri, fotokimyasal olarak başlatılan polimerizasyon sonucu hazırlanırlar. Yapı içinde bulunan fotobaşlatıcılar UV ışınları ile uyarılarak reaktif parçacıklar oluşturmaktadırlar. Serbest radikal adı verilen bu reaktif parçacıklar, ortamda bulunan olefinik oligomer ve monomerlerle tepkime verip, serbest radikal mekanizma ile polimerleşmeyi başlatmaktadırlar. Birçok yüzey, dekoratif ve koruma amacıyla boya yada kaplama adı verilen malzemeler ile işlem görmektedir. Yaygın olarak kullanılan sentetik, su bazlı ve toz boyalar yanında 1960'lı yılların başından bugüne UV ışınları ile sertleştirilen boya ve kaplamaların kullanımı güncel hale gelmiştir. Konu üzerinde yapılan çalışmalar ve her geçen gün avantajlarının ortaya çıkması, UV ışınları ile sertleştirilen kaplama kullanımını yaygınlaştırmaktadır. UV ışınları ile sertleşebilen kaplamaların düşük enerji maliyeti, % 100 katı madde içeriğine sahip olmaları, organik uçucu solvent içermemeleri ve çevre sağlık açısından olumsuz bir etkiye sahip olmamaları, kaliteli ürünler verebilmeleri, düşük yatırım ve üretim maliyetine sahip olmaları, dışçilikten yer döşemesine kadar geniş bir uygulama alanına sahip olmaları bu tür kaplamaları cazip hale getirmiştir. UV ışınları ile sertleştirilen kaplamalar başlıca; kağıt, plastik, ahşap, metal, optik fiberlerin kaplanmalarında kullanılmaktadır. Bununla birlikte hassas çalışma gerektiren ve ısıya karşı duyarlı lens, elektronik devreler gibi yüzeylerin kaplanması bu tür kaplamalar kullanılır.

Bu kaplamaların hazırlanmasında fotobaşlatıcılar, oligomerler ve reaktif seyrelticiler (monomerler) kullanılmaktadır.

Kaplamanın hazırlanmasında kullanılan malzemeler arasında en önemlileri oligomerlerdir. Oligomer seçimi, kaplamaya verilmesi istenilen özelliğe ve uygulama alanına göre yapılmaktadır.

Bu çalışmada diglisidil eter bisfenol A epoksi reçine ile akrilik asitin reaksiyonundan sentezlenen epoksi akrilat, UV ile sertleştirilen kaplamalarda kullanılan temel oligomerlerdendir. Epoksi akrilatlar terminal akrilat fonksiyonallitesi nedeniyle UV kürleme reaksiyonlarında yüksek reaktivite göstermektedirler. Bu seçimde epoksi akrilat oligomerler reaktivite, parlaklık, yapışma, kimyasal dayanım, çizilme ve aşınma dayanımı, sararmama özelliklerine göre seçilirken bu özelliklerin oluşumunda oligomerlerin kimyasal yapısı, fonksiyonallitesi ve molekül ağırlığı rol oynar. Epoksi akrilatlar kağıt, plastik, ahşap, metal için şeffaf kaplama ve üst baskı cilası ve aynı malzemeler için pigmentli kaplamalarda, elektronik uygulamalar için devre levhası üretiminde, kağıt için UV kurumalı ve ıslak ofset litografik, fleksografik ve ipeksi mürekkeplerde, kağıt, film ve foil için laminasyon katkılarında ve kompozitlerde kullanılmaktadırlar.

Monomerler kürlenme hızının artırılması, viskozitenin düşürülmesi ve çapraz bağlanma yoğunluğunun artırılması amacıyla kullanılırlar. Monomerlerin seçiminde oligomerle uyumu, fonksiyonallite, kimyasal yapı, molekül ağırlığının yanı sıra toksite ve tahriş edici özellikleri önemlidir.

Fotobaşlatıcılar belirli dalga boyundaki UV ışını ile aktivite olan ve çapraz bağlanmayı başlatan moleküllerdir. Fotobaşlatıcı ve monomer son film özellikleri üzerinde önemli etkiye sahip olduğundan bu kimyasalların seçiminde ürünün kullanım alanı belirleyicidir.

Polimerik malzemeler, koruyucu ve dekoratif amaçla kaplandıkları yüzeylere kolay tutuşurluk gibi istenmeyen bir özellikte kazandırılırlar. Bilindiği gibi çoğu polimerik malzemenin ve epoksi akrilat kaplamaların yanıcı özelliği vardır ve bu yüzden UV ile sertleştirilen kaplamalara yanma geciktirici özelliğinin verilmesi gerekmektedir. Kaplama teknolojisinde polimerik malzemelerde yanma geciktiriminin sağlanması iki metotla olabilmektedir. İlk metotta yanma geciktirici olarak kullanılan maddeler, sisteme katkı malzemeleri olarak fiziksel şekilde eklenmektedirler. Bu şekilde sisteme dahil edilen metal hidroksit, halojen, fosfor, nitojen ve sülfür içeren bileşikler fiziksel karışım sırasında sisteme iyi şekilde dahil olamadıklarından, kaplamanın mekanik ve yüzey özelliklerini bozabilmektedirler. Ayrıca UV ışınlarını absorbe ederek verimin düşmesine, kürlenme hızının yavaşlamasına neden olabilmektedirler. Bu bileşikler sistem içerisinde homojen olarak karışmamakta; çökme veya faz ayrımları gözlenmektedir. Bu dezavantajlarından dolayı UV ışınları ile sertleştirilen kaplamalarda, polimerik zincire içermiş olduğu doymamış çift bağları ile çapraz bağ oluşturarak kimyasal olarak dahil olabilen bileşiklerin kullanılması ikinci bir metot olarak kullanılmaktadır.

Günlük hayatımızda her yönü ile giren, pekçok alanda alternatifsiz olarak kullanılan bor elementi, stratejik ve ekonomik bir öneme sahiptir. Borun endüstriyel kullanımı elementel bor yanında daha çok bor türevleri şeklinde olmaktadır. Bor türevlerinden biri olan borik asit esterleri çeşitli endüstriyel proseslerde doğrudan reaktif olarak veya reaksiyon kontrol kimyasalları şeklinde bir çok alanda kullanılmaktadır. Borik asit kullanılarak sentezlenen bor türevlerinden biri olan borik asit esterleri genellikle

polimerizasyon reaksiyonlarında katalizör, polimer stabilizatörleri ve yangın geciktirici olarak kullanılır. Bor içeren bileşiklerin polimerik malzemelere etkisi hem kimyasal hem de fiziksel olmaktadır. İnorganik bir madde olan bor elementini içeren bileşiklerin termal özelliklerinin daha iyi olduğu bilinmektedir. Bor elementi karbon ve silisyum elementlerine benzerliği en fazla ve oksijene karşı kimyasal reaksiyona girme isteği çok yüksek olan bir elementtir. Bu nedenle çok sayıda ve değişik özelliklere sahip olan bor-oksijen bileşikleri bulunmaktadır.

Son yıllarda, etkinliği ve güvenilirliği artırılmış, fiziksel, kimyasal ve mekanik özellikleri geliştirilmiş, daha hafif, daha ucuz ve yeni uygulamalarda istenen işlevleri yerine getirebilecek malzemelere olan talep artmıştır. Özellikle, uygulamalarda malzemelerin yüzey özellikleri büyük önem taşımaktadır, malzemenin kendisinin gerekli koşulları sağlayamadığı durumlarda, yüzey modifiye edilerek uygun özellikler kazandırılmaktadır. Bu kaplamalar, fiziksel işlemler ve yüzeyde atom, iyon ya da moleküllerin implantasyonu gibi çeşitli yöntemlerle yapılmaktadır. Uygulanan kaplama yöntemlerinden biri de sol-jel yöntemidir.

Sol-jel yönteminde çeşitli (organik-inorganik ve inorganik-organik) hibrit malzemeleri hazırlanır. Hibrit malzemelerin özellikleri; organik ve inorganik bileşenlere ve bu iki fazın birbiriyle etkileşmesine bağlıdır. Organik ve inorganik kısımlar arasında güçlü kovalent bağların oluşmasıyla hibrit malzemeler elde edilir. Günümüzde bu malzemeler çeşitli kaplamalarda; optik kaplamalar (antirefleksif, optoelektronik), elektronik kaplamalar (foto anodlar, yüksek sıcaklığa dayanıklı süper iletkenler), koruyucu kaplamalar (sert, korozyona dayanıklı) ve dış materyallerinde geniş uygulama alanı bulmuştur. Sol-jel tekniği ile hibrit malzemelerin hazırlanmasında inorganik bileşen olarak kullanılan Si, Ti, Zr, Al gibi metal alkoksitlerin hidroliz ve kondenzasyon reaksiyonları sonucunda camı ağ yapı oluşturulur. Fonksiyonel yapı içeren organik kısım, bahsedilen camı ağ yapı ile termal veya fotopolimerizasyon teknikleri ile polimerleştirilerek aralarında kimyasal bağlanma sağlanır. Bu tip hibrit materyallerin hazırlanması ile inorganik maddelerin yüksek ısıl direnci, mekanik ve optik özellikleri ile organik polimerlerin esneklik, kolay işlenebilirlik, çözünürlük gibi özellikleri bir matriks içinde bir araya getirilmektedir.

Yanmazlık artırıcı ve alev geciktirici olarak fosfor bileşikleri yaygın olarak kullanılmaktadır. Bu katkı maddesi polimerin oksijen ile temasını engelleyen bir koruyucu tabaka oluşturarak alevlenmeyi engelleyici yönde etkinlik gösterir. Ayrıca bu bileşikler aktif grupların oluşumunu engelleyici özellik göstererek alevlenmeyi engeller. Fosfor maddelerinin alevlenmeyi geciktirme mekanizması malzemenin yüzeyinin oksijen ve alev ile temasını engelleyecek biçimde bir koruyucu tabaka oluşturması, kömürleşen bir tabaka oluşturması ve aktif grupların oluşumunu engelleyen özellikleri ile açıklanmakta olup polimerin türüne ve kullanılan fosfor içerikli bileşiğine göre değişiklik gösterir.

Bu çalışmanın amacı  $\alpha$ - $\beta$ -etilen doymamış monokarboksilik asit, borik asit ve doymamış alifatik hidrokarbon grubundan yola çıkarak polimerleşebilen bir bor metakrilat monomerinin (bor ester) sentezlenmesi ve bu bileşiğin UV ile kürleşebilen epoksi akrilat kaplamalarda kullanılıp, termal ve mekanik özelliklerinin incelenmesidir. Ayrıca sol-jel metoduyla TEOS ve MAPTMS bileşiklerinin hidroliz

ve kondenzasyonu ile hazırlanan UV ile sertleşebilen organik-inorganik hibrit kaplamaların da termal ve mekaniksel özellikleri incelenecektir. Elde edilen ürünün karakterizasyon çalışmaları FTIR, NMR ve ısıl davranışları termal analiz yöntemleri ile incelenecektir. Bu çalışmada termo gravimetrik analiz yöntemi kullanılarak elde edilen kaplamaların termal davranışları incelenmiştir.

## 1.INTRODUCTION

Epoxy acrylate resins are commercially used in coatings and various structural applications. By proper selection of epoxy acrylate resin and monomers, the cured thermosetting product can be tailored to specific performance characteristics. The choice depends upon the cost, processing and performance requirement. Cured epoxy acrylate resins exhibit excellent adhesion to a variety of substrates, good chemical and corrosion resistance, excellent electrical insulation, high tensile, flexural strength, good compressive strength and thermal stability. The largest single use is in coatings, where high chemical, corrosion resistance and adhesion are important. The exceptional adhesion performance is due to the presence of polar hydroxyl and ether groups in the backbone structure of epoxy resins [1]. The presence of unsaturation at the end of the polymer backbone (due to reaction with acid functional acrylic monomers) has shaped epoxy resins for the radiation curing industry. Terminal unsaturated double bonds are the reactive sites for coatings and paints [2]. The main drawback of epoxy resins, like many other organic polymers, is their flammability. Recent developments in the chemistry of halogen-free flame retardant polymers involve polymers or reactive monomers that are inherently flame retarding such as those containing P, Si, B, N and other miscellaneous elements. Boric acid and borate salts have been used as flame retardant additives since early 1800s. The flame retardant action of boron-containing compounds on polymeric materials is chemical as well as physical [3].

However, additives have the disadvantage that they have to be used in relatively high concentrations (typically 30% by weight, or more) and this may affect the physical and mechanical properties of the polymers. Also, additives may be leached or may volatilised from the polymer during service. The alternative strategy is to use reactive flame retardants, via copolymerisation some other type of chemical modification (i.e. flame retardant groups that are inherently part of the polymer backbone or that are covalently attached as side groups to the polymer) [4].

In general, the UV curing process results in three dimensional network formations. The curing process is fast and depends on the radiation dose and the time of radiation. UV curing, i.e., the process of photo initiated conversion of polymeric materials from a liquid to a solid is a popular alternative to conventional thermal curing. UV curing systems had recently succeeded in a large number of new applications and expanded toward new markets [5]. Many of these become possible because of the development of new UV-curable system that is commercially available. UV curing process has attractive advantages over thermal curing. Its major advantages are high-speed process, low energy consumption (as the operation at room temperature), and environmental friendly as there is no solvent exposure [6].

In recent years, organic–inorganic hybrid materials have drawn tremendous attention since they combine the advantages of both organic polymers (elasticity, ease of processing, good impact resistance, etc.) and inorganic compounds (hardness, chemical stability, optical properties, thermal stability, etc.). Thus, they are considered innovative advanced materials and have found promising applications in many fields, such as optics, electronics, membranes, and coatings. To construct an organic– inorganic hybrid, an inorganic phase is formed within an organic polymer matrix using a sol-gel process consisting of hydrolysis and condensation of alkoxy derivatives of metals such as silicon, titanium, aluminum and zirconium. The advantage of the sol-gel method is that the reaction that produces hybrid materials proceeds at ambient temperature, in contrast to traditional methods, which require high temperatures. In this method, a suitable coupling agent is employed in order to obtain a strongly interconnected network, preventing macroscopic phase separation. The coupling agent provides bonding between the organic and the inorganic phases [7].

This thesis will be interested in preparation of polymerizable boron methacrylate monomer and boron methacrylate oligomer. Then, series of UV-curable boron containing epoxy acrylate coatings were set up. The flame retardant performance of boron element was investigated with thermal gravimetric analysis. Furthermore, coating performances are examined with various tests, such as pencil hardness, contact angle, gel content, tensile test, solvent resistance. For that purpose, several formulations were prepared in different ratios.

## **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, water resistance, etc. [8]. 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 epichlorohydrin.

#### **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 [9].

The most widely used pair of monomers to prepare an epoxy prepolymer are 2,2-bis(4-hydroxyphenyl)propane (referred to as bisphenol-A) and epichlorohydrin, the epoxide 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 [10].

The two ring-opening reactions occur almost exclusively by attack of the nucleophile on the primary carbon atom of the oxirane group [11]. 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 processability behavior before crosslinking is focused on this oligomer [12].

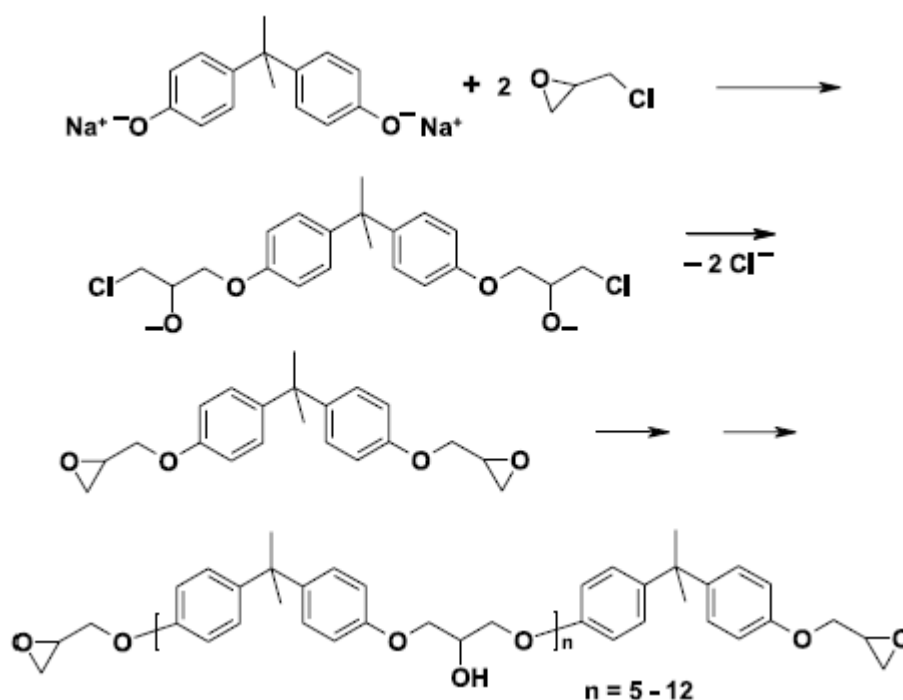
The initial product is the monoglycidyl ether of Bisphenol A. Analogous reaction of the phenolic group of Bisphenol A with NaOH and epichlorohydrin gives the diglycidyl ether of Bisphenol A. The epoxy groups react with Bisphenol A-to extend the chain, these reactions introduce alcohol groups on the backbone. 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 [9].

### **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



**Figure 2.1:** Bisphenol A epoxy resin

groups is low, and so they are cured with materials that react with the hydroxyl groups along the backbone [13].

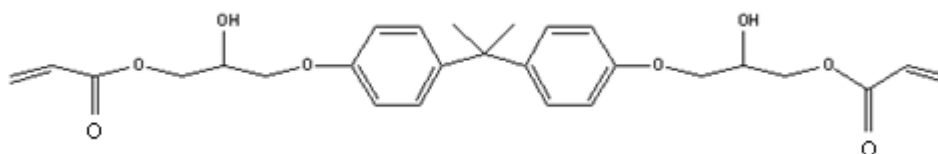
## 2.1.4 Epoxy Acrylates

### 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 phosphine) 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 Tg 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 [15].

#### **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.

#### **Acrylated 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 from 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 [16]. 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 UV Coatings**

### **2.2.1 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 [17].

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 [18].

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. 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 [19].

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.

### 2.2.2 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 vibrational energy ( $E_v$ ), and the rotational energy ( $E_r$ ) as follows:

$$E = E_e + E_v + E_r$$

where,

$$E_e > E_v \gg E_r$$

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

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

where,  $I_0$  is the intensity of the incident light

$I$  is the intensity of transmitted light

$\epsilon$  is the molar extinction coefficient ( $\text{cm}^{-1} \text{mol}^{-1}$ )

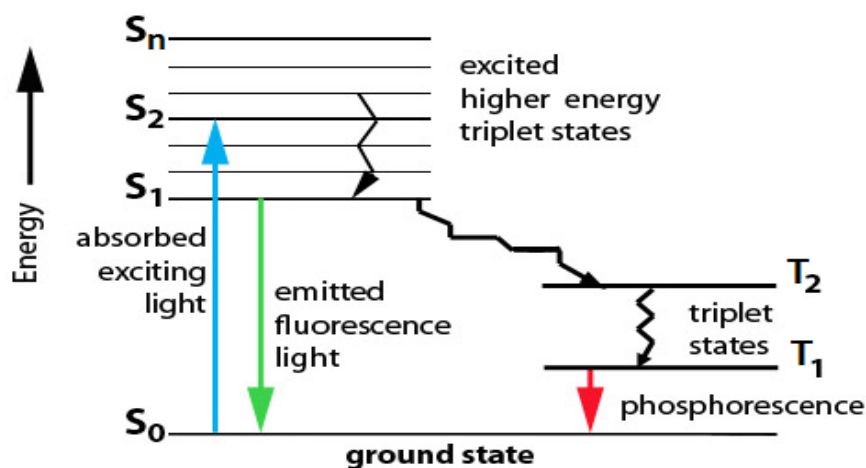
$c$  is the concentration of absorbing species

$d$  is the optical path length

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

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 [20].

The Jablonsky diagram, as Shown in Figure 2.3, can represent the structure of various electronically excited states and the most important photochemical processes involved with these states.



**Figure 2.3:**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  $S_1, S_2 \dots S_n$ , 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  $T_1, T_2 \dots T_n$  with two unpaired spins [21]. 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. 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  $\nu$ ,  $\nu'$ , and  $\nu''$  respective frequencies of the absorbed or emitted light.

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 [22] or degrade polymers, particularly in the presence of oxygen [23]. 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 cointiators; and, if necessary, other coating additives, like surface active additives, slip additives, fillers, pigments, light stabilizers, etc.

### 2.2.3 Raw materials for UV coating systems

#### 2.2.3.1 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.

$PI \rightarrow PI^* \rightarrow \text{Reactive species (free radicals or ions), or}$

$S \rightarrow S^*$

$S^* + PI \rightarrow S + PI^*$  Energy to 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  $I_0$ :

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

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 photoinitiators**

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 [24, 25].

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 a 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 [26]. 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 [27].

### **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 [28]. Initially, diazonium salts were used, but they were replaced by more thermally stable iodonium and sulfonium salts [29].

### **Anionic photoinitiators**

Tertiary amine salts of ketocarboxylic acids [30] were used initially. Newer systems based on peptide chemistry have been described and used in microlithography [31].

#### **2.2.3.2 Oligomers**

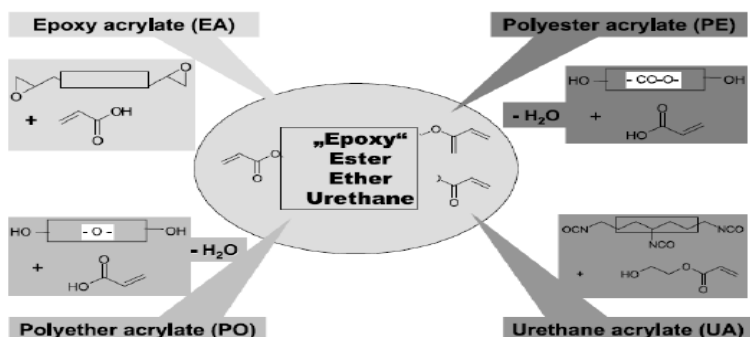
##### **Epoxies**

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 diglycidylether 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 [32].

## Saturated acrylate terminated oligomers

The acrylate resins now dominate the market. The schematic structure of the main acrylate terminated resin classes is shown in Figure 2.4.



**Figure 2.4:** 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.

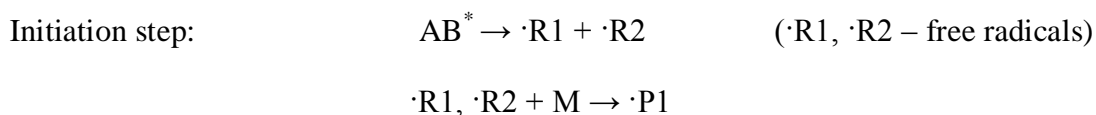
The epoxy acrylates are distinguished by a high reactivity and the cured coatings exhibit good chemical stability. The epoxy component contributes to adhesion to nonporous substrates and enhances chemical resistance of the film [10]. Main uses are paper coatings and inks as well as wood coatings.

### 2.2.4 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  $\Phi$  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 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  $[\cdot P]$ . The quantity  $k_p$  is the propagation rate constant.

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

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

Chain termination occurs by combination or disproportionation of different polymer radicals. The termination rate  $v_t$  is proportional to the polymer radical concentration  $[\cdot P_n]$  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:  $\cdot P_n + \cdot P_m \rightarrow P_n - P_m$

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

Termination rate:  $v_t = k_t [\cdot P]^2$

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

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

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

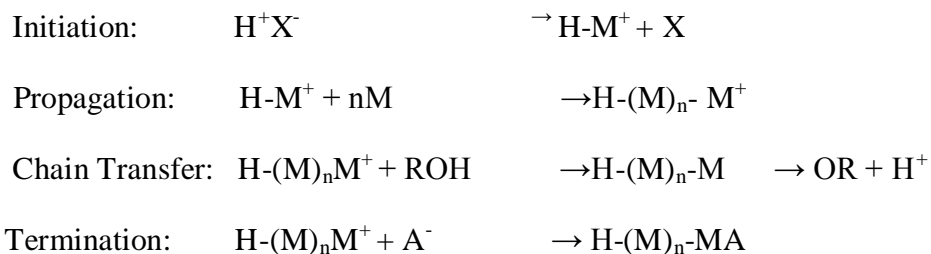
- The light used is monochromatic and is absorbed by the photoinitiator exclusively.
- The absorption is small and homogeneous within the irradiated volume.
- As the polymerization proceeds, a stationary radical concentration is obtained.
- All polymer radicals exhibit the same reactivity toward propagation and termination [10].

### 2.2.5 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  $H^+BF_4$ ,  $H^+PF_4$  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 [34].

Reaction steps in a photoinduced cationic polymerization are as follows:



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

## 2.2.6 UV coating process

### 2.2.6.1 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.

### 2.2.6.2 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 [35]:

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.

### **2.2.6.3 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.) [18].

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.

### **2.2.7 Advantages and drawbacks of UV coatings**

From the many advantages and disadvantages mentioned in the literature, some of the most important are listed below [35]:

#### **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  $>5\text{ }\mu\text{m}$ )

#### **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.

## **2.2.8 UV curing applications**

### **2.2.8.1 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.

### **2.2.8.2 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 [36].

### **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 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 [37].

#### **2.2.8.3 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 [38].

#### **2.2.8.4 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.

#### **2.2.8.5 Adhesives**

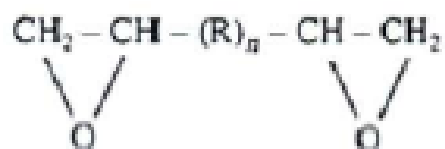
Adhesives are well established, mostly in lamination. Radiation-curable adhesives represent a small but growing segment of the overall radiation curing market because they represent an attractive alternative to solvent based, water-based and hot-melt adhesives. Structural adhesives, pressure-sensitive 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 [39].

## 2.2.9 Raw materials for radiation curable systems

### 2.2.9.1 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. If we generalize an epoxy as:



**Figure 2.5:** Epoxy

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.

### 2.2.9.2 Reactive diluents

Diluents are materials used to reduce the viscosity of formulation to levels suitable for the required method of printing. They may also be 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 units. 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 2.1 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 diol with acrylic acid.

**Table 2.1.:** 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

**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.

**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.

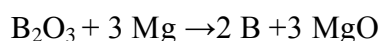
**2.2.9.3 Photoinitiators**

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.

**2.3 Boron and Borates**

Boron, is shown by symbol B in the periodic table, has an atomic number of 5, atomic mass of 10.81 and boron's position in the periodic table, on the border of

metals Be and nonmetals C, determines its physical properties. The melting point of boron is about 2300 °C; its boiling point is 2250 °C. Being a semiconductor, it conducts electrical current only slightly; its conductivity increases rapidly increasing temperature [40]. Boron was discovered in 1808 by Louis-Joseph-Gay-Lussac and Louis Jacques Thénard in France, and independently by Sir Humphrey Davy in England, as the product of the reduction of boric acid (H<sub>3</sub>BO<sub>3</sub>) with potassium. In 1892, H. Moissan obtained purer samples by reducing B<sub>2</sub>O<sub>3</sub> with magnesium. Amorphous boron of lower purity is obtained by as a brown powder with reaction as below:



The name of boron is derived from borax, which had been known since ancient times, and ‘‘carbon’’, to indicate the similarity of two elements.

Elemental boron is a metalloid that has limited commercial applications. Although the term ‘‘boron’’ is commonly referenced, it does not occur in nature in an elemental state [41]. Boron has a very high affinity to oxygen and is therefore [41] boron has a ability to form boron-oxygen compounds which are called ‘‘borates’’ [42] naturally occurring boron consists of 19.10-20.31% <sup>10</sup>B and 80.90-79.69% <sup>11</sup>B. Both isotopes may be obtained from commercially, and find application in NMR spectroscopy.

About 230 naturally occurring borate minerals were identified as of 1996 and the increasing sophistication of analytical instruments, computer assistance, and crystallographic identification ensures that many new ones will be found in the future. Most of the newly reported minerals contain multiple cations or anions, are very large molecules, or have changed cation or anion proportions in large families of borates such as borosilicates, rare earths, boracites, and others. The number of nonmineral borates produced in the laboratory is also very large. Its tri- and tetra (negatively charged)-bonded groups with oxygen can combine in a very large number of geometric combinations and polymer types. Also, the borates can combine with any cation, as well as form double or multiple salts with many other compounds. Boron readily crystallizes with silicates, and can replace aluminum or silicon in varying proportions in some minerals. Because of this, there are more than

8 Na-borate minerals (>27 in the laboratory) and more than 23 Ca-borates with no other cations or anions [42].

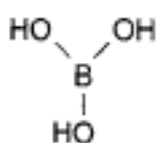
Boron minerals contain different amount of  $B_2O_3$  in their structures. The important factor for industrial application of boron minerals are  $B_2O_3$  content, so they can replace each other in use. This means that one boron mineral can be trade competitor the other one. The most commercially important and frequently traded minerals (salts or borates) are tincal, colemanite, ulexite and kernite [43].

### 2.3.1 Physical properties of boron

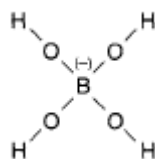
#### Borate crystal structure

The crystal structure of borate minerals and synthetic borates has been rather thoroughly studied, providing some general rules about their structure. Crystallographers also have systematized the possible automatic arrangements of the borates and helped to explain the very large number of borate compounds. All borates contain combinations of the three-(triangular) or four-bond (tetragonal); negatively charged) B-O structures Figure 2.6. Boron always maintains its valance state of +3, so the tetrahedral bonding has a negative charge and seeks attachment to a cation (which helps to make its structures more stable). Cations may occasionally replace hydrogen on some of boron's OH groups at very high temperatures (i.e.,szaibelyite) [42].

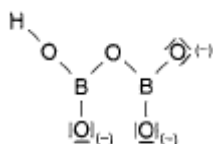
#### 1. Monoborates



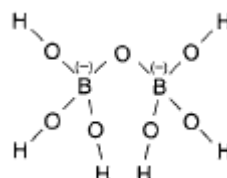
Boric acid Teepleite



#### 2. Diborates

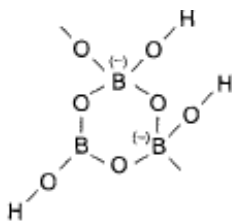


Szaibelyite



Pinnoite

#### 3. Triborates



Colemanite

**Figure 2.6:** Examples of first three compounds of borates.

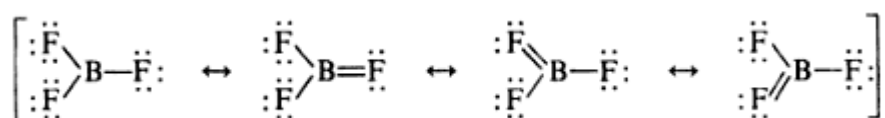
### Coordination Numbers of Boron

Boron can have any coordination number from one to nine; the numbers 3 and 4 are most commonly seen. In the following examples of compounds given for each coordination number and configuration: one BF; two, O=B-B=O (linear) and BF<sub>2</sub> (angular); three, BF<sub>3</sub>, B(OR)<sub>3</sub>, B(NR)<sub>2</sub>, B<sub>2</sub>Cl<sub>4</sub> (trigonal planar); four, BF<sub>4</sub><sup>-</sup>, B<sub>4</sub>Cl<sub>4</sub> (tetrahedral); five, B<sub>5</sub>H<sub>9</sub>, B<sub>6</sub>H<sub>6</sub><sup>-2</sup> (square pyramidal); six, B<sub>6</sub>H<sub>10</sub>; seven, B<sub>11</sub>H<sub>11</sub><sup>-2</sup>; eight, Be<sub>2</sub>B (cubic); nine, Re<sub>3</sub>B.

### Bonds

As a member of the third main group of the periodic system, boron has three outer electrons. Its compound with monovalent group X thus have the composition BX<sub>3</sub>; they are planar molecules with sp<sup>2</sup> hybridized boron and X-B-X angles of 120°. In these compounds, the boron atom has only a sextet of electrons. It therefore attempts to achieve valence saturation by forming an electron octet in three different ways: by p<sub>x</sub>p<sub>y</sub> bonding, by three center bonding, or by formation of adducts.

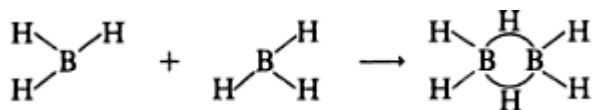
- i) The first route, the formation of  $\pi$  bonds, is observed in compounds BX<sub>3</sub> when X has electron lone pairs, e.g. where X is a halogen, OR or NR<sub>2</sub>; this is illustrated in the following scheme with X=F. In these compounds, a p electron lone pair from the halogen, oxygen or nitrogen serves to fill the fourth, unoccupied p orbital on the boron atom.



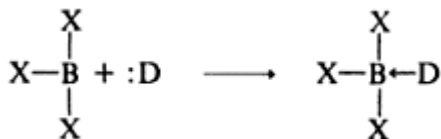
- ii) In the case of the compound BH<sub>3</sub>, in contrast to BF<sub>3</sub>, this kind of valence stabilization is not possible because the H has no electron lone pairs. Instead, the boron forms a two-electron, three-center bond, in which two hydrogen atoms serve



as bridges between two boron atoms and the electron on each is shared not with one, but with two boron atoms.



iii) Instead of intramolecular valence equalization as in (i) and (ii), the boron atom in  $\text{BX}_3$  molecules can also gain its octet by intermolecular donation of an electron lone pair from a donor molecule D, and form a  $\sigma$  bond; this involves a change from  $\text{sp}^2$  to  $\text{sp}^3$  hybridization at boron:



D may be, e.g.  $\text{NR}_3$ ,  $\text{OR}_2$ ,  $\text{OR}^-$ ,  $\text{F}^-$ ,  $\text{H}^-$ . The boron compounds  $\text{BX}_3$  are here acting as lewis acids [40]

Hydrogen bonding is also especially strong with the borates, forming many hydrates, double salts and polymers. In all cases except for the comparatively few mono- and diborates, the b-o grouping tends to form one or more ring structures, allowing electrons to resonate around the ring, thus strengthening its bonds. Ring structures can also form with borates and many organic compounds especially those with adjacent OH or groups that are similar ( $=\text{O}$ ,  $-\text{COOH}$ , etc.)

With all of the borates, hydrogen bonding (and Van der Waals attraction) is particularly strong. It provides the force to hold the isolated, chain, and sheet borate structures together, as well as to attach the double salts and water of hydration. It also keeps the rings stable while they are cleaved and OH and H groups from water during dehydration, thus creating more complex structures [44].

## 2.3.2 Organic Compounds of Boron

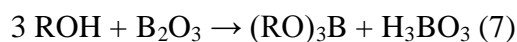
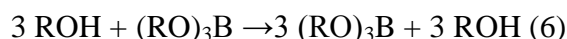
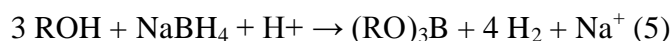
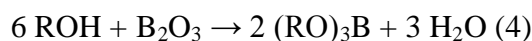
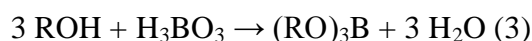
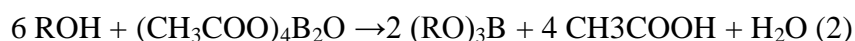
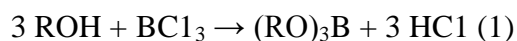
### 2.3.2.1 Introduction

The best known and most stable of the organic derivatives of boric acid are the trialkyl and triaryl orthoborates (borate ester)  $\text{B}(\text{OR})_3$ . Unsymmetrical esters,  $\text{ROB}(\text{OR}')_2$ , are known but tend to disproportionate to the symmetrical forms. The acid ester derivatives of boric acid,  $\text{HOB}(\text{OR})_2$  and  $\text{ROB}(\text{OH})_2$ , have never with

certainity been isolated, although they have been postulated as intermediates in both hydrolysis and dealkylation by hydrogen halides of trialkyl borates [45].

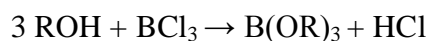
### 2.3.2.2 Preparation of orthoborates

A number of methods for preparing borate esters have been described. They include: reaction of an alcohol (or phenol) with boron trichloride (Equation 1) ; boron acetate (Equation 2) ; boric acid (Equation 3) ; boron oxide (Equation 4) ; or sodium borohydride (Equation 5) ; and trans-esterification with a lower boiling borate ester (Equation 6). When water is a product of the esterification, it has been removed by azeotropic distillation with an excess of the alcohol or an inert medium; or by dehydration with sulfuric acid, copper sulfate, or boron oxide (Equation 7) [46].

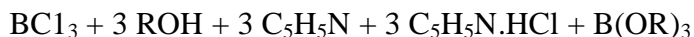


### Boron trichloride

Ebelmen and Bouquet in 1846 were the first workers to mention orthoborates. They prepared trimethyl, triethyl, and triamyl borates by heating the appropriate alcohol with the trichloride in the sealed tube. Michaelis and Hillringhaus in 1901 prepared the first triaryl borates when they obtained the borates of phenol, m-cresol, and  $\beta$ -naphthol by employing the sealed-tube method at 100 °C; chlorinated products were also isolated. More recently it has been showed that heating is unnecessary, triaryl borates being obtained in nearly quantitative yield at -80 °C by the addition of 1 mole of boron trichloride to 3 moles of phenol in methylene dichloride. Wiberg and Sütterlin investigated the reaction sequences in the boron trichloride-methanol and boron tri chloride-ethanol systems, employing a high vacuum apparatus at -80 °C., and showed that quantitative yields of the orthoborates were obtained in both systems when the correct proportion of reagents was used.



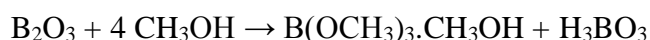
Triborates may be obtained more suitable for larger scale preparations, by addition in an inert solvent such as n-pentane. The method was applicable to all the primary alcohols [n-C<sub>3</sub>H<sub>7</sub>OH; n-C<sub>4</sub>H<sub>9</sub>OH, i-C<sub>4</sub>H<sub>9</sub>OH; (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>OH, n-C<sub>8</sub>H<sub>17</sub>OH; ClCH<sub>2</sub>CH<sub>2</sub>OH, Cl<sup>-</sup> (CH<sub>2</sub>)<sub>4</sub>OH ; CCl<sub>3</sub>CH<sub>2</sub>OH ; C<sub>2</sub>H<sub>5</sub>OOCCH<sub>2</sub>OH, C<sub>2</sub>H<sub>5</sub>OOCCH<sub>2</sub>CH<sub>2</sub>OH, (CH<sub>3</sub>)<sub>3</sub>CCHOHCH<sub>3</sub>; and to secondary alcohols[CH<sub>3</sub>CH<sub>2</sub>CHOHCH<sub>3</sub> ; i-C<sub>3</sub>H<sub>7</sub>CHOHCH<sub>3</sub> C<sub>2</sub>H<sub>5</sub>OOCCH<sub>2</sub>CHOHCOOC<sub>2</sub>H<sub>5</sub> ; (CCl<sub>3</sub>)<sub>2</sub>CHOH ], except those which had a powerfully electron-releasing group, such as a phenyl group attached to the alcoholic carbon atom, when the major product was the alkyl chloride. An example of such a case was 1-phenylethanol. An alkyl chloride was the only product if the method was applied to a tertiary alcohol, e.g., tertiary butyl alcohol. Boron trichloride has been used for the preparation of tertiary alkyl borates, as well as of many other types, in almost quantitative yields by the addition of boron trichloride (1 mole) to a mixture of the alcohol and pyridine (3 moles of each) in an inert solvent at low temperature. The reaction was again rapid.



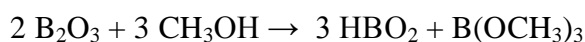
### **Boron trioxide**

Schiff introduced the use of boron trioxide for the preparation of methyl, ethyl, and n-amyl borates, by heating with the appropriate alcohol in a digester. Later, n-propyl, isopropyl, isobutyl, and allyl borates were prepared by heating the oxide with the alcohols in an autoclave at 110-170 °C. For the preparation of very pure methyl and ethyl borates a pressure bottle has been used, which was constantly agitated to avoid caking of the hygroscopic boron trioxide. A 68 per cent yield of crude trimethyl borate was obtained, but this was an azeotrope of the borate (70 per cent) and methanol (30 per cent), from which the alcohol was removed by treatment with calcium chloride. The formation of an azeotrope, which has only been observed in the case of the methyl compound, has proved a constant source of difficulty. A further modification, particularly for borates of high molecular weight, comprised heating boron trioxide and the alcohol with an inert solvent (e.g., toluene) and allowing the condensed vapors to percolate through anhydrous copper sulfate in a Soxhlet extractor, thus removing the water formed in the reaction. The method has been considered to be the most convenient for the preparation of trialkyl borates, when about 20-100 g. was required, and was also extended in its range of application. The method was unsuccessful for the borates of tertiary alcohols.

Recently, an almost quantitative yield of trimethyl borate on a large scale has been achieved; the best results were obtained when the oxide (1 mole) and methanol (4 moles) were used.

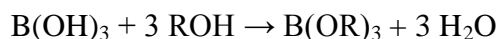


The most recent method employing boron trioxide recommends adding it (2 moles) to methanol (3 moles) at 35-60 °C. and digesting the mixture for 1 hr. at 25 °C.; this procedure afforded trimethyl borate (77 per cent pure) in 92 per cent yield.



### **Orthoboric acid**

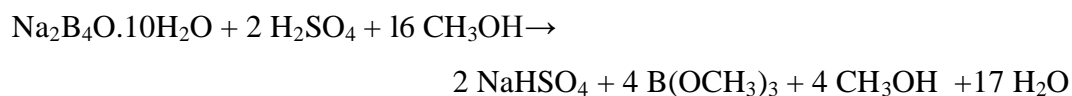
Cohn was the first to use boric acid for the preparation of orthoborates (methyl, ethyl, n-propyl, and isobutyl).



Esterification with alcohols was carried out in the presence of either hydrogen chloride or concentrated sulfuric acid. Later, it was suggested that the water of esterification be removed as an azeotrope with excess alcohol, which could later be recovered. Subsequent workers have shown that the method gives excellent yields for a wide range of trialkyl borates and for triphenyl borate, but is unsuccessful in the case of those borates whose parent alcohols do not form azeotropes with water and for the tertiary alkyl borates, although impure samples of these have been obtained. It has been suggested that the method is in general the most suitable if large quantities of a borate are required, and a further modification, the incorporation of an inert solvent, such as benzene, toluene, or carbon tetrachloride, has been recommended, the water being thus removed as a ternary azeotrope. For trimethyl borate the method has been modified still further; the lowest boiling constituent in this system is the borate-methanol azeotrope and careful fractionation permits esterification to proceed.

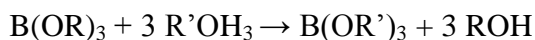
### **Metallic borates**

Trimethyl borate have been synthesized by using borax and the concentrated sulfuric acid employing a large excess of methanol.



## Orthoborates

Easily obtainable trialkyl borates, e.g., n-butyl or n-propyl, have been used to obtain borates which are less readily prepared by other methods.

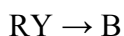


The method was first used by Schiff. Trimethyl borate has been prepared by heating under reflux a mixture of methanol and tributyl borate and subsequently separating the methyl ester from the azeotrope by washing with concentrated sulfuric acid. A wide range of trialkyl borates and also triphenyl borate were obtained by heating under reflux the appropriate alcohol or phenol with tri-n-propyl borate, using benzene as solvent. Triphenyl borate has also been used as a starting material (e.g., for trimethyl borate), but with tertiary butyl alcohol, isobutylene and diisobutylene were isolated and no tri-tert-butyl borate was obtained. This borate has, however, been obtained from triethyl borate and tertiary butyl alcohol in the presence of a trace of sodium, a fractionating column of high efficiency being used. From trimethyl borate, the ethyl, isopropyl, and tert-butyl esters have been made.

### 2.3.3 Heterocyclic Organic Boron Compounds

#### 2.3.3.1 Introduction

The chemistry of cyclic organic molecules with an annular boron, including those with one or two other heteroatoms in the ring as well. A large number of compounds also are known in which a cyclic molecule is formed by chelation between the boron and a donor group, each at one end of an acyclic molecule



(where R represents the carbon chain and Y is usually  $-\text{NR}_2$ ,  $-\text{OR}'$ ,  $=\text{O}$ , etc).

The nomenclature of boron compounds is very confused and a unified system has to be adopted. The standard Ring Index names and numbering will be applied to most of the cyclic systems here, using the normal prefixes for heteroatoms which are shown in Table 2.2:

**Table 2 2 : Nomenclature of rings containing boron and other heteroatoms**

Ring Size	Rings containing nitrogen		Rings containing no nitrogen	
	Unsaturated	Saturated	Unsaturated	Saturated
5	-borole	-borolidine	-borole	-borolane
6	-borine	-boracyclohexane	-borin	-borinane
7	-borepine	-boracycloheptane	-borepin	-borepane

The special properties and high reactivities of boron-containing molecules stem from the fact that normal trigonal boron is electron deficient.

Great interest has therefore centered recently on the preparation of more stable and less reactive boron compounds, most of cycling systems.

### **2.3.3.2 Saturated Rings Containing carbon, boron and one two or three other**

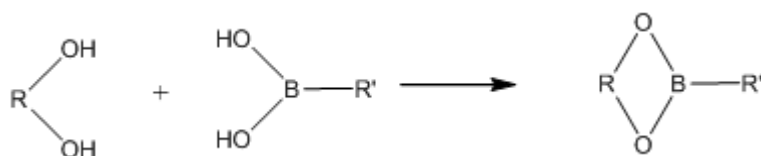
#### **Heteroatoms (Cyclic Borate Ester)**

The only dioxaboracycloalkanes known are the cyclic borate esters of boric acid and borinic acids. The most usual preparatory route is directly from the diol and the boronic or boric acid. Reactions in which six-membered rings (1,3,2-dioxaborinanes), are formed easily, even aqueous solution; formation of five membered rings (1,3,2-dioxaborolanes) is more difficult and does not usually proceed under aqueous conditions unless the product is very insoluble. The water formed in the latter reaction is usually removed as an azeotrope.

A modification of the above reaction uses the borate ester and a diol; transesterification occurs on heating and removal of the alcohol. No catalyst are necessary. Five-, six- and seven-membered rings are all readily formed from diols in which there is no restriction to rotation about the carbon-carbon bonds. The six-membered ester of phenylboronic acid and 2,3- butane-diol was formed in higher yield than the five- and seven-membered esters from other butanediols, suggesting that the former is more easily formed. Dale, Hubert and Hargitay have confirmed earlier suggestions that the six-membered esters of boric acid and ethylene and 1,3-propylene glycols.

The compounds which fall into this category are those in which aromatic stabilization of the heteroring cannot occur, and mainly consist of rings in which the heteroatoms are adjacent, which are cyclic borate esters or amides.

Preparation : (a) The most usual preparatory route is directly from the diol and the boronic or boric acid. Reactions in which six-membered rings (1,3,2-dioxaborinanes, are formed proceed easily, even in aqueous solution; formation of five-membered rings (1,3,2-dioxaborolanes) is more difficult and does not usually proceed under aqueous conditions unless the product is very insoluble. The water formed in the latter reaction is usually removed as an azeotrope.



**Figure 2.7:** Schematic representation of cyclic borate ester

b) A modification of the above reaction uses the borate ester and a diol; transesterification occurs on heating and removal of the alcohol. No catalysts are necessary.

(c) Reaction of a diol with boron trichloride in an inert solvent gives the 2-chloro-1,3,2-dioxaboracycloalkanes; the chlorine can be replaced by primary or secondary amines or alcohols. Alkoxydichloroboranes have been used in place of boron trichloride (3). (d) B-Methyldioxaborolanes have been prepared by heating 1,2-diols with trimethylborane at 340°C.

(e) Cyclic borate esters and their complexes with sodium borate were formed in the reduction of 1,2- and 1,3-diketones by sodium borohydride [47].

## 2.4 Organic-Inorganic Hybrid Materials By The Sol-Gel Method

In recent years, organic–inorganic hybrid materials have drawn tremendous attention since they combine the advantages of both organic polymers (elasticity, ease of processing, good impact resistance, etc.) and inorganic compounds (hardness, chemical stability, optical properties, thermal stability, etc.). Thus, they are considered innovative advanced materials and have found promising applications in many fields, such as optics, electronics, membranes, and coatings. To construct an organic– inorganic hybrid, an inorganic phase is formed within an organic polymer matrix using a sol-gel process consisting of hydrolysis and condensation of alkoxy derivatives of metals such as silicon, titanium, aluminum and zirconium. The advantage of the sol-gel method is that the reaction that produces hybrid materials

proceeds at ambient temperature, in contrast to traditional methods, which require high temperatures. In this method, a suitable coupling agent is employed in order to obtain a strongly interconnected network, preventing macroscopic phase separation. The coupling agent provides bonding between the organic and the inorganic phases, yielding well-dispersed, nanostructured phases. The nanostructures and the properties of the hybrid materials depend greatly on the particle size of the inorganic phase, the uniformity of the distribution of the inorganic phase throughout the organic phase, and the interfacial forces between the two phases [48].

#### **2.4.1 Synthesis of Nanosilica Particles by Sol-Gel Process**

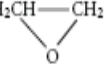
For decay, the sol-gel process is widely applied to produce silica, glass, and ceramic materials due to its ability to form pure and homogenous products at mild conditions. The process involves hydrolysis and condensation of metal alkoxides ( $\text{Si(OR)}_4$ ) such as tetraethylorthosilicate (TEOS,  $\text{Si(OC}_2\text{H}_5)_4$ ) or inorganic salts such as sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) in the presence of mineral acid (e.g., HCl) or base e.g.,  $\text{NH}_3$ ) as catalyst.

The hydrolysis of TEOS molecules forms silanol groups. The condensation/polymerization between the silanol groups or between silanol groups and ethoxy groups creates siloxane bridges ( $\text{Si-O-Si}$ ) that form entire silica structure.

**Chemical Modification of Silica Surface:** The chemical modification of silica surface with organo functional groups is an important step towards the preparation of silica-polymer nanocomposites. More precisely, the surface modifications have been reported to enhance the affinity between the organic and inorganic phases and at the same time improve the dispersion of silica nanoparticles within the polymer matrix. Modification of silica surface with silane coupling agents is one of the most effective techniques available. Silane-coupling agents ( $\text{Si(OR)}_3\text{R}$ ) have the ability to bond inorganic materials such as silica nanoparticles to organic resins. In general, the  $\text{Si(OR)}_3$  portion of the silane-coupling agents reacts with the inorganic reinforcement, while the organofunctional group (R) reacts with the resin. Table 2.3 shows some of the common silane coupling agents used for modification of silica surface [49].

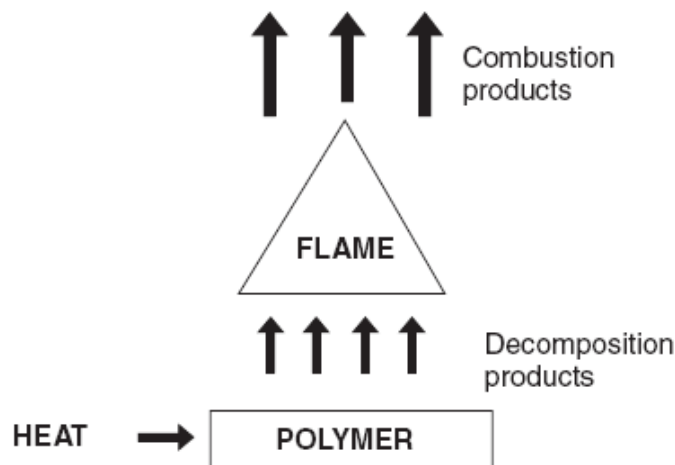


**Table 2.3 : Silane-coupling agents commonly used**

Name (acronym)	Formula
Vinyltriethoxysilane (VTS)	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{CH}=\text{CH}_2$
Methacryloxypropyltriethoxysilane (MPTS)	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CO}-\text{C}(\text{CH}_3)=\text{CH}_2$
3-Glycidyloxypropyltrimethoxysilane (GPTS)	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}-\text{CH}_2$ 
3-Aminopropyltrimethoxysilane (APTS)	$(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
3-Mercaptopropyltriethoxysilane (McPTS)	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$
Chloropropyltriethoxysilane (CPTS)	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

## 2.5 Flame Retardancy in Polymers

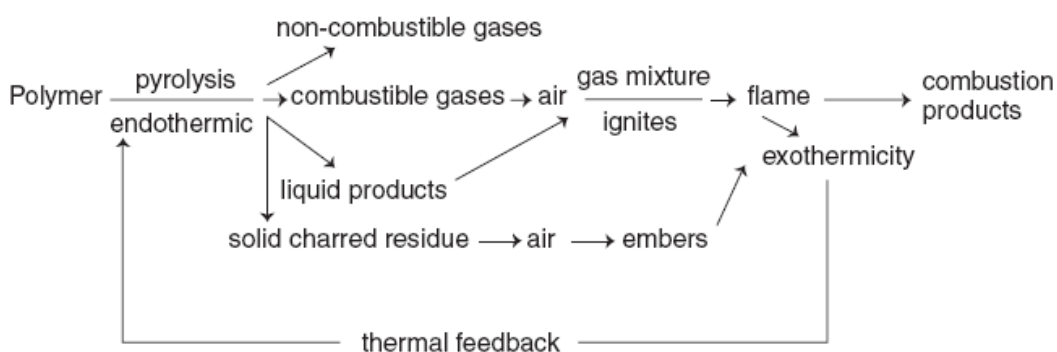
Organic polymers degrade to give volatile combustible products when they are heated above certain critical temperatures, which in turn depend on their chemical structures. If the gaseous mixture resulting from the mixing of degradation volatiles with air is within the flammability limits, and the temperature is above the ignition temperature, then combustion begins. The combustion of a polymeric material is a highly complex process involving a series of interrelated and/or independent stages occurring in the condensed phase and the gaseous phase, and at the interfaces between the two phases. Natural and synthetic polymers, when exposed to a source of sufficient heat, will decompose or ‘pyrolyse’ evolving flammable volatiles. These mix with the air and, if the temperature is high enough, ignite. Ignition occurs either spontaneously (autoignition) or due to the presence of an external source such as a spark or a flame (flash ignition). If the heat evolved by this ignited flame is sufficient to keep the decomposition rate of the polymer above that required to maintain the concentration of the combustible volatiles, i.e. the ‘fuel’, within the flammability limits for the system, then a self-sustaining combustion cycle will be established. Figure 2.8 is a simple representation of this behaviour[50].



**Figure 2.8 :** Simple representation of polymer combustion processes

### 2.5.1 Polymer flames

Combustion reactions liberate the energy stored in the chemical bonds of the molecules of the fuel. A fuel is any substance that will release energy during its reaction with oxygen, usually in air, generally initiated by an external heat source. Typical fuels are wood, hydrocarbons, coal and animal fats. In the main, they are organic materials as are most synthetic polymers. Polymer combustion is a complex process involving a multitude of steps and is best described in qualitative terms. Figure 2.9 is a schematic diagram of the various steps which combine to establish the polymer combustion process.



**Figure 2.9 :** Schematic representation of many processes involved in polymer combustion

The three essential stages required to initiate the combustion are heating, thermal decomposition or pyrolysis and ignition. Ignition is normally caused by the presence of an external heat source such as a flame or a spark or, if the temperature is high enough, occurs spontaneously.

The temperature of the solid polymer is raised either due to an external heat source such as radiation or a flame, or by thermal 'feedback' as indicated in Fig. 2.8. During the initial exposure to heat thermoplastics, which have a linear chain structure, soften or melt and start to flow. On the otherhand, thermosetting plastics have a three-dimensional cross-linked molecular structure which prevents softening or melting. Additional heat causes both types of polymer to pyrolyse and evolve smaller volatile molecular species. Because of their structure this occurs at higher temperatures for thermosetting as opposed to thermoplastic polymers. Since most plastics are organic in nature the evolved species will also be organic and thus flammable. Such flammable evolved species provide the fuel to sustain the flame. Thus we see that the mechanism of combustion contains both a condensed phase and a vapour phase contribution.

Pyrolysis is an endothermic process which requires the input of sufficient energy to satisfy the dissociation energies of any bonds to be broken (200–400 kJ mol<sup>-1</sup>) plus any activation energy requirements of the process. As individual polymers differ in structure, their decomposition temperature-ranges vary within certain limits. The limits will again change somewhat when a polymer is compounded with various additives and subsequently processed to produce what are commonly known as 'plastics'. The fuel generating pyrolysis reactions that control polymer combustion occur in the condensed phase.

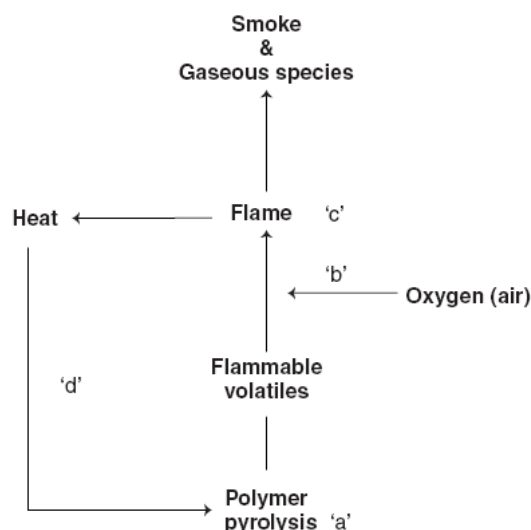
Fires involving organic polymers lead essentially to the same hazards as those fed by other fuels. The flammability and destruction of property are not the only problem. More important are fire fatalities due to the evolved smoke and toxic gases, exacerbated in some cases by poisonous fumes emitted from the synthetic organic polymers [51, 52]. This has led to the introduction of stricter legislation and safety standards concerning flammability, and extensive research into the area of flame retardants for polymers has been the result. Real fires involve not only substantially 'pure' polymers but also polymeric materials that contain considerable amounts of

other constituents, such as artificially introduced fillers or plasticisers or naturally associated non-polymeric substances. Furthermore, polymers involved in a fire may be in the form of fabricated articles containing other materials; these products can take a variety of shapes, sizes and forms. Indeed, the whole of the surrounding system containing combustible articles in which a fire occurs is another aspect that needs to be considered. Therefore, in dealing with the combustion of organic polymers, in the broadest sense, it is necessary to consider the combustion behaviour of a wide range of polymers, and not to confine attention to those which are normally regarded as flammable.

### **Factors affecting flammability and its reduction**

Successful strategies to reduce the flammability of a polymeric material interrupting the complex stages of the combustion process at one or more points to reduce the rate and/or change the mechanism of combustion at that point. From a practical point of view, this is achieved either by the mechanical blending of a suitable flame-retardant compound with the polymeric substrate (i.e. by introducing an additive) or by the chemical incorporation of the retardant into the polymer molecule by simple copolymerisation or by chemical modification of the preformed polymer (i.e. using a reactive component).

Currently, synthetic polymers are usually made more flame retardant by incorporating additives. Such additives often have to be used at high loadings to achieve a significant effect, e.g. 30% by weight or more, which occasionally can have a more detrimental effect on the physical and mechanical properties of a polymer than that produced by reactive flame retardants. Nevertheless, additives are more generally used as they are often cheaper and more widely applicable [53]. A simple schematic representation of the self-sustaining polymer combustion cycle is shown in Figure 2.10. Flame retardants act to break this cycle, and thus extinguish the flame or reduce the burning rate, in a number of possible ways:



**Figure 2.10 :** Schematic representation of the self-sustaining polymer combustion cycle.

- by reducing the heat evolved to below that required to sustain combustion
- by modifying the pyrolysis process to reduce the amount of flammable evolved in favour of increasing the formation of less flammable char which also acts as a barrier between the polymer and the flame ('a')
- by isolating the flame from the oxygen/air supply ('b')
- by introducing into the plastic formulations compounds which will release chlorine or bromine atoms if the polymer is heated to near the ignition temperature. Chlorine and particularly bromine atoms are very efficient flame inhibitors ('c')
- by reducing the heat flow back to the polymer to prevent further pyrolysis. This can be achieved by the introduction of a heat sink, e.g. aluminium oxide trihydrate (ATH,  $\text{Al}(\text{OH})_3$ ) which decomposes endothermically or by arranging that a barrier, e.g. char or intumescent coating, is formed when the polymer is exposed to fire conditions ('d')
- by developing inherently flame retarded polymer systems

Most flame retardant systems in use today have been developed empirically. Current interest in obtaining a better understanding of polymer combustion and interaction of flame retardants therewith is motivated by the requirement to develop environmentally friendly flame retardant systems.

### **2.5.2 Boron containing flame retardants**

Borates and boric acid have been well established as flame retardants which have a synergistic effect, particularly with halogenated polymers and halogen additive/polymer systems. Boron compounds act in the condensed phase by redirecting the decomposition process in favour of carbon formation rather than CO or CO<sub>2</sub>. It is also postulated that the flame retardancy is related to the formation of a surface layer of protective char, which acts as a barrier to the access of oxygen to prevent the oxidation of carbon. Boron compounds are also useful in reducing or eliminating after-glow in halogenated flame retardant polymer systems. Boron containing flame retardants are developed as cheaper, yet less toxic alternatives to such traditional flame retardants as antimony oxide. The borate in the foam behaves like a typical polymer chain extender causing the structure to become ordered. It favours reduction of brittleness with no decrease in rigidity. The chemical modification of polymer chain by boron containing groups leads to significant improvement in flame retardancy. It was found that the additives, such as boric acid, phenylboric acid and a number of other boronated compounds have no significant effect on PS flame retardancy. The same research group also found improved flame retardancy in boric acid to surface treated PVOH and poly(ethylene-co-vinyl alcohol) (EVOH). [54].

### **2.5.3 Silicon containing flame retardants**

Research has shown that the addition of relatively small amount of silicon compounds to various polymeric materials can significantly improve their flame retardancy, through both char forming in the condensed phase and the trapping of active radicals in the vapour phase. They are considered to be environmentally friendly additives because their use leads to a reduction in the harmful impact on environment when compared with existing materials. Organic-inorganic nano-composites, from silicon materials such as clay, kaolin, emerge in the literature as a new concept. Organic-inorganic nano-composites made from the sol-gel process that involves covalent bonding are included.

#### **2.5.4 Phosphorus containing flame retardants**

The range of phosphorus containing flame retardants is extremely wide and the materials versatile, since the element exists in several oxidation states. Phosphines, phosphine oxides, phosphonium compounds, phosphonates, elemental red phosphorus, phosphites and phosphate are all used as flame retardants. The reactive type organophosphorus flame retardants, which attract most attentions in polymer chemistry, can be broadly divided into three categories: simple reactive phosphate monomers; linear polyphosphazenes; and aromatic cyclic phosphazenes. All compounds discussed here are either complete polymer chains, or form part of the copolymer chain through covalent bonding. They may be incorporated into the polymer chains through homopolymerization, copolymerization, surface modification or blending; simple organic or inorganic additives are not included. These compounds mostly perform their flame retardant function in the condensed phase by increasing the amount of carbonaceous residue or char. There are two char forming mechanisms: (a) redirection of the chemical reactions involved in decomposition in favour of reactions yielding carbon rather than CO or CO<sub>2</sub> and (b) formation of a surface layer of protective char. The chemical transformations of phosphorus containing compounds and their participation in all stages of the polymer combustion process are not yet fully understood; nevertheless evidence of their practical importance in the development of halogen-free flame retardants is abundant in the literature. Sometimes, the phosphorus flame retardants still retain some halogens, which may have synergistic effects in polymeric materials provided their environmental impact is minimal [55].





### 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 bis(4-fluorophenyl) phenyl phosphine oxide (BFPPPO), 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-hydroxyethoxy)phenyl]phenyl phosphine oxide (BOHEPPO), Ethylene carbonate (Riedel-de Haen), Sodium carbonate (Merck) were used.

For the synthesis of acrylated phenyl phosphine oxide oligomer (APPO), Triethylamine (Acros Chemicals), Acryloyl chloride (Merck) were used.

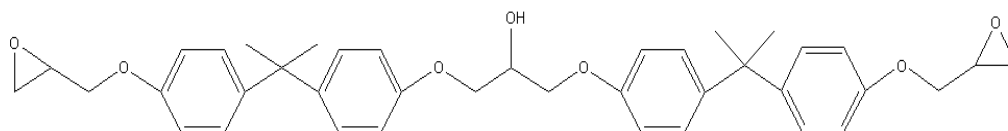
For the synthesis of 2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yloxy)ethylmethacrylate (Boron Methacrylate), Neopentylglycol (Merck), 2-Hydroxyethylmethacrylate (HEMA) (Merck), Boric acid (Sigma Aldrich), Methylhydroquinone (MeHQ) (Sigma Aldrich), Toluene (Merck) were used.

For the synthesis of 4,4'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(10-methyl-9-oxo-3,5,8-trioxa-4-boraundec-10-ene-4,1-diyl)bis(2-methylacrylate) (Boron methacrylate oligomer), Boric acid (Sigma Aldrich), 2-Hydroxyethylmethacrylate (HEMA) (Merck), Diethylene glycol (Merck), Methylhydroquinone (MeHQ), Hypophosphorus acid solution ( $\text{H}_3\text{PO}_2$ ) (Sigma Aldrich), Toluene (Merck) were used.

For the preparation of the silane precursor; Tetraethyl orthosilicate (TEOS) (Sigma Aldrich), 3-Methacryloxypropyltrimethoxysilane (MAPTMS) (Merck), Ethanol (EtOH) (Merck), distilled water, p-toluenesulfuric acid (Sigma Aldrich) were used.

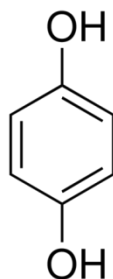
For the UV curing formulation, Dipropylene glycoldiacrylate (DPGDA, Cytec Chemicals), 1,6-hexanedioldiacrylate (HDDA, from Sartomer Chemicals), Darocur 1173 (from CIBA Chemicals). As commercial resins, Ebecryl 605 (Cytec Chemicals) was used.

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 250°C.



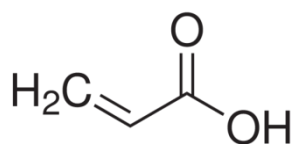
**Figure 3. 1 :** Bisphenol A diglycidyl ether resin

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



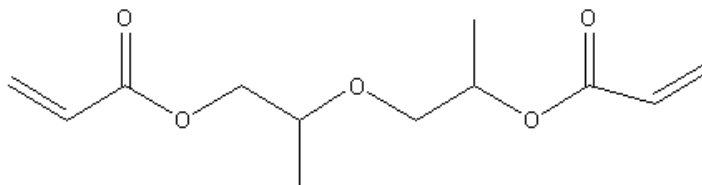
**Figure 3.2 :** Hydroquinone

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.



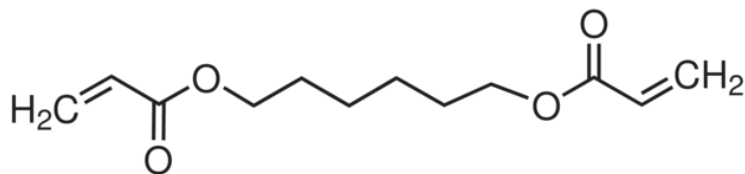
**Figure 3.3 :** Acrylic acid

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<sub>g</sub>, and fast cure speed. It was used as a crosslinking agent in photopolymerization system.



**Figure 3.4 :** Dipropylene glycol diacrylate

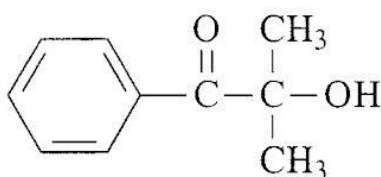
HDDA (1,6-hexanedioldiacrylate) is a fast curing monomer. It has a low viscosity, low volatility. It has a hydrophobic backbone and good solvency for use in free radical polymerization. It was used for lower viscosity and crosslinking in polymerization.



**Figure 3.5 :** 1,6-hexanedioldiacrylate

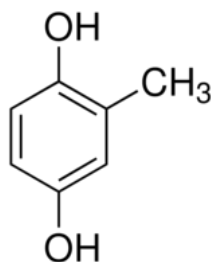
EBECRYL<sup>™</sup> 605 is a bisphenol A epoxy diacrylate oligomer diluted with 25% of tripropyleneglycol diacrylate monomer. Films of EBECRYL<sup>™</sup> 605 cured by UV or EB exhibit high gloss, high surface hardness and the good solvent resistance typical of an epoxy resin.

DAROCUR 1173 (2-Hydroxy-2-methyl-1-phenyl-propan-1-one ) is a versatile highly efficient liquid photoinitiator which is used to initiate the photopolymerisation of chemically unsaturated prepolymers - e.g. acrylates - in combination with mono- or multifunctional monomers.



**Figure 3.6 :** DAROCUR 1173

Methylhydroquinone was used as inhibitor.



**Figure 3.7 :** Methylhydroquinone

### **3.2 Equipments**

#### **Infrared Analysis (IR)**

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

#### **Nuclear Magnetic Resonance (NMR)**

<sup>1</sup>H-NMR analyses were performed with a Agilent VNMRS 500 MHz.

#### **Thermogravimetric Analysis (TGA)**

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

#### **Contact Angle Meter**

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

#### **Pendulum Hardness Tester**

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

#### **Tensile Loading Machine**

Instron 3345 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,  $\text{CaCl}_2$  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 set to  $50^\circ\text{C}$ . Then at  $50^\circ\text{C}$  2.07 mL of triethylamine is added to the flask and was left stirring and the heat is set to  $60^\circ\text{C}$ . Then 33.45 mL acrylic acid was added to mixture as dropwise at  $60^\circ\text{C}$  and the system was stirred until the addition was completed. Then the mixture was heated until the system is reached to  $80^\circ\text{C}$ . 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 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  $5^\circ\text{C}$  88 g (54,7 ml) pbromofluorobenzene 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  $5^\circ\text{C}$  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 [56].

### **3.3.3 Synthesis of bis(4-hydroxyphenyl)phenyl phosphine oxide (BOHPPO)**

BOHPPO was synthesized by hydrolyzing BFPPPO using potassium hydroxide in DMSO. For example, 10 g BFPPPO 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°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°C overnight, and then purified using fractional recrystallization from 1:5 v/v ratio of methanol/water [57].

### **3.3.4 Synthesis of bis[(4-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°C under nitrogen for 2 h. The crude product was washed with water several times to remove unreacted ethylene carbonate. A light brown viscous liquid was obtained [58].

### **3.3.5 Synthesis of acrylated phenyl phosphineoxide oligomer (APPO)**

BOHEPPO (6.7 g; 0.0168 mol) dissolved in dichloromethane was charged into a three-necked flask, equipped with a stirrer, a thermometer, a dropping funnel, and a condenser. Five milliliters of triethylamine was added and the system was cooled to 0°C in an ice bath. Acryloyl chloride weighing 3.6 g (0.04 mol, 3.25 mL) was slowly dropped into the flask and the mixture was reacted at 0°C for 4 h. The solution was microfiltered to remove triethylamine hydrochloride. The filtrate was washed with aqueous sodium carbonate and water respectively, to remove traces of HCl and to neutralize the system. Then the filtrate was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated off under vacuum and a clear, viscous product was obtained [59].

### 3.3.6 Synthesis of 2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yloxy)ethylmethacrylate

#### (Boron Methacrylate Monomer) (BM-M)

2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yloxy)ethylmethacrylate monomer was synthesized by esterification reactions. 5 g of boric acid, 10.54 g of HEMA, 8.45 g neopentylglycol, toluene, aqueous  $\text{H}_3\text{PO}_2$  was added to a 100 ml two-necked round bottom flask equipped with a Dean-Stark and a condenser. To the reaction MeHQ was added as a inhibitor. The reaction mixture was stirred and heated to reflux temperature for 3 h and the water was removed by azeotrope distillation with Dean-Stark. The solvent was then removed by vacuum distillation. Air must be sparged during the esterification reaction to avoid polymerization of the HEMA because MeHQ is efficient only in presence of oxygen. The product was transparent, colorless liquid (yield: 99%) [60, 61].

### 3.3.7 Synthesis of 4,4'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(10-methyl-9-oxo-3,5,8-trioxa-4-boraundec-10-ene-4,1-diyl)bis(2-methylacrylate)

#### (Boronmethacrylate oligomer) (BM-O)

To a 100 ml two-necked round bottom flask equipped with a Dean-Stark and a condenser, 5 g of boric acid, 14.7 g of HEMA, 6.8 g diethyleneglycol, toluene, MeHQ was added. Aqueous  $\text{H}_3\text{PO}_2$  was added to the reaction as a catalyst, under the air medium the reaction was stirred and heated to reflux temperature for 5 h, the water was collected with Dean-Stark. The solvent was removed by vacuum distillation. Boron methacrylate oligomer was obtained transparent, colorless and a viscous liquid (yield: 99%) [61].

### 3.3.8 Preparation of the silane precursor (silica sol)

The precursor sol was prepared by using TEOS (3 g, 0.014 mol) and MAPTMS (3.6 g, 0.0145 mol) as the precursor alkoxides, EtOH (1.4g) as solvent, distilled water (1.1 g, 0.06 mol) and p-toluensulfonic acid (0.038 g) as a catalyst for hydrolysis. Initially, TEOS, MAPTMS and EtOH were mixed into a glass vial and then water which had been acidified by p-toluensulfonic acid was added dropwise into the vial under stirring. The whole mixture was allowed for partial hydrolysis approximately for 12 h at room temperature. The pH of the silane precursor was adjusted to be between 4 and 5 [62].

### 3.4 Preparation of Formulations

Thirty different formulations were prepared for UV curable coating. The compositions of formulas were given at below tables.

**Table 3.1 :** Formulations containing epoxy acrylate and BM-M

Sample (wt.%)	F1	F2	F3	F4
Epoxy Acrylate	80	77.5	75	70
BM-M	-	2.5	5	10
HDDA	5	5	5	5
DPGDA	10	10	10	10
Darocur 1173	5	5	5	5

**Table 3.2 :** Formulations containing epoxy acrylate and BM-O

Sample (wt.%)	F1	F5	F6	F7
Epoxy Acrylate	80	77.5	75	70
BM-O	-	2.5	5	10
HDDA	5	5	5	5
DPGDA	10	10	10	10
Darocur 1173	5	5	5	5

**Table 3.3 :** Formulations containing Ebecryl 605 and BM-M

Sample (wt.%)	F8	F9	F10	F11
Ebecryl 605	80	77.5	75	70
BM-M	-	2.5	5	10
HDDA	5	5	5	5
DPGDA	10	10	10	10
Darocur 1173	5	5	5	5



**Table 3.4 :** Formulations containing ebecryl 605 and BM-O

Sample (wt.%)	F8	F12	F13	F14
Ebecryl 605	80	77.5	75	70
BM-O	-	2.5	5	10
HDDA	5	5	5	5
DPGDA	10	10	10	10
Darocur 1173	5	5	5	5

**Table 3.5 :** Formulations containing epoxy acrylate, BM-M, APPO

Sample (wt.%)	F15	F16	F17	F18	F19
Epoxy Acrylate	60	60	60	60	60
BM-M	-	2.5	5	7.5	10
APPO	20	17.5	15	12.5	10
HDDA	5	5	5	5	5
DPGDA	10	10	10	10	10
Darocur 1173	5	5	5	5	5

**Table 3.6 :** Formulations containing Ebecryl 605, BM-M,APPO

Sample (wt.%)	F20	F21	F22	F23
Ebecryl 605	60	60	60	60
BM-M	2.5	5	7.5	10
APPO	17.5	15	12.5	10
HDDA	5	5	5	5
DPGDA	10	10	10	10
Darocur 1173	5	5	5	5

**Table 3.7 :**Formulations containing Ebecryl 605, BM-M, silica sol

Sample (wt.%)	F24	F25	F26	F27
Ebecryl 605	60	60	60	60
BM-M	-	2.5	5	10
Silane precursor	20	17.5	15	10
HDDA	7	7	7	7
DPGDA	10	10	10	10
Darocur 1173	3	3	3	3

**Table 3.8 :** Formulations containing Ebecryl 605, BM-O, silica sol

Sample (wt.%)	F27	F28	F29	F30
Ebecryl 605	60	60	60	60
BM-O	-	2.5	5	10
Silane precursor	20	17.5	15	10
HDDA	7	7	7	7
DPGDA	10	10	10	10
Darocur 1173	3	3	3	3

### 3.4 Preparation of test samples

#### 3.4.1 Free films

Free film formulations were stirred until become clear and homogeneous. Then solutions were kept under vacuum 30 minutes to remove bubbles. Free films were prepared by pouring viscous liquid formulations on a teflon mold having 10mm x 50mm x 1mm spaces. Viscous liquid formulations except containing silane precursor were cured under EMA UV machine for four pass and kept waiting for a couple of days before further tests. Containing silane precursor formulations were cured under EMA UV machine for four pass at and the hybrid coated teflon molds were annealed at 65 °C four 12 h to achieve high degree cross-linking via condensation of remaining silanol groups. After that thermal and characterization analysis, chemical resistance and strain-stress tests were applied on these free films.

### 3.4.2 Coated plexiglass plates

1g of film solution for each plates was prepared. Then the formulations were applied onto Plexiglass plates using a bar gauged wired applicator obtaining a layer thickness of 30  $\mu\text{m}$ . Finally plexiglass plates were cured under EMA UV machine in analogy to free films UV curing way. Pencil hardness, contact angle and pendulum hardness tests were applied on these plates.

## 3.5 Analyses

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

### 3.5.1 Infrared Analysis

Infrared 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.

$$E = h\nu$$

where,

$h$  = Planck's constant

$\nu$  = 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,  $\mu$ , whose displacement from its equilibrium position is equal to the change of the internuclear distance. The term  $\mu$  is called the reduced mass and is given by:

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

where,  $m_1$  and  $m_2$  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.

### 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 through 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/2 $\pi$  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.,  $^{12}\text{C}$ ,  $^{16}\text{O}$ ) have zero spin and are of no interest to NMR spectroscopy. Nuclei with odd mass numbers (e.g.,  $^{17}\text{O}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ) have half-integer spins and are of most interest here. Nuclei with even mass numbers and odd charge (e.g.,  $^2\text{H}$ ,  $^{14}\text{N}$ ) 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  $I, I - 1, I - 2, \dots, -I$ . 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,  $\delta$ , 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.

### 3.5.3 Thermogravimetric Analysis

TGA is widely used to evaluate the thermal stability and thermal degradation behaviour of polymers [64]. 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 [65].

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.

In this study, thermal stability was evaluated using a Q50 TGA from TA Instruments. Film samples of 15-19 mg were placed in the sample pan and heated from 30 °C to 850°C under N<sub>2</sub> (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.

#### **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,

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

Where  $m_1$  is the weight of the cured film sample;  $m_2$  is the residual weight of the cured film sample.

#### **3.5.5 Solvent resistance**

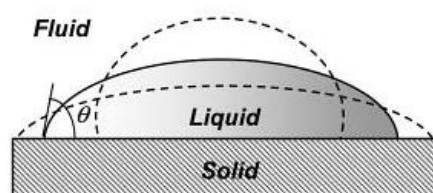
The solvent resistance of the cured films was determined by immersing in various solvents ( $m_1$ , 0.005-0.03g g/10 ml) for one day. After than cured films were dried until its weight were constant. After drying, the films were reweighted ( $m_2$ ) and weight loss was calculated.

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

#### **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.



**Figure 3.8 :** Scheme of a sessile-drop contact angle

### 3.5.7 Pendulum hardness test

Standard hardness tests relate oscillation damping to surface hardness. The König test for hard coatings measures the time taken for the amplitude to decrease from  $6^\circ$  to  $3^\circ$ . 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 [68]. It is described in the ISO Recommendation 1522 as follows:

The pendulum rests on two stainless steel balls,  $5 \pm 0.005$  mm diameter, of hardness HRC  $63 \pm 3$ ,  $30 \pm 0.2$  mm apart, and is counterpoised (to adjust the natural frequency of oscillation) by means of a weight sliding on a vertical rod attached to a cross bar. The period of oscillation should be  $1.4 \pm 0.2$  s on a polished plate glass panel; the

time for damping from a 60 displacement to a 30 displacement, on the same substrate, should be  $250 \pm 10$  s. The total weight of the pendulum should be  $200 \pm 0.2$ g.

### **3.5.8 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 hardness values are forced against a coated surface in a precisely defined manner until one lead marks the surface. Surface hardness is defined by the hardest pencil grade which fails to mark the organic coating surface.

Pencils are available in different grades of hardness, ranging from the softest, and 6B, to the hardest. 6H, although hardnesses 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:

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

### **3.5.9 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  $\nu$  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.

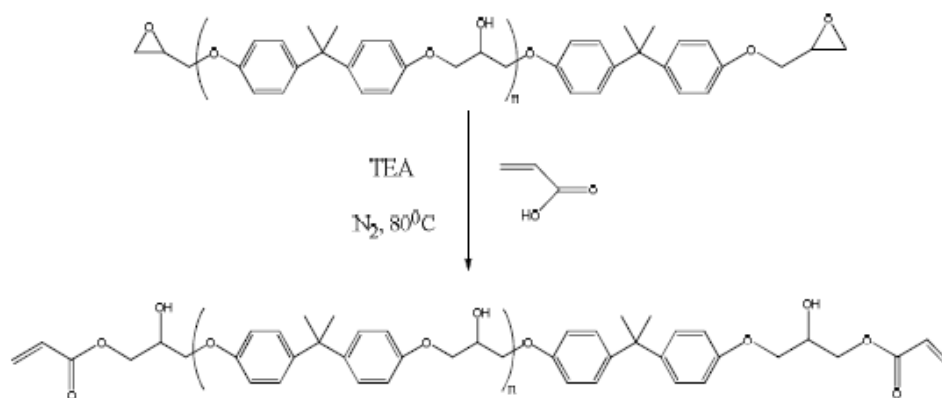


## 4. RESULT AND DISCUSSION

This thesis will be interested in preparation of polymerizable boron methacrylate monomer and the boron methacrylate oligomer. Then, series of UV-curable boron containing epoxy acrylate coatings were set up. The flame retardant performance of boron element was investigated with thermal gravimetric analysis. Furthermore, coating performances are examined with various tests, such as pencil hardness, contact angle, gel content, tensile test, solvent resistance. For that purpose, several formulations were prepared in different ratios.

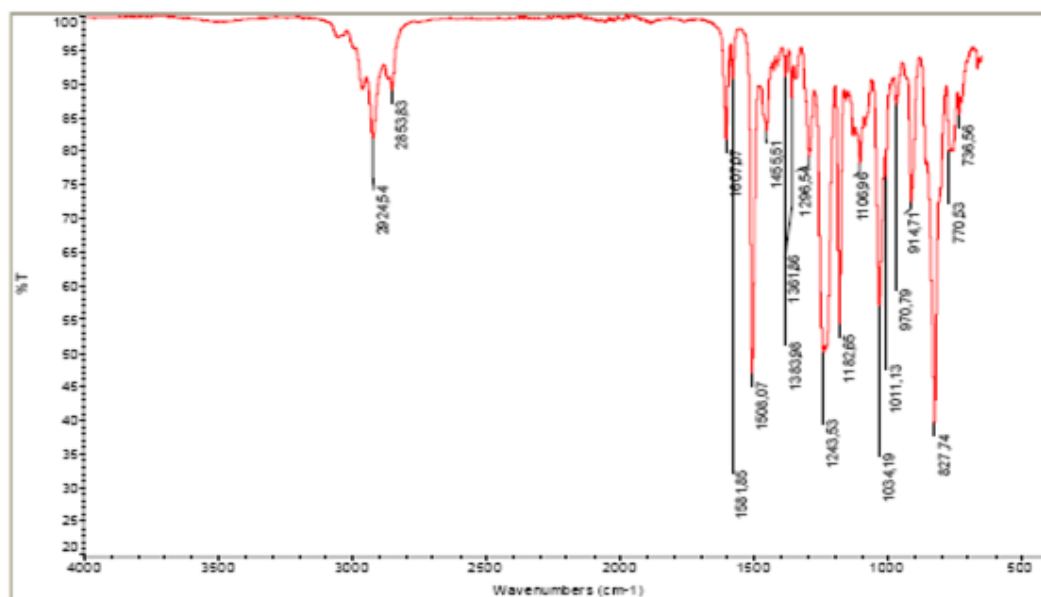
### 4.1 Synthesis of Epoxy Acrylate

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.



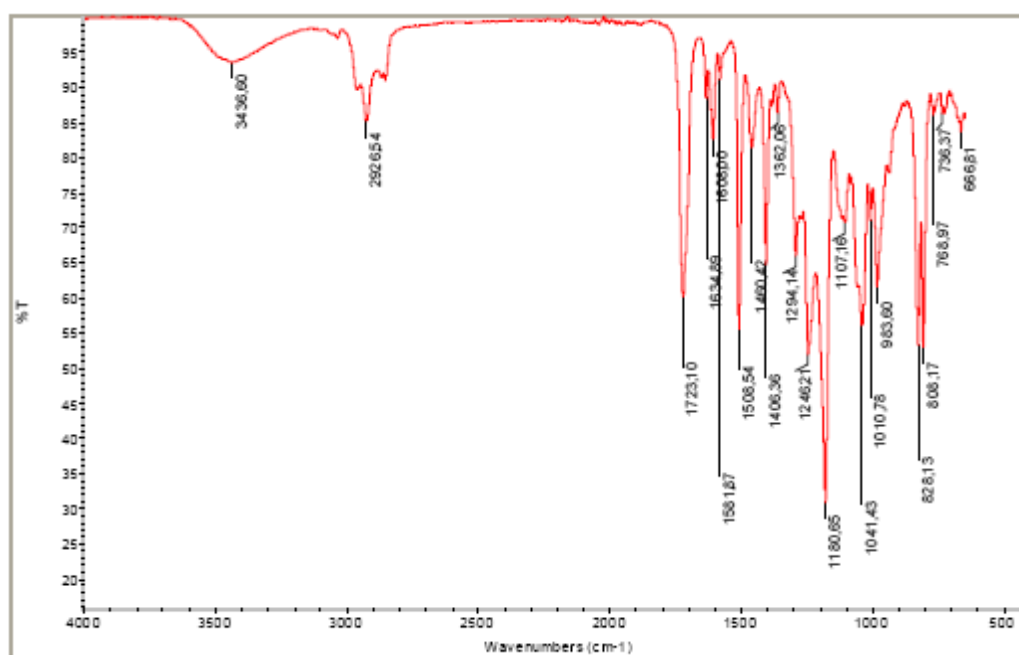
**Figure 4.2 :** Synthesis of epoxy acrylate

The FT-IR spectrum analysis of epoxy resin in Figure 4.2 contains characteristic epoxy group at  $915\text{ cm}^{-1}$ . 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 4.2.



**Figure 4.3 : FT-IR Spectra of epoxy resin**

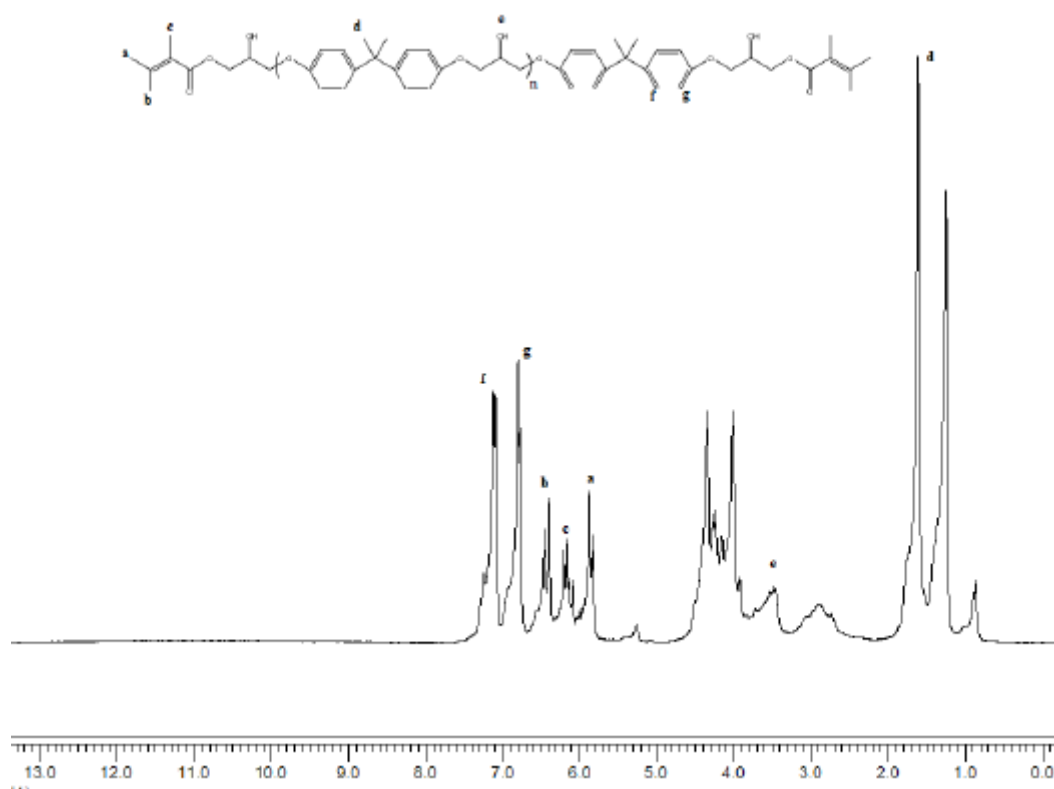
Also at the end of epoxy acrylate reaction FT-IR spectrum analysis of epoxy acrylate in Figure 4.3 contains characteristic broad band  $\text{-OH}$  at  $3437\text{ cm}^{-1}$ ,  $\text{-C=O}$  at  $1723\text{ cm}^{-1}$ ,  $\text{-C=C}$  at  $1606\text{ cm}^{-1}$  and  $\text{-CH}$  at  $2927\text{ cm}^{-1}$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



**Figure 4.4 : FT-IR Spectra of epoxy acrylate**

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

$^1\text{H}$ -NMR spectrum of epoxy acrylate was taken in  $\text{CDCl}_3$  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  $-\text{OH}$  was discerned at 3.48 ppm. And the epoxy aromatic ring have signals at 6.78-6.81.



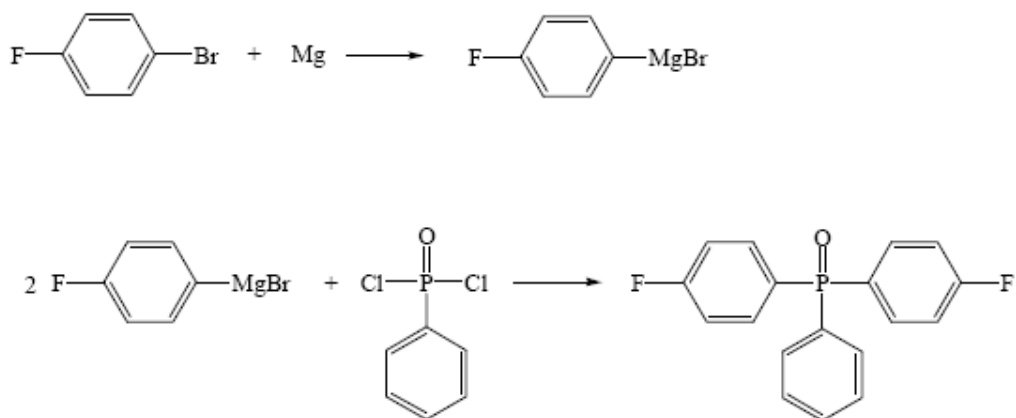
**Figure 4.5 :**  $^1\text{H}$ -NMR Spectra of epoxy acrylate

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

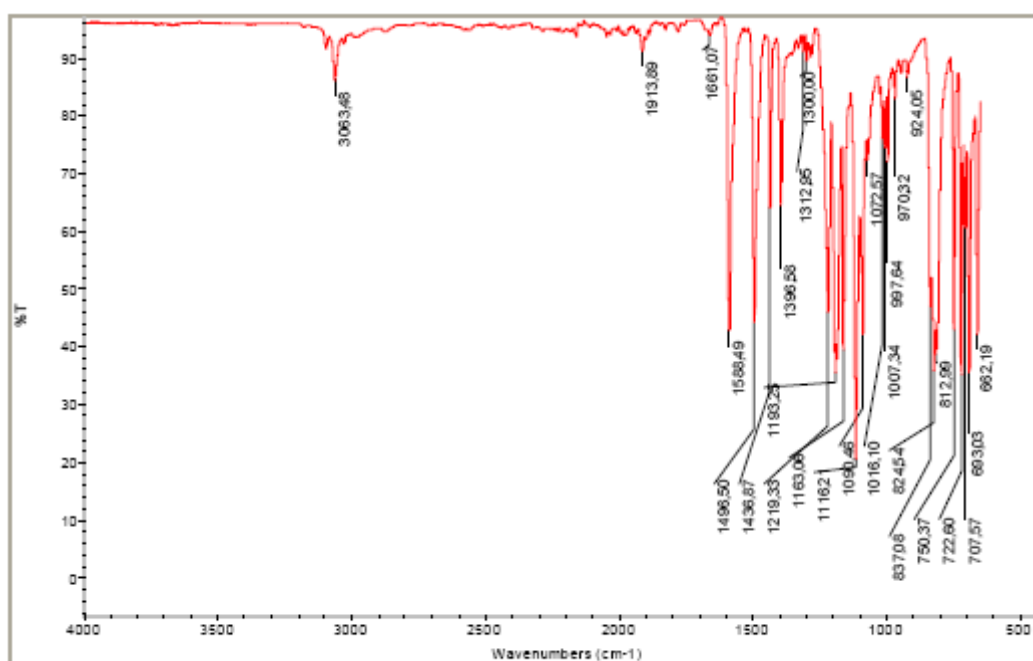
In this part, BFPPO was synthesized according to the procedure [56] in Figure 4.5.

The structure of product was confirmed by FT-IR spectrum.

The FT-IR spectrum of BFPPO in Figure 4.6 contains the characteristic broad band  $\text{P}=\text{O}$  at  $1397\text{ cm}^{-1}$ ,  $\text{P}-\text{Ph}$  at  $1437\text{ cm}^{-1}$ ,  $\text{C}-\text{F}$  at  $1219\text{ cm}^{-1}$ ,  $-\text{CH}$  at  $3063\text{ cm}^{-1}$ , and  $\text{C}=\text{C}$  at  $1437\text{-}1588\text{ cm}^{-1}$ .



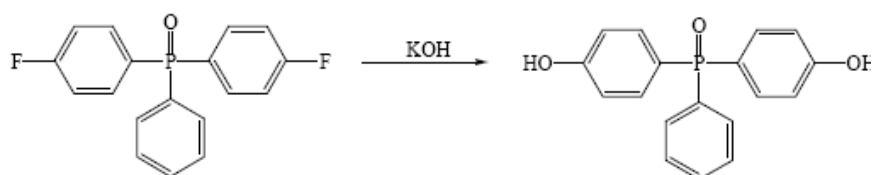
**Figure 4.6 : FT-IR Spectra of BFPPPO**



**Figure 4.7 : FT-IR Spectra of BFPPPO**

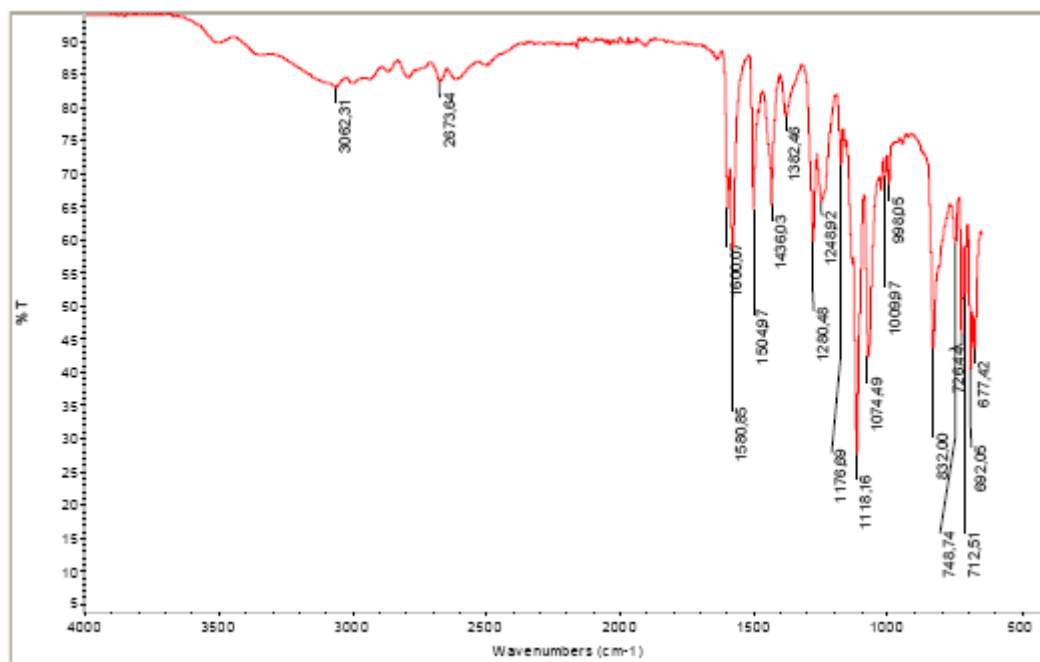
### 4.3 Synthesis of Bis(4-hydroxyphenyl)phenyl Phosphine Oxide (BOHPPO)

In this part, BFPPPO was synthesized according to the procedure [57] in Figure 4.7.



**Figure 4.8 :Synthesis scheme of BOHPPO**

The chemical structures of the resulting material (BOHPPO) was characterized by FT-IR (Figure 4.8). The characteristic absorption peak of the functional group Ph-OH  $3062\text{ cm}^{-1}$  was detected for BOHPPO. Peaks at  $1280\text{ cm}^{-1}$  -P=O,  $1436\text{ cm}^{-1}$  -P-Ph,  $1118\text{ cm}^{-1}$  C-O, and  $1581\text{-}1600\text{ cm}^{-1}$  C=C proved the existence of phenyl phosphine oxide and hydroxy structure.

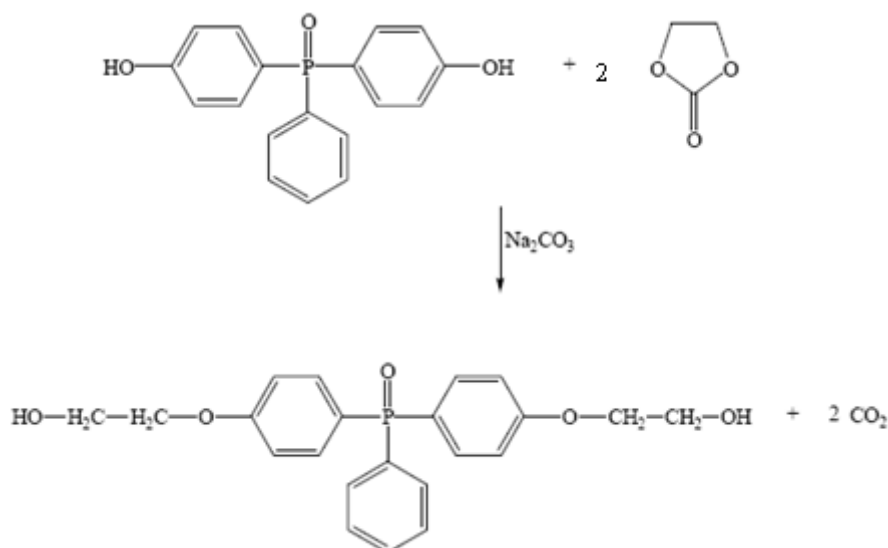


**Figure 4.9 : FT-IR Spectra of BOHEPPO**

#### **4.4 Synthesis of Bis[(4-.hydroxyethoxy)phenyl]phenyl Phosphine Oxide (BOHEPPO)**

In this part, BOHEPPO was synthesized according to the procedure [58] in Figure 4.9.

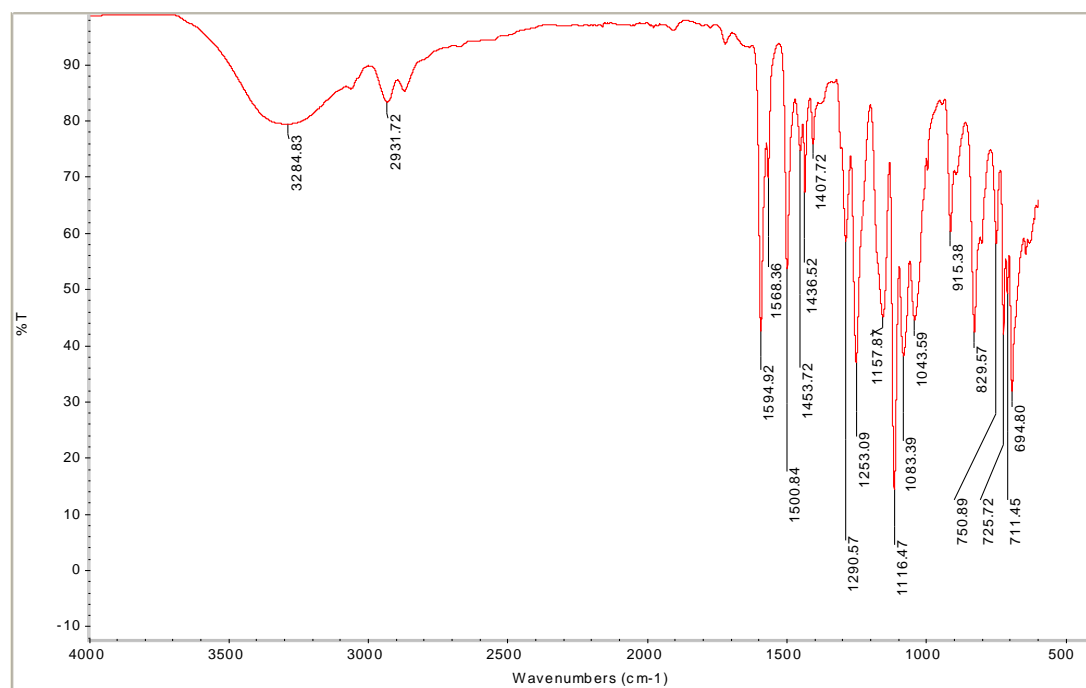
The structure of BOHEPPO was confirmed by IR and  $^1\text{H-NMR}$ . Figure 4.10 presents the FT-IR spectra of BOHEPPO.



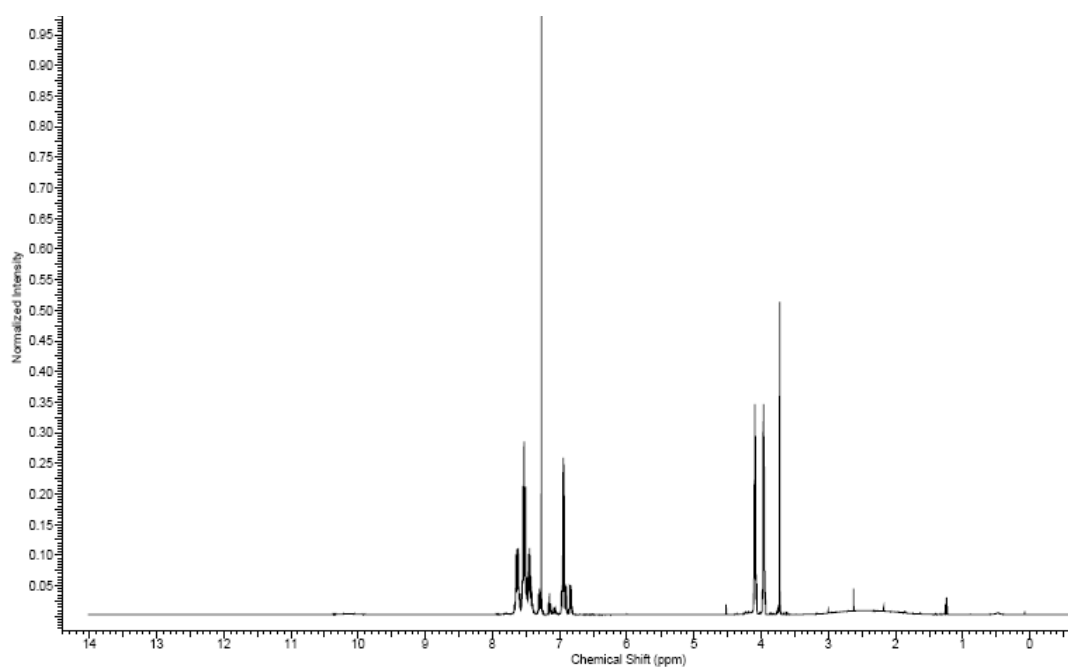
**Figure 4.10 :** Synthesis scheme of BOHEPPO

In the IR spectra, absorptions due to hydroxyl groups  $\text{-CH}_2\text{-OH}$  was observed at  $3284\text{ cm}^{-1}$ ,  $\text{-C-O}$  at  $1157\text{-}1043\text{ cm}^{-1}$ ,  $\text{-CH}$  at  $2931\text{ cm}^{-1}$ ,  $\text{C=C}$  at  $1594\text{-}1500\text{ cm}^{-1}$  and an absorption based on triphenylphosphine was observed at  $1436.52\text{ cm}^{-1}$ .

Figure 4.11 shows  $^1\text{H-NMR}$  spectra of BOHEPPO. The peak at  $3.92\text{ ppm}$  was due to  $\text{CH}_2$  protons near to hydroxyl group and  $4.05\text{ ppm}$  was due to  $\text{CH}_2$  protons near to etheric oxygen atom. The hydroxyl groups were observed at  $3.6\text{ ppm}$ . The aromatic protons of BOHEPPO near to etheric oxygen atom appeared at  $\delta = 6.6\text{-}7\text{ ppm}$ , and the other aromatic protons bonded to phosphine oxide group appeared at  $\delta = 7.7\text{-}7.7\text{ ppm}$ .



**Figure 4.11 : FT- IR Spectra of BOHEPPO**



**Figure 4.12 :  $^1\text{H}$ -NMR Spectra of BOHEPPO**

#### 4.5 Synthesis of acrylated phenyl phosphineoxide oligomer (APPO)

In this part, APPO was synthesized according to the procedure [59] in Figure 4.12.

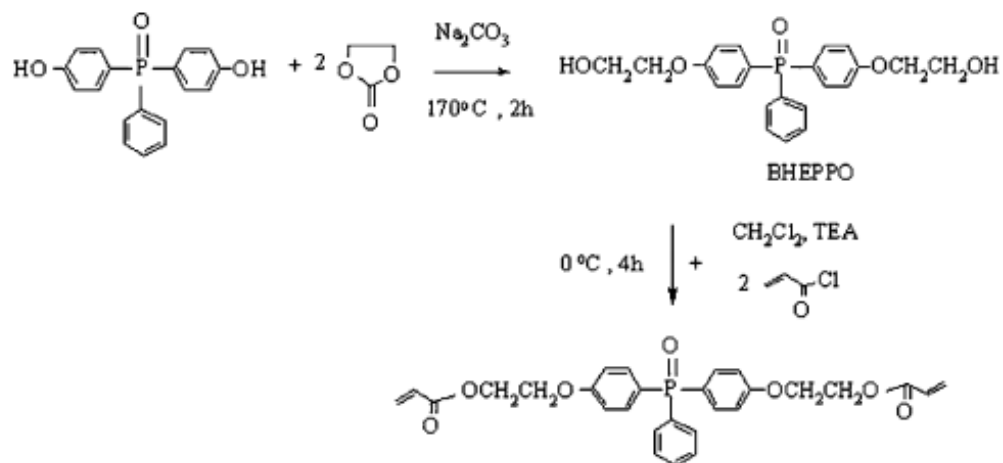


Figure 4.13 : Synthesis scheme of APPO

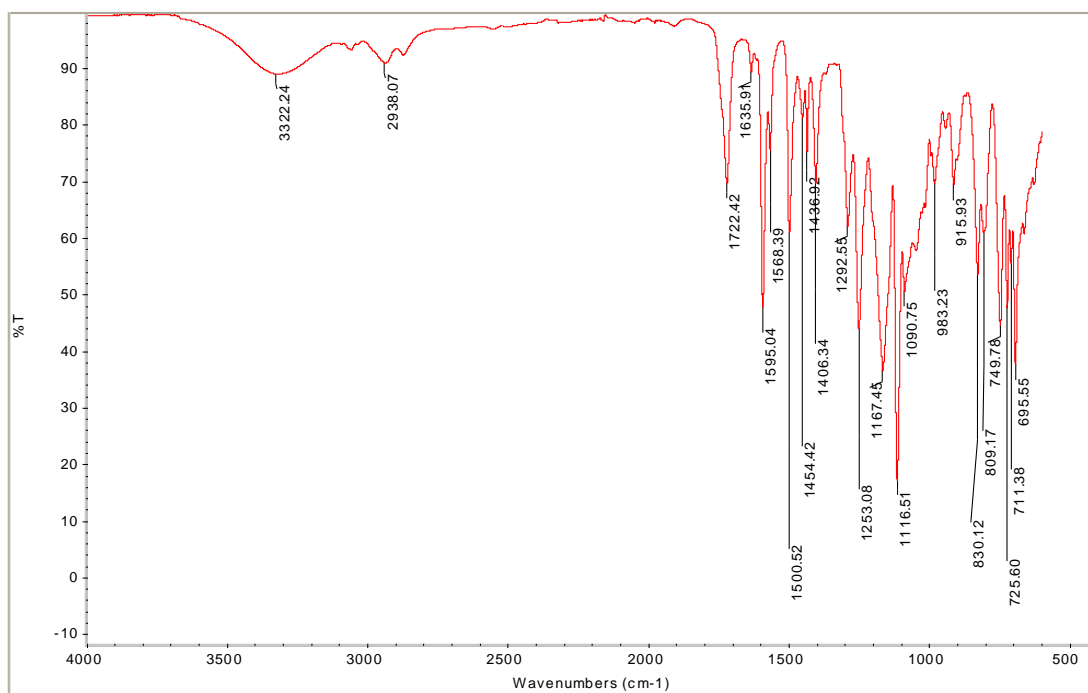
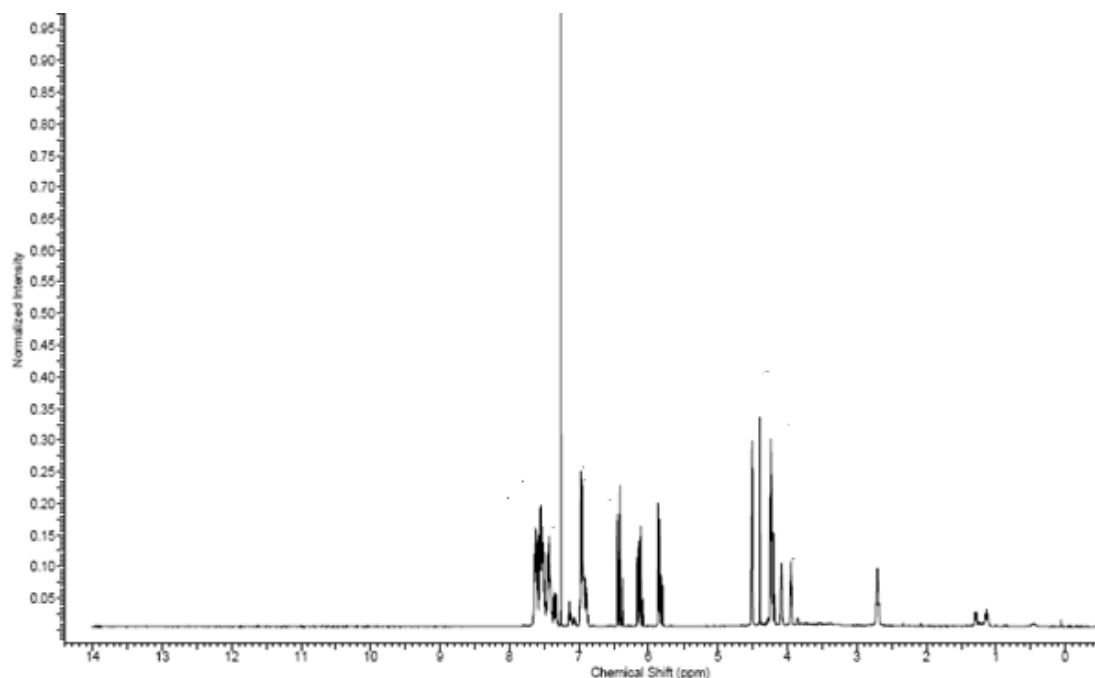


Figure 4.14 : FT-IR Spectra of APPO

Peaks at  $1721.68\text{ cm}^{-1}$  C=O,  $1636.47\text{ cm}^{-1}$  C=C,  $1437\text{ cm}^{-1}$  triphenylphosphine,  $2970\text{ cm}^{-1}$  -CH,  $1293\text{ cm}^{-1}$  P=O,  $1117\text{ cm}^{-1}$  C-O proved the structure of APPO.



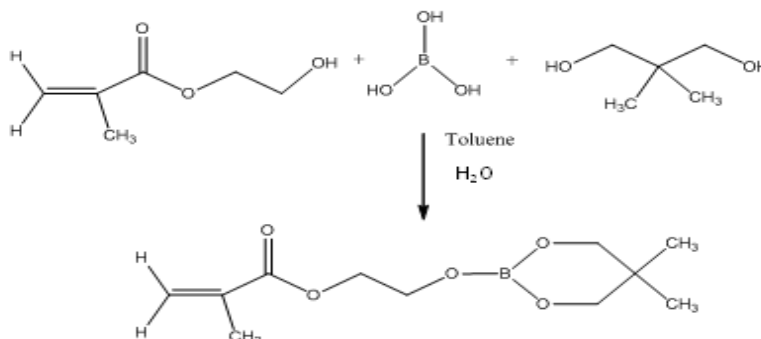


**Figure 4.15 :**  $^1\text{H}$ -NMR Spectra of APPO

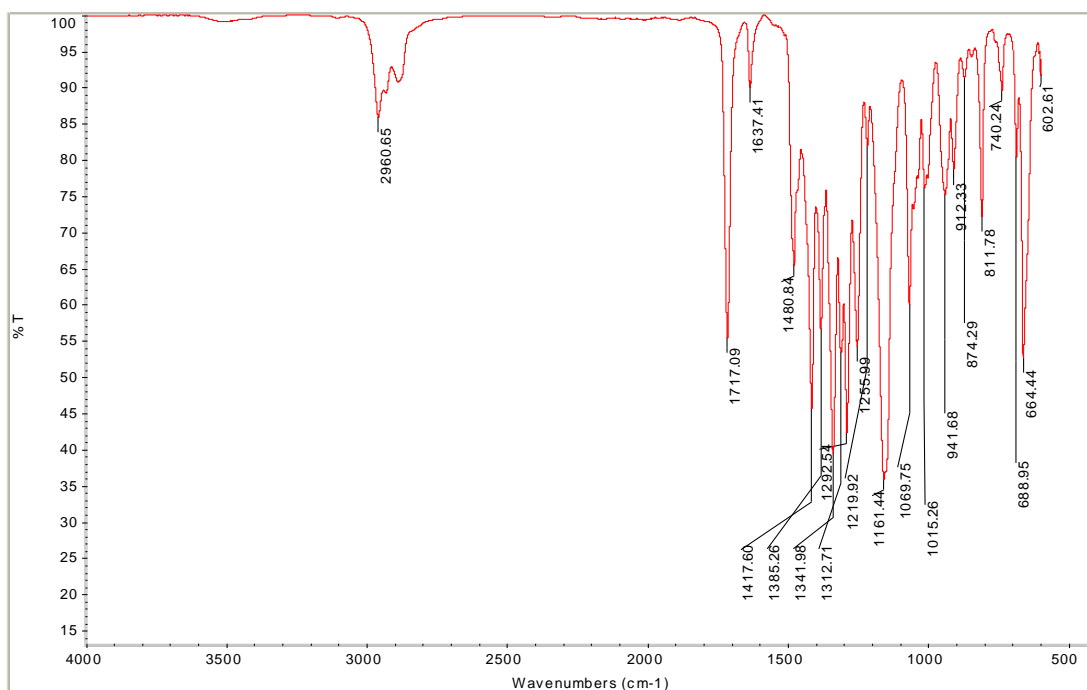
The chemical shifts appearing 7.4 and 7.8 ppm ( $\text{O}=\text{P}-\text{C}_6\text{H}_5$ ), 7.0 ppm ( $-\text{O}-\text{C}_6\text{H}_5-\text{P}=\text{O}$ ) were aromatic protons in Figure 4.14. The shifts from 5.7 to 6.4 ppm were due to the three olefinic protons from acrylate functionality. Methylene groups that are bounded to the oxygen atom and acrylate group was appeared at 4.2-4.5 ppm.

#### 4.6 Synthesis of 2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yloxy)ethylmethacrylate (Boron Methacrylate Monomer) (BM-M)

2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yloxy)ethylmethacrylate monomer which is classified as a saturated cyclic borate ester, was synthesized from boric acid and 2,2-dimethyl-1,3-propanediol by esterification reactions.



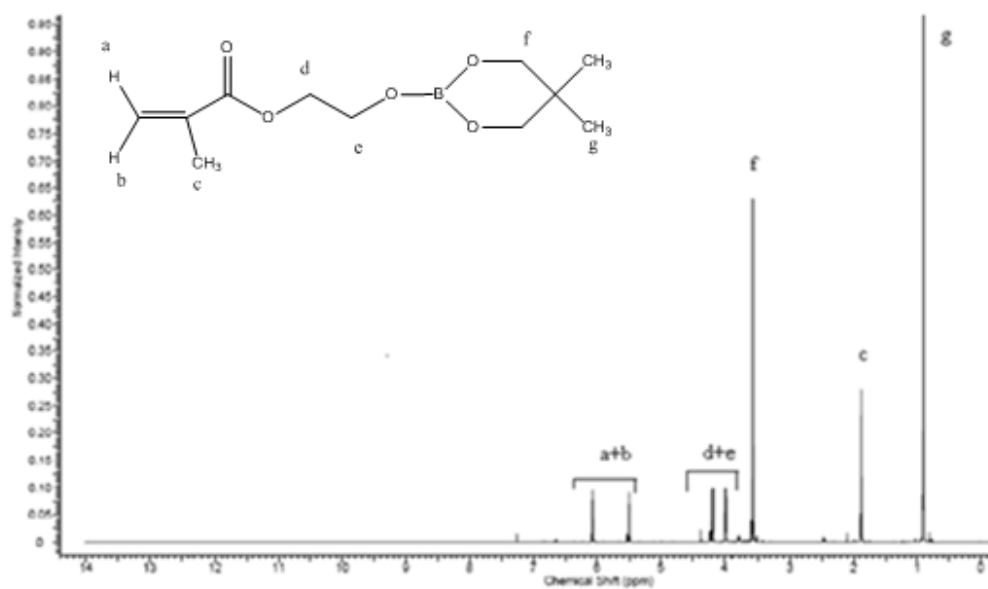
**Figure 4.16 :** Synthesis scheme of BM-M



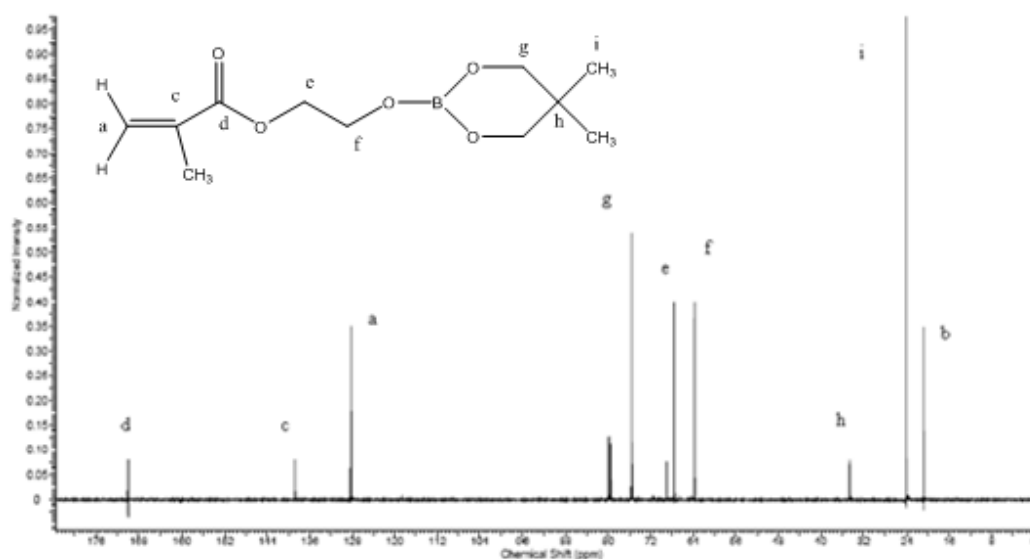
**Figure 4.17 : FT-IR Spectra of BM-M**

Peaks observed at Figure 4.16 shows  $2960\text{ cm}^{-1}$   $-\text{CH}$ ,  $1717\text{ cm}^{-1}$   $-\text{C}=\text{O}$ ,  $1637\text{ cm}^{-1}$   $\text{C}=\text{C}$ ,  $1417\text{ cm}^{-1}$   $\text{B}-\text{O}$  group.

Figure 4.17 was represented the  $^1\text{H}$ -NMR Spectra of BM-M



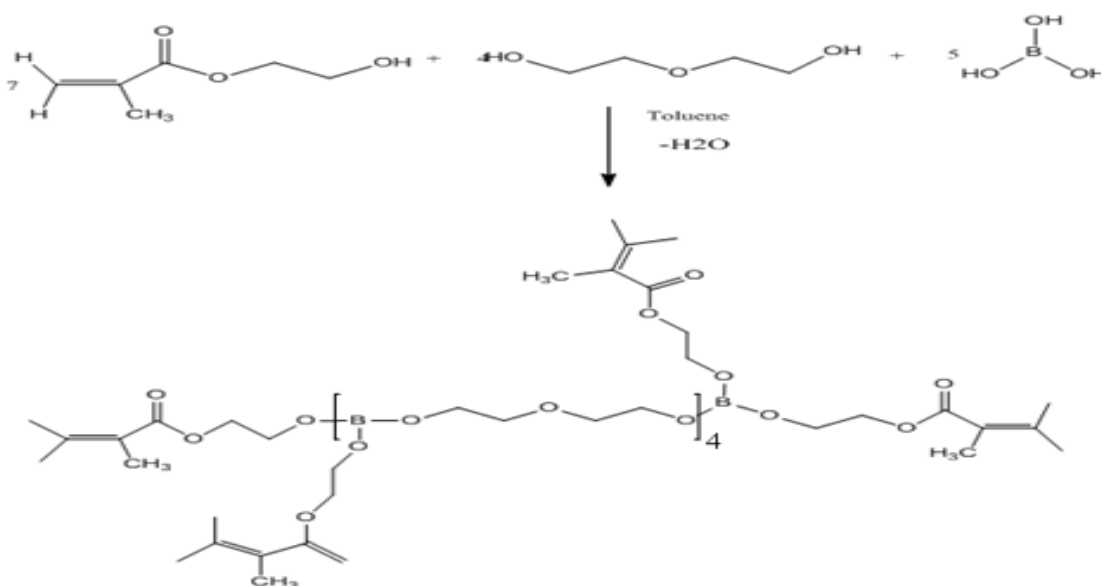
**Figure 4.18 :  $^1\text{H}$ -NMR Spectra of BM monomer**



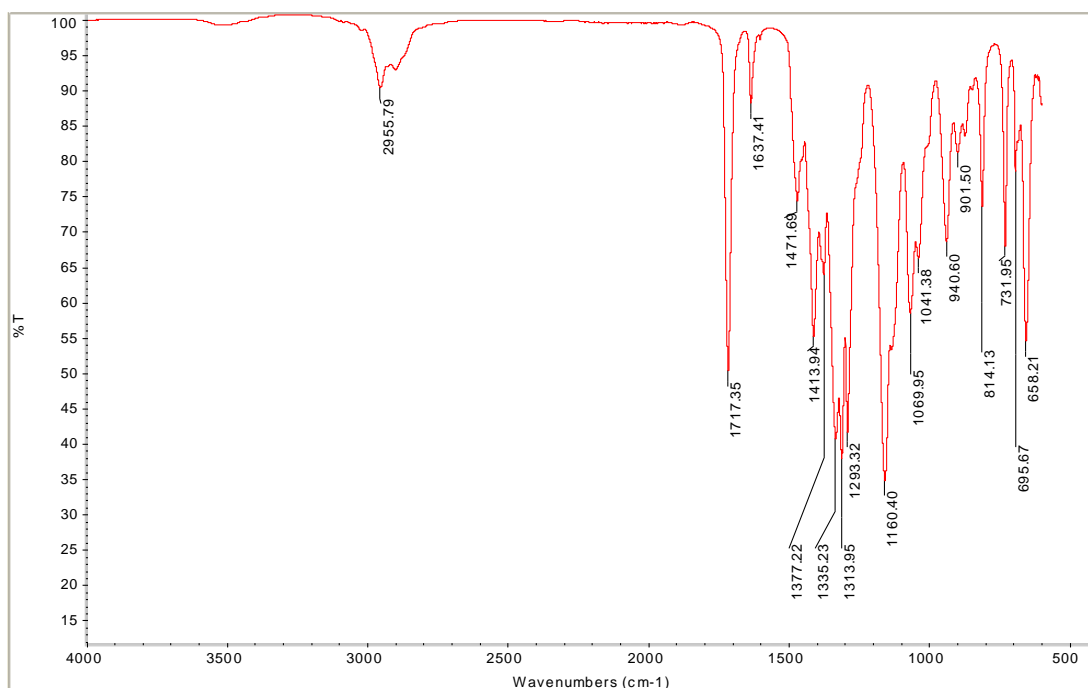
**Figure 4.19 :**  $^{13}\text{C}$ -NMR Spectra of BM-M

#### 4.7 Synthesis of 4,4'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(10-methyl-9-oxo-3,5,8-trioxa-4-boraundec-10-ene-4,1-diyl)bis(2-methacrylate) (Boron Methacrylate Oligomer) (BM-O)

4,4'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))bis(10-methyl-9-oxo-3,5,8-trioxa-4-boraundec-10-ene-4,1-diyl)bis(2-methylacrylate) was synthesized by the esterification reactions of boric acid, HEMA and diethyleneglycol.



**Figure 4.20 :** Synthesis scheme of BM-O

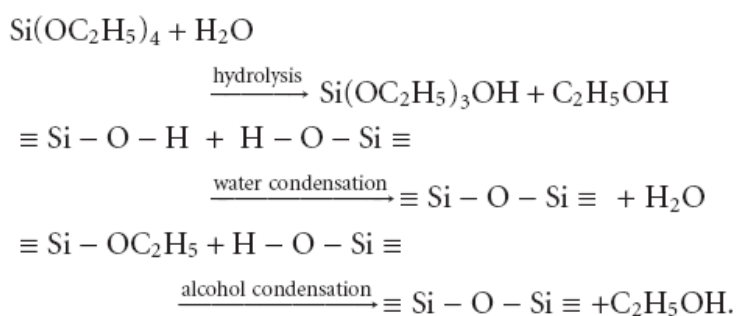


**Figure 4.21 : FT-IR Spectra of BM-O**

Figure 4.21 presents the FT-IR spectra of BM-O. In the FT-IR spectra, absorptions due to the  $\text{-CH}$  groups was observed at  $2955\text{ cm}^{-1}$ ,  $\text{-C=O}$  at  $1717\text{ cm}^{-1}$ , B-O at  $1413\text{ cm}^{-1}$ .

#### 4.8 Preparation of Silane precursor

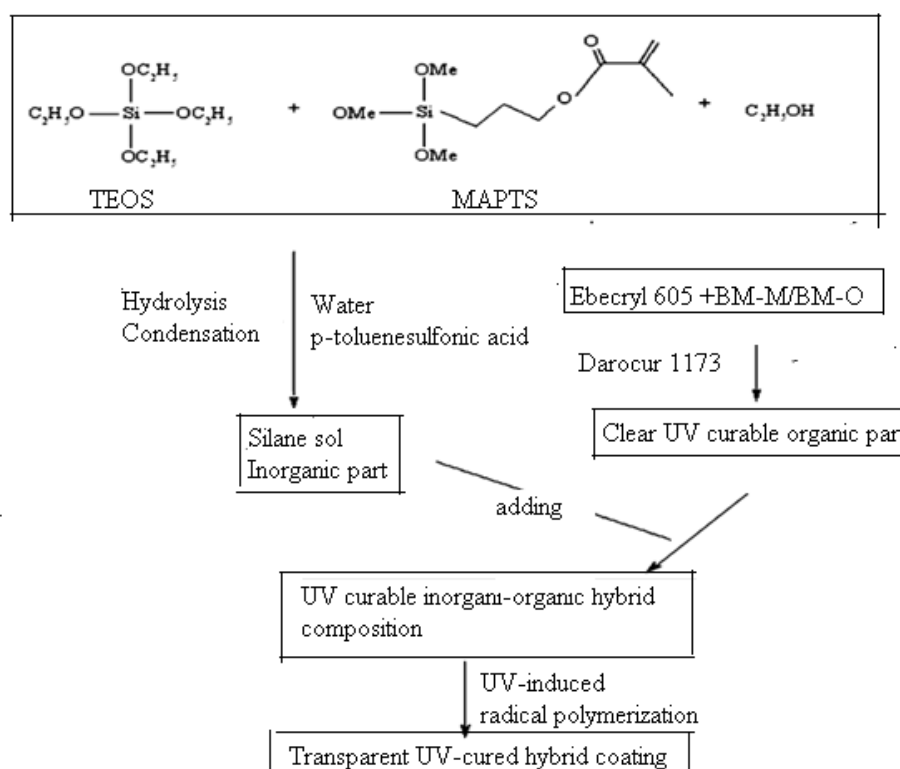
The general reactions of TEOS that leads to the formation of silica particles in the sol-gel process can be written as Figure 4.21:



**Figure 4.22 : Preparation of silane precursor**

The hydrolysis of TEOS molecules forms silanol groups. The condensation/polymerization between the silanol groups or between silanol groups and ethoxy groups creates siloxane bridges ( $\text{Si-O-Si}$ ) that form entire silica structure.

## 4.9 Preparation of UV-cured Hybrid Coating Material



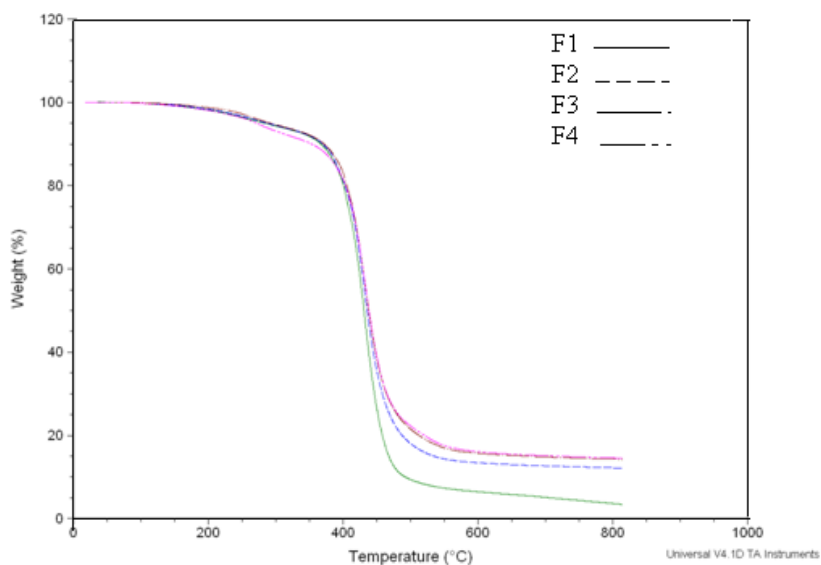
**Figure 4.23 :** Schematic representation of the formation of the UV-cured organic-inorganic hybrid coating material.

## 4.10 Film Formation

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

### 4.10.1 Thermogravimetric Analysis

TGA analysis were carried out in a nitrogen atmosphere at a heating rate of  $20^\circ\text{C}/\text{min}$  between  $30^\circ\text{C}$  and  $850^\circ\text{C}$  for analysing thermal stabilities of the boron containing epoxy acrylate films. Tables which are placed below indicated TGA values of TGA thermograms.

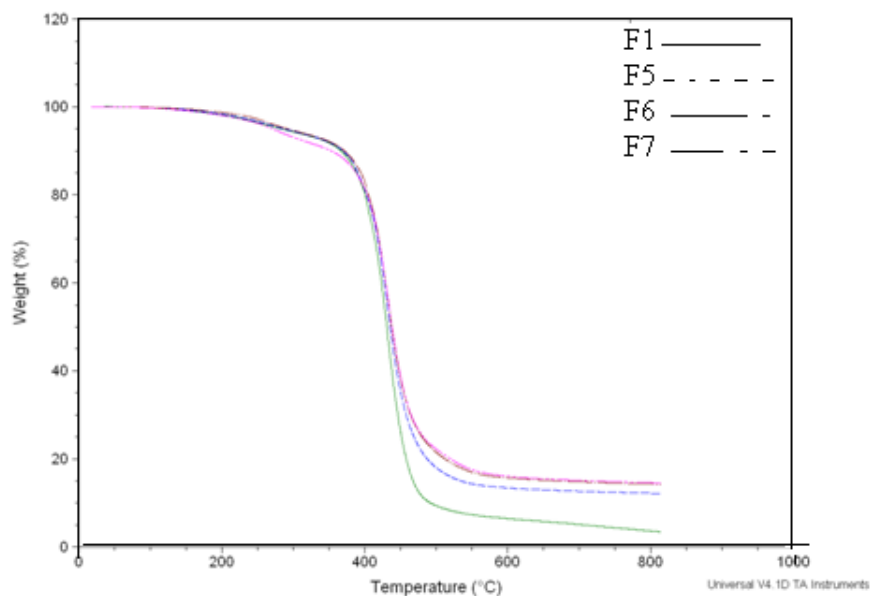


**Figure 4.24 :** TGA thermogram of samples F1-F4

**Table 4.1 :** TGA analysis values of F1-F4

Sample Code	5% Weight Loss Temperature (°C)	50% Weight Loss Temperature (°C)	Char Yield (%)
F1	284	430	4.3
F2	283	433	11.68
F3	284	436	13.89
F4	294	438	14.87

The samples containing boron compounds (F2, F3, F4 ) have higher char yield values due to the flame retardant action of boron compound. Borates are effective flame retardants because they have formed glassy coatings when they have thermally degradate. The glass coatings have formed on the surface and have caused the decreasing thermal conductivity of the surface of a burning material. Therefore, char yield is increased and the flammability of the material has reduced.

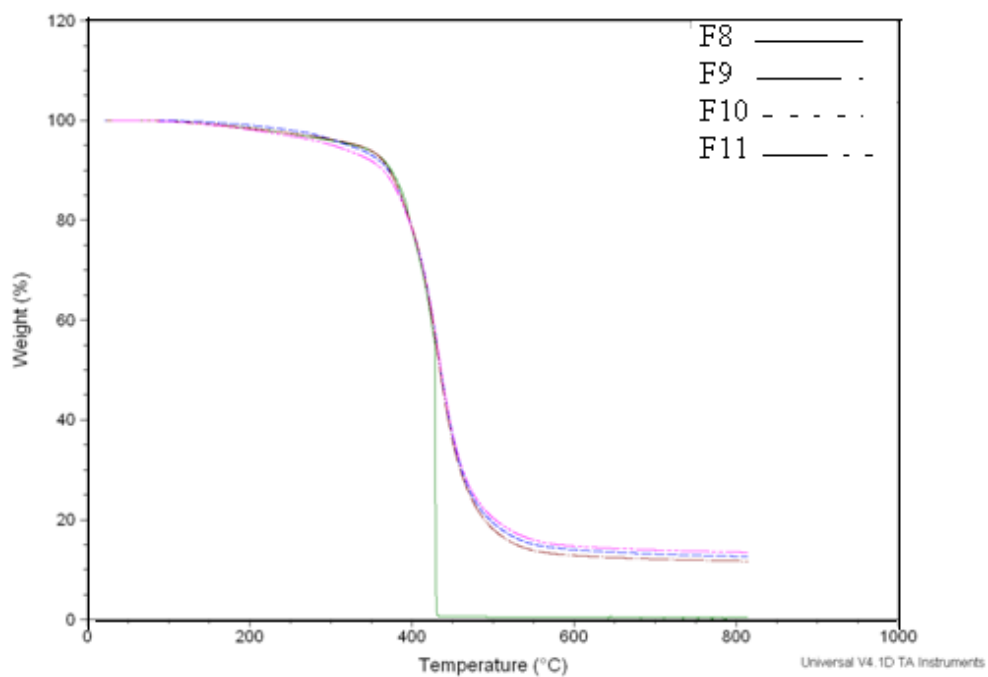


**Figure 4.25 :** TGA thermogram of samples F1-F7

**Table 4.2 :** TGA analysis values of F1-F7

Sample Code	5% Weight Loss Temperature (°C)	50% Weight Loss Temperature (°C)	Char Yield (%)
F1	284	430	4.3
F5	287	435	12.41
F6	292	437	14.52
F7	272	438	14.83

Sample containing boron methacrylate oligomer, F6, has higher first thermal degradation value than F3 sample because of the high content B-O bonds. Because the first weight-loss peak corresponds the bond breakage of the polymer chains and the F6 containing more B-O bond content. B-O bonds have high thermodynamic stability than C-O bonds. As a result of higher content of B-O bonds, 5% weight loss temperature has increased in this table ,especially at F6 sample. Beside the temperatures increasing, also boron is increased the barrier effect and gave better protective performance on char yield.

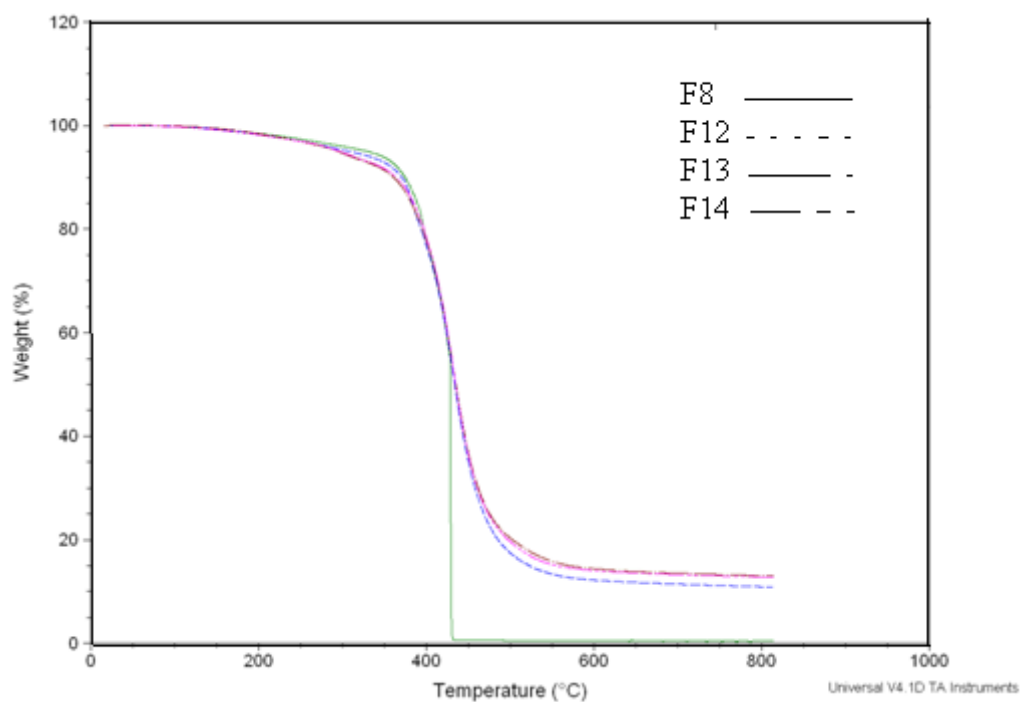


**Figure 4.26 :** TGA thermogram of samples F8-F11

**Table 4.3 :** TGA analysis values of F8-F11

Sample Code	5% Weight Loss Temperature (°C)	50% Weight Loss Temperature (°C)	Char Yield (%)
F8	329	428	0.43
F9	333	434	11.9
F10	322	436	12.9
F11	302	436	13.7



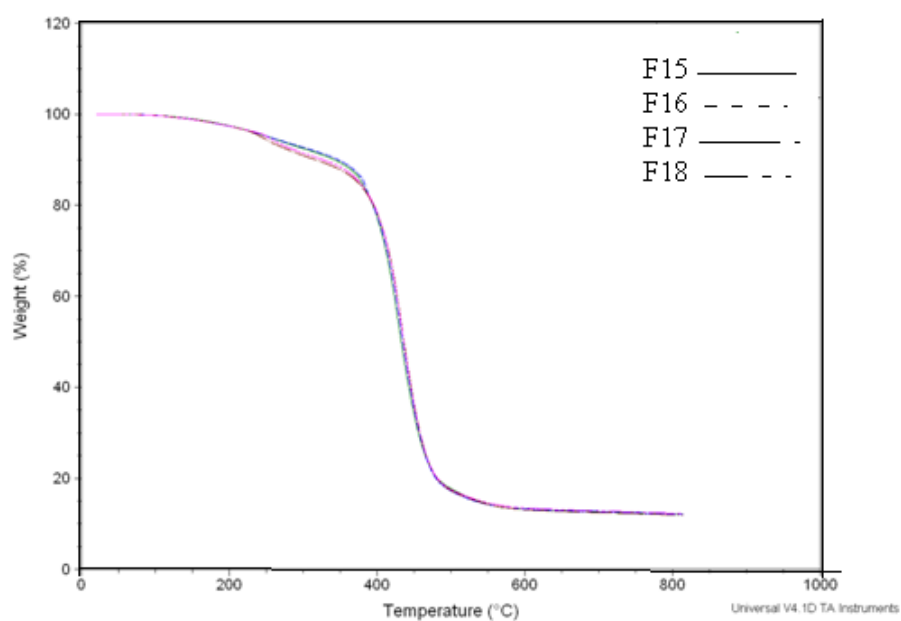


**Figure 4.27 :** TGA thermogram of samples F8-F14

**Table 4.4 :** TGA analysis values of F8-F14

Sample Code	5% Weight Loss Temperature (°C)	50% Weight Loss Temperature (°C)	Char Yield (%)
F8	329	428	0.43
F12	321	434	12
F13	296	434	13
F14	295	435	13.8

Sample F8 is containing only epoxy acrylate which has burned completely and no give any char yield. From Table 4.3 and Table 4.4 it can be seen obviously, samples which are containing boron compound have higher char yields to the respect of penetrating borates' flame retardancy effect. When the glassy coatings form on the surface and can contribute to the intumescent effect, because they exclude oxygen and prevent further propagation of combustion. By forming a boron to oxygen bond (such as a borester  $\text{-B-O-CH}_2\text{-}$ ), it is known that boron can inhibit oxidation at  $\text{-CH}_2\text{-}$  positions. Also, there has been increasing at 50% weight loss temperatures because of borate ester in the coating.

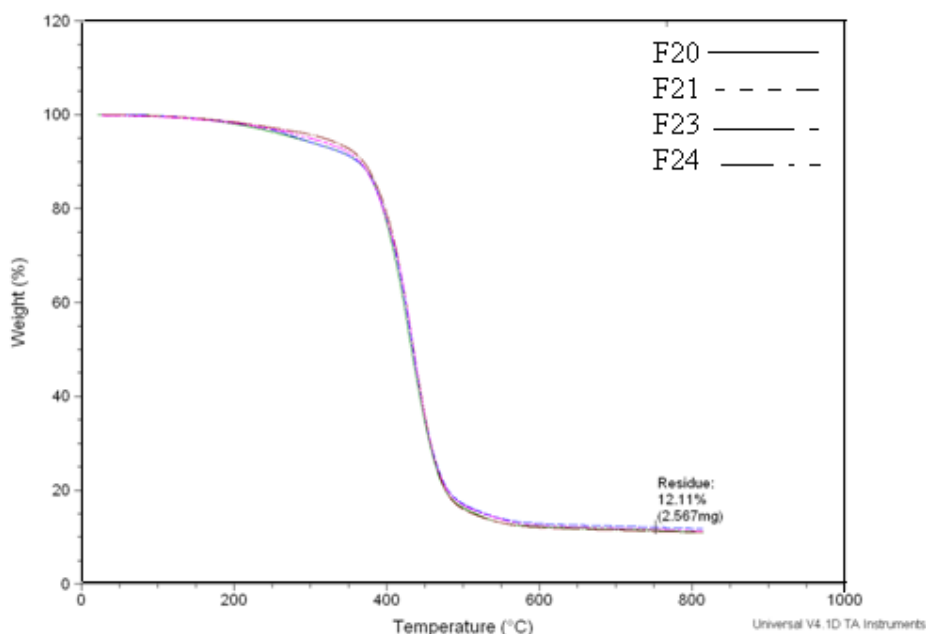


**Figure 4.28 :** TGA thermogram of samples F15-F18

**Table 4.5 :** TGA analysis values of F15-F19

Sample Code	5% Weight Loss Temperature (°C)	50% Weight Loss Temperature (°C)	Char Yield (%)
F15	266	432	10
F16	252	432	12.4
F17	254	434	12.43
F18	245	436	12.23
F19	251	436	12.6

Sample, F15, is containing phosphorus material that has high char yield. It is assumed that phosphorus content increase flame resistant of coating and act as physical barrier that prevent further combustion. When a comparison made between with samples F15 and F16, F16 has considerable char yield more than F15 due to the content of boron compound 2.5 %.



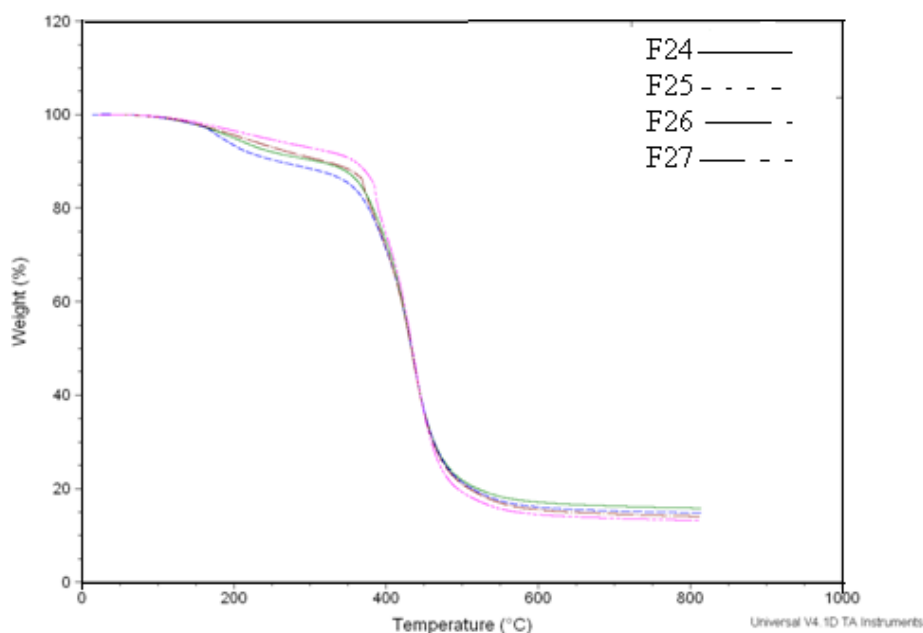
**Figure 4.29 :** TGA thermogram of samples F20- F24

**Table 4.6 :**TGA analysis values F20-F23

Sample Code	5% Weight Loss Temperature (°C)	50% Weight Loss Temperature (°C)	Char Yield (%)
F20	281	432	11.45
F21	284	434	12.11
F22	299	435	11.64
F23	317	435	11.24

Table 4.6 can be shown increasing at 5% and 50% weight of temperatures of the samples with addition of boron compound. The higher thermal degradation temperatures indicate the higher amounts of resins' residual with good antivolatile characteristics so thermal stability of epoxy acrylate is enhanced. With reducing the amount of flammable volatiles evolved, the formation of less flammable char increasing which also acts as a barrier between the polymer chain and the flame.

When phosphorus and boron compounds are used together, they can prevent the combustible gases from transferring to the surface of the materials, increase thermal stability at higher temperatures and improve flame retardancy



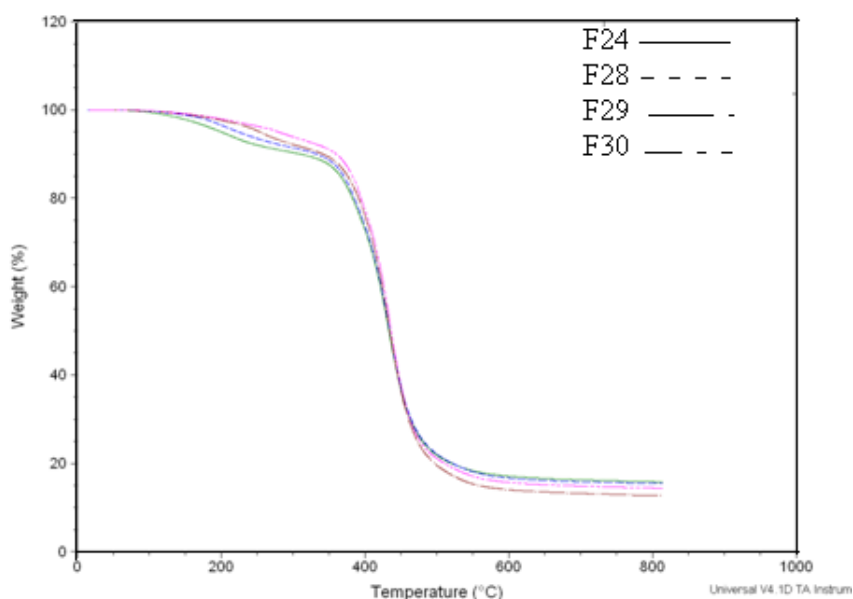
**Figure 4.30 :** TGA thermogram of samples F24-F27

**Table 4.7 :** TGA analysis values of F24-F27

Sample Code	5% Weight Loss Temperature (°C)	50% Weight Loss Temperature (°C)	Char Yield (%)
F24	200	433	16
F25	205	433	15
F26	212	432	14
F27	240	434	13

Hybrid materials have strong interaction between organic and inorganic components. Table 4.7 is shown 5% weight loss temperature is increased with incorporation of boron methacrylate monomer, this would indicate bonds between organic and inorganic networks could improve the thermal stability. The minor weight loss stage to 200 °C for samples due to the evaporation of physically absorbed water, residual solvent, and some volatile organic compounds. The weight losses of UV-cured hybrid coating material is started after 200 °C, this weight loss is attributed to breakage of the polymeric chain. The first weight loss stage is raised with boron content. From

200 °C to 650 °C belongs to the decomposition of other parts organic network. The third step after 650 °C complete decrosslinking and the thermal degradedates of the polymer. And these temperatures are increased with boron content.



**Figure 4.31** : TGA thermogram of samples F24-30

**Table 4.8** : TGA analysis values of F24-F30

Sample Code	5% Weight Loss Temperature (°C)	50% Weight Loss Temperature (°C)	Char Yield (%)
F24	200	433	16
F28	224	434	15.6
F29	254	434	13
F30	278	436	14.6

The thermal degradation temperatures of samples at Table 4.8, especially 5% weight loss temperatures, is increased much when comparing with Table 4.7. The reason, for these increasing can be based on the boron methacrylate oligomer structure which has high boron content, accordingly interaction between components have more strong. Thus, thermal degradation temperatures more than the samples at Table 4.7.

#### 4.10.2 Gel Content Measurement

This test was applied to measure the polymerization degree of the system. This procedure was proceeded as mentioned in section 3.5.4 and gel content values are listed in Table 4.

**Table 4.9 :** Gel content of UV-cured films

Sample code	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10
Gel Content (Wt %)	99	96	98	96	97	97	98	99	97	98
Sample code	F11	F12	F13	F14	F15	F16	F17	F18	F19	F20
Gel Content (Wt %)	98	98	98	98	97	97	96	98	99	97
Sample code	F21	F22	F23	F24	F25	F26	F27	F28	F29	F30
Gel Content (Wt %)	98	99	98	97	98	98	98	99	97	97

This results show us that unreacted part of cured materials are mostly under wt. 4%. It may be attributed that gel content values of the films increase because of high polymerization degree. The results of hybrid film samples from F21 to F30, found between 99 wt.% and 97 wt.%. These results verify the strong interaction between acrylate based organic and silica precursor.

#### 4.10.3 Solvent Resistance

This test was applied according to section 3.5.5. The solvents and the results were listed in tables. The solvent resistance of coatings was examined by immersing films samples in various such as xylene, methanol and chloroform for a 24 h time period. Chemical resistance of UV-cured coatings were studied in 10% acetic acid, 10% HCl, 10% NaOH solutions.

**Table 4.10 :Solvent resistance of F1**

Solvents	Weight loss (%)	Appearance
Xylene	-	Good
Chloroform	-	Good
Methanol	>10	Good
10% NaOH	2	Good
10% CH <sub>3</sub> COOH	-	Good
10% HCl	-	Good

**Table 4.11 : Solvent resistance of F2**

Solvents	Weight loss (%)	Appearance
Xylene	-	Good
Chloroform	-	Good
Methanol	5	Good
10% NaOH	<1	Good
10% CH <sub>3</sub> COOH	1.5	Good
10% HCl	1.5	Good

**Table 4.11 :Solvent resistance of F3**

Solvents	Weight loss (%)	Appearance
Xylene	<1	Good
Chloroform	1.8	Good
Methanol	4	Good
10% NaOH	0	Broken
10% CH <sub>3</sub> COOH	1.6	Good
10% HCl	1.5	Good

**Table 4.12 :Solvent resistance of F4**

Solvents	Weight loss (%)	Appearance
Xylene	1.8	Good
Chloroform	5	Good
Methanol	8.6	Good
10% NaOH	1	Broken
10% CH <sub>3</sub> COOH	1.8	Good
10% HCl	1.7	Good

From Table 4.11, Table 4.12, Table 4.13, Table 4.14 UV-cured coating materials including epoxy acrylate/boron methacrylate, low boron content samples higher solvent resistance.

**Table 4.13 : Solvent resistance of F8**

Solvents	Weight loss (%)	Appearance
Xylene	-	Good
Chloroform	-	Good
Methanol	-	Good
10% NaOH	-	Good
10% CH <sub>3</sub> COOH	-	Good
10% HCl	2	Good



**Table 4.14 : Solvent resistance of F9**

Solvents	Weight loss (%)	Appearance
Xylene	-	Good
Chloroform	-	Good
Methanol	-	Good
10% NaOH	-	Good
10% CH <sub>3</sub> COOH	-	Good
10% HCl	-	Good

**Table 4.15 : Solvent resistance of F10**

Solvents	Weight loss (%)	Appearance
Xylene	-	Good
Chloroform	-	Good
Methanol	-	Good
10% NaOH	-	Good
10% CH <sub>3</sub> COOH	-	Good
10% HCl	-	Good

**Table 4.16 : Solvent resistance of F11**

Solvents	Weight loss (%)	Appearance
Xylene	1	Good
Chloroform	-	Good
Methanol	-	Good
10% NaOH	-	Good
10% CH <sub>3</sub> COOH	>10	Broken
10% HCl	-	Good

From tables UV-cured coating materials containing commercial epoxy acrylate resin have high solvent resistance and better appearance.

**Table 4.17 : Solvent resistance of F15**

Solvents	Weight loss (%)	Appearance
Xylene	1.5	Good
Chloroform	>6	Good
Methanol	>8	Good
10% NaOH	>10	Broken
10% CH <sub>3</sub> COOH	1.5	Good
10% HCl	2	Good

**Table 4.18 : Solvent resistance of F16**

Solvents	Weight loss (%)	Appearance
Xylene	2	Good
Chloroform	>6	Good
Methanol	>10	Good
10% NaOH	>9	Broken
10% CH <sub>3</sub> COOH	1.5	Good
10% HCl	1	Good

**Table 4.19 : Solvent resistance of F17**

Solvents	Weight loss (%)	Appearance
Xylene	1.5	Good
Chloroform	>6	Good
Methanol	>10	Good
10% NaOH	>10	Broken
10% CH <sub>3</sub> COOH	2	Good
10% HCl	2	Good

**Table 4.20 : Solvent resistance of F18**

Solvents	Weight loss (%)	Appearance
Xylene	3	Good
Chloroform	>6	Good
Methanol	>10	Good
10% NaOH	>10	Broken
10% CH <sub>3</sub> COOH	3	Good
10% HCl	1	Good

**Table 4.22 : Solvent resistance of F19**

Solvents	Weight loss (%)	Appearance
Xylene	<1	Good
Chloroform	>6	Good
Methanol	-	Broken
10% NaOH	>10	Good
10% CH <sub>3</sub> COOH	-	Good
10% HCl	-	Good

APPO containing UV-cured coating materials are lower results of solvent resistance comparing with coatings materials non-containing APPO compound can be seen obviously in Tables 4.15, 4.16, 4.17, 4.18, 4.19.

#### 4.10.4 Contact Angle Measurement

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

**Table 4.21 :Contact angle values of F1-F7**

Sample Code	Water Contact Angle (°)	Sample Code	Water Contact Angle (°)
F1	73	F1	73
F2	77	F5	75.6
F3	79	F6	75
F4	79	F7	74

From the Table 4.23, water contact angles are smaller than 90° so the UV-cured coatings have shown hydrophilic effect. Epoxy acrylate coating with no additive has a fairly polar surface. Boron monomer has decreased the hydrophilicity in F2, F3, F4 samples. When compared with tables boron methacrylate oligomer containing samples have higher hydrophilicity due to the more content of polarity groups in F5, F6, F7 samples.

**Table 4.22 :Contact angle values of F8- F14**

Sample Code	Water Contact Angle (°)	Sample Code	Water Contact Angle (°)
F8	70	F8	70
F9	69	F12	69
F10	69	F13	68
F11	70	F14	67

From the Table 4.24 commercial epoxy acrylate resin has more hydrophilic effect and boron compound has increased the hydrophilic effect.

**Table 4.23 : Contact angle values of F15-F23**

Sample Code	Water Contact Angle (°)	Sample Code	Water Contact Angle (°)
F15	72	F20	66
F16	71	F21	65
F17	70	F22	70
F18	69	F23	66
F19	69		

Again commercial epoxy resin has higher hydrophilic effect and boron compound has caused increase in the hydrophilic effect.

**Table 4.24 :Contact angle values of F24-F30**

Sample Code	Water Contact Angle (°)	Sample Code	Water Contact Angle (°)
F24	60	F24	60
F25	59	F28	58
F26	58	F29	60
F27	56	F30	61

Silica containing hybrid coatings show hydrophilic properties. These results suggested residual polar groups derived from sol-gel silane solution affinity to water.

#### 4.10.5 Pendulum Hardness Test (Oscillation)

Instron pendulum hardness test is applied after all formulations coated plexiglass plat

**Table 4.25 : Oscillation results of F1-F7**

Sample Code	Pendulum Hardness	Sample Code	Pendulum Hardness
F1	85	F1	85
F2	89	F5	90
F3	86	F6	85
F4	87	F7	86

Pendulum hardness depends on the crosslinking density of the UV-cured films and the chemical structure of UV curable resin. According to the Table 4.27 boron containinf cured films have higher hardness and sample F2 and F3 can be said that show best effect.

**Table 4.26 :** Oscillation results of F8-F14

Sample Code	Pendulum Hardness	Sample Code	Pendulum Hardness
F8	101	F8	101
F9	96.7	F12	82
F10	93	F13	89
F11	94	F14	84

Commercial epoxy acrylate with no additive shows the better hardness, this result may be suggested that because of remaining some non-crosslinked structures due to the high acrylic content.

**Table 4.27 :**Oscillation results of F15-F23

Sample Code	Pendulum Hardness	Sample Code	Pendulum Hardness
F15	92	F20	90
F16	94	F21	84
F17	93	F22	86
F18	92	F23	94
F19	91		

Increasing the pendulum hardness in F16, F17, F23 expected to be due to the rigid structure of APPO and the higher acylate content of the coating because of boron methacrylate oligomer.

**Table 4.28 : Oscillation results of F24-F25**

Sample Code	Pendulum Hardness	Sample Code	Pendulum Hardness
F24	83.5	F24	83.5
F25	81	F28	85
F26	81	F29	85
F27	81	F30	85

Boron methacrylate oligomer is clearly increased the hardness of coating due to its high acrylic content so high crosslink density in Table 4.30.

#### 4.10.6 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.

**Table 4.29 : Pencil hardness of F1-F7**

Sample Code	Pencil Hardness	Sample Code	Pencil Hardness
F1	6H	F1	6H
F2	6H	F5	7H
F3	6H	F6	7H
F4	6H	F7	7H

**Table 4.30 : Pencil hardness of F8-F14**

Sample Code	Pencil Hardness	Sample Code	Pencil Hardness
F8	6H+	F8	5H
F9	6H+	F12	5H
F10	6H+	F13	5H
F11	7H+	F14	6H

**Table 4.31 : Pencil hardness of F15-F23**

Sample Code	Pencil Hardness	Sample Code	Pencil Hardness
F15	4H	F20	5H
F16	5H	F21	5H
F17	5H	F22	7H+
F18	5H	F23	7H+
F19	6H		

**Table 4.32 : Pencil hardness of F24-F30**

Sample Code	Pencil Hardness	Sample Code	Pencil Hardness
F24	7H	F24	7H
F25	6H	F28	7H
F26	6H	F29	7H
F27	6H	F30	7H

**4.10.7 Tensile Strength**

The mechanical specification of free films, prepared at 50x10x1mm dimensions, made clearly with measurement of stress-strain values.

**Table 4.33 : Stress-Strain Analysis of F1-F4**

Sample Code	E-Modulus (N/mm <sup>2</sup> )	Tensile strength (Mpa)	Elongation at break (%)
F1	734	10	2.74
F2	840	11	4
F3	853	13	5
F4	939	19	6



**Table 4.34 : Stress-Strain Analysis of F1-F7**

Sample Code	E-Modulus (N/mm <sup>2</sup> )	Tensile strength (Mpa)	Elongation at break (%)
F1	734	10	2.75
F5	899	22	3
F6	748	19	5.5
F7	769	23	8.5

Modulus value is a measure of the stiffness of material, it can give information about rigidity too. And the tensile strength gives result about material elastic or brittle. According to Table 4.47 and 4.48 modulus and tensile strength has increased with high content of borate compounds. Therefore stiffness and the brittle properties also increasing. Sample F5 has better value than others because of the high boron content than others.

**Table 4.35 : Stress-Strain Analysis of F8-F11**

Sample Code	E-Modulus (N/mm <sup>2</sup> )	Tensile strength (Mpa)	Elongation at break (%)
F8	994	28	3.5
F9	956	27	4.5
F10	881	2	2
F11	1019	14	14

**Table 4.36 : Stress-Strain Analysis of F8-F14**

Sample Code	E-Modulus (N/mm <sup>2</sup> )	Tensile strength (Mpa)	Elongation at break (%)
F8	994	28	3.5
F12	1003	7	7.3
F13	1021	30.5	5.9
F14	1054	31	4.2

In samples F12, F13, F14 modulus and the tensile strength is increased due to the boron methacrylate oligomer, thus, it can be seen clearly boron-oxygen bond strength is affected the stiffness of the coating.

**Table 4.37 :Stress-Strain Analysis of F15-F19**

Sample Code	E-Modulus (N/mm <sup>2</sup> )	Tensile strength (Mpa)	Elongation at break (%)
F15	793	17	4
F16	828	20	4
F17	841	24	3.5
F18	513	1	24
F19	852	17	6.15

**Table 4.38 : Stress-Strain Analysis of F20-F23**

Sample Code	E-Modulus (N/mm <sup>2</sup> )	Tensile strength (Mpa)	Elongation at break (%)
F20	924	40	5.6
F21	1138	5.7	11.61
F22	887	31	4.6
F23	963	4	5.3

**Table 4.39 :Stress-Strain Analysis of F24-F27**

Sample Code	E-Modulus (N/mm <sup>2</sup> )	Tensile strength (Mpa)	Elongation at break (%)
F24	735	4	6.6
F25	642	14	6
F26	766	3.5	2
F27	533	6.5	3.5

**Table 4.40 : Stress-Strain Analysis of F24-F30**

Sample Code	E-Modulus (N/mm <sup>2</sup> )	Tensile strength (Mpa)	Elongation at break (%)
F24	735	4	6.6
F28	730	3	6.9
F29	670	7.4	5
F30	591	8	14.53



## 5. CONCLUSION

The aim of this study was to prepared UV-curable boron containing epoxy acrylate coatings and investigated their mechanical and thermal properties. For this purpose polymerizable boron acrylate monomer and boron methacrylate oligomer was synthesized. The resulting material used in UV-curable coating formulations which were included organic–inorganic hybrid coating materials containing silica sol and phosphorus containing oligomer APPO.

Formulations with containing boron methacrylate monomer and boron methacrylate oligomer were increased the char yield which plays an important role in improving flame retardancy. Furthermore, hybrid coatings give higher results at the 5% weight loss temperature with boron methacrylate compounds. Then, it can be seen clearly APPO with boron methacrylate monomer gave the best result where the boron methacrylate monomer has 2.5 % weight ratio in the formulations. There was not any positive or negative affect at the mechanical properties on the epoxy acrylate coat



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