İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

URETHANE ACRYLATE COATING ON COAGULATED POLYURETHANE SURFACES BY UV RADIATION

M.Sc. Thesis by
Chem. Eng. Esra KIRAYLAR

Department : Polymer Science and Technology

Programme: Polymer Science and Technolgy

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POLİÜRETAN KOAGÜLE ZEMİNLERE ÜRETAN AKRİLAT TİPİ OLİGOMERLERİN UV RADYASYONLA KAPLANMASI VE ÖZELLİKLERİNİN İNCELENMESİ

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ABBREVIATIONS

DMF : Dimethyl Formamide

PU : Polyurethane

ALUA : Aliphatic Urethane Acrylate

ARUA : Aromatic Urethane Acrylate

CPS : Coagulated Polyurethane Surfaces

PEG : Polyethyleneglycol

PPG : Polypropyleneglycol

UV : Ultraviolet

VOC : Volatile Organic Compounds

EB : Electron Beam

UA : Urethane Acrylate

CIE : International Commission of Illumination

NVP : N- vinyl pyrollidone

IDA : Isodecylacrylate

NPGDA : Propoxylated neophentylglycoldiacrylate

GPTA : Propoxylated glyceryltriacrylate

TMPTA : Trimethylolpropanetriacrylate

vs. : versus

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LIST OF SYMBOLS

Al **:** Aluminium

R **:** Reflectance

λ **:** Wavelength

Tg **:** The glass transition temperature

COAGULATED POLYURETHANE SURFACE COATING by URETHANE ACRYLATES via UV RADIATION

ABSTRACT

Polyurethane (PU) resins are used in aerospace industry, transportation, buildings, wood, plastic coating applications but especially in synthetic leather industry as coagulated polyurethanes because of their high performances. Polyurethane systems are widely used in coating applications because of their high chemical resistance, gloss and excellent mechanical properties. Coagulated polyurethane surfaces are produced by coagulation process of diluted polyurethane resins on fabric substrates.

The fast and easiest way to obtain crosslinked polymer network out of multifunctional liquid acrylate monomers and viscous oligomers is photopolymerization. Radiation curing is the polymerisation of a chemical system which is initiated by incident radiation. The curing, the transformation from a liquid into a non-tacky solid, is very fast and occurs in less than 1 s. UV curing creates polymers from monomers of low-molecular weight oligomers initially present. Their mechanism of drying depends upon some of their chemical constituents being sensitive to UV-light of certain wavelengths. In modern time, there are two major reasons for the current rapid advance of UV-curing technology; one of them is energy and matter conservation and the other is environment pollution control.

In this thesis, the aim is to develop some formulations with urethane prepolymer to improve mechanical properties of coagulated polyurethane surfaces with desired properties. Like most oligomers, the urethane acrylates are typically high in molecular weight and viscosity. Diluents, particularly multifunctional acrylate monomers, are used to reduce viscosity to manageable levels and to provide crosslinking. The formulated solutions are coated on coagulated PU surfaces and cured under UV light. Furthermore, coated cogulated PU surfaces are tested for their physical and mechanical properties.

POLİÜRETAN KOAGÜLE ZEMİNLERE ÜRETAN AKRİLAT TİPİ OLİGOMERLERİN UV RADYASYONLA KAPLANMASI ve ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Poliüretan kaplamalar yüksek parlaklık, iyi kimyasal dayanım ve fiziksel özelliklerinin mükemmelliğinden dolayı havacılık, taşımacılık, bina, kumaş ve plastik kaplama konularında oldukça geniş kullanım alanı bulmuştur. Poliüretan koagüle zeminler ise seyreltilmiş poliüretan reçinelerin kumaş üzerine kaplanması ile elde edilmektedir. Poliüretan koagüle zeminler, en çok suni deri üretiminde kullanılmaktadır.

Çok fonksiyonlu sıvı akrilat monomerler ile viskoz oligomerlerden, çapraz bağlı polimer ağı elde etmenini en etkili ve kolay yöntemi fotopolimerizasyondur. Hızlı polimerizasyonunun yanında; çözücü içermeyen formülü, düşük enerji tüketimi, reaksiyonun oda sıcaklığında yapılabilmesi de fotopolimerizasyonun diğer avantajları arasında sayılabilir. UV radyasyonla bir sıvının yapışmayan bir katıya dönüşmesi olayı, bir saniyeden kısa bir sürede meydana gelir. Kürleme mekanizması ise, malzemenin, belirli dalga boyundaki UV ışığa duyarlı, kimyasal bileşenlerine dayanır. UV ile kürlemenin iki güçlü yönü vardır; biri madde ve enerjinin korunması, diğeri ise çevresel atık kontrolüdür.

Bu çalışmada, suni deri uygulamasına yönelik, alifatik ve aromatik üretan akrilat oligomerlerden, UV ışınları ile, istenilen özelliklerde, polimerik kaplamalar çalışılmıştır. Akrilat monomerleri, oligomerin viskozitesini düşürerek uygulamayı kolaylaştırmanın yanında elde edeceğimiz polimerik filmin mekanik özelliklerini belirlemede de oldukça etkin bir rol oynadığından, istenilen özelliklerde film eldesi için çeşitli oranlarda değişik fonksiyonlu monomer ilavesi ile karışım formülasyonu hazırlanarak, uygun fotobaşlatıcı ortamında kaplama yüzeyine uygulanarak, UV ile kürleştirilmiş, daha sonra da fiziksel ve mekanik özellikleri incelenmiştir.

1. INTRODUCTION

Polyurethane resins are widely used in coating applications especially in production of coagulated polyurethane surfaces, because of their high performances. Coagulated polyurethane surfaces are used as synthetic leather which is an important commodity that is widely used in shoes, luggage carriers, bags and as sheaths for couches etc.

Urethane acrylate oligomers have been extensively investigated in the past two decades as photocurable coatings useful for protecting some material surfaces such as papers, woods and plastics [1]. They are high molecular weight, reactive materials that can be photopolymerized (cured) using a free radical mechanism called ultraviolet (UV) radiation. Photoinitiated free radical polymerization of urethane acrylate oligomers require reactive multifunctional diluents that enhanche mechanical properties and an appropriate photoinitiator that starts photopolymerization [2].

UV-radiation curing has become a well accepted technology which has found a large variety of industrial applications because of its distinct advantages. Light-induced polymerization of multifunctional oligomers and monomers is indeed a powerful method to achieve a quasi-instantaneous transformation of a liquid resin into a solid polymer. The steady development of the UV-curing technology in the past 20 years has opened the way to an increasing number of end uses. The most important ones are to be found in the coating industry for enhancing final properties and surface protection of the product.

This thesis will concern the preparation of aliphatic and aromatic urethane acrylate formulations which will be applied on coagulated polyurethane surfaces and their polymerization by UV light. The aim is enhancing mechanical properties of coagulated surfaces. Therefore, physical and mechanical properties of the treated and untreated surfaces will be investigated.

2. THEORETICAL PART

2.1 Coagulated Polyurethane Coatings

Polyurethane (PU) resins are widely used in coating applications especially in synthetic leather industry because of their high performances. Synthetic leather is an important commodity that is widely used in shoes, luggage carriers, bags, belts, tents, purses and as sheaths for couches etc.

Coagulated polyurethane coating process is a specialized process requires special apparatus and considerable capital investment which includes solvent recovery. Development started over 40 years ago and there are several hundred patents involving many of the major textile and chemical companies e.g. DuPont, Bayer [3].

Reproducing the properties of leather is not easy; many products have appeared over years. The essential process involves polyurethane which is dissolved in a solvent and is then thrown out of solution under controlled conditions to form a precipitate or coagulation. This material is a soft, has a pore-like structure and is the basis of imitation leather. Commercial processes use polyurethane in dimethylformamide (DMF) solvent which is applied to the fabric carrier. This coated material is then brought into contact with a bath containing a DMF/water mixture in which the polyurethane is insoluable and is therefore coagulated. The coagulated material is washed and dried and the potentially toxic DMF solvent has to be recovered [3].

Consequently, it began with the treatment of nonwovens with polyurethane dissolved in DMF. After immersion and squeezing, the impregnated nonwoven web was successively diluted by passing it through various water baths until the DMF, which can be mixed with water in any ratio, was no longer able to keep the PU in solution. It therefore coagulated in situ, thus forming a film with an immense number of micropores, which were vapour permeable but at the same time water proof. After drying the treated nonwoven was usually emerized or suede finished.

Figure 2.1: Coagulated Polyurethane Surface (CPS)

As DMF poses health risk, the whole finishing has to be carried out on closed machines and all DMF has to be recovered from water by distillation [4]. There are numerous variations in process design and conditions which have to be optimised such as polymer type, base fabric design, additives, viscosity, coagulation bath conditions, washing and drying conditions, but most of the commercially available artificial leathers are made using this type of process [3]. One example of commercial coagulated polyurethane surface (CPS) is shown in Figure 2.1.

2.2 Acrylate Oligomers

The acrylate oligomers used in UV radical polymerization are typically viscous liquids ranging from a few thousand to greater than one million centipoise in viscosity at 25°C. They typically possess two to six acrylate groups per molecule and range in molecular weight from approximately 500 to 20,000. The acrylate oligomers provide film properties superior to what can be achieved with monomers alone. This variety of oligomer types yields UV-cured polymers with a wide range of physical properties. There are oligomers that form hard, rigid polymers with high tensile strength and modulus and others that form soft, extensible polymers with high elongation [19].

Low to zero volatile organic compound (VOC) content, improved performance, and significantly decreased drying times can be achieved when specialty acrylic functionalized oligomers are used in formulating cure-in-place coatings, inks, adhesives, and electronic products to name a few [5]. Cure-in-place coatings are coatings that are applied and immediately cured or polymerized on the substrate, as the name implies. Methods of curing-in-place include free radical initiated curing such as in ultraviolet light or electron beam radiation systems etc. [5].

All of these technologies allow coatings to be cured-in-place using specialty acrylic esters - acrylate and methacrylate monomers and oligomers. Formulations for cured-in-place coatings, inks, adhesives, and electronics, typically consist of a blend of an oligomer, a monofunctional monomer, multifunctional monomer, photoinitiator (for UV), and often additives and pigments. The oligomer imparts most of the basic properties of the final cured material [5].

Urethane acrylate oligomers are among the most widely used products in radiation cure applications. Urethane acrylates provide water resistance, high gloss, hardness and/or flexibility, and chemical resistance for a wide variety of applications [5].

2.2.1 Urethane Acrylate Oligomer Chemistry

Urethane acrylate oligomers offer improved performance properties in coatings, electronics, adhesives, inks, elastomers, photopolymers, polymer concrete, flooring and flexible packaging [5]. Urethane acrylate oligomers are high molecular weight, reactive materials that play a significant role in cure-in-place technology. Urethane acrylate oligomers can be cured (polymerized) using any of several free-radical mechanisms, ultraviolet radiation (UV), including electron beam (EB). Key determinants of urethane acrylate oligomer performance lie in the structural elements of the molecule. As an example Figure 2.2 shows the chemistry of an urethane acrylate oligomer. The mechanical properties of a coating can be adapted to the requirements by optimizing the raw material. UV curable urethane acrylates provide a large property spectrum, where hardness and elasticity can be adjusted to the application [6].

The urethane acrylate oligomers are synthesized from polyols (polyesterols and/or polyetherols) which have an influence on the mechanical properties of the UV-cured coatings. Examples of polyols, 1,4 butanediol polyadipate and polyethyleneglycol, are given in Table 2.1.

Urethane acrylates can be divided into two main categories: Aliphatic and aromatic urethane acrylate oligomers. The aliphatic or aromatic nature of the urethane acrylate is determined by the choice of diisocyanate An aromatic diisocyanate, such as bis(4-isocyanatophenyl)methane , will yield an aromatic urethane acrylate oligomer.

An aliphatic urethane acrylate will result from the selection of an aliphatic diisocyanate, such as hexamethylene diisocyanate [5]. Examples of aromatic and aliphatic diisocyanates are given in Table 2.1.

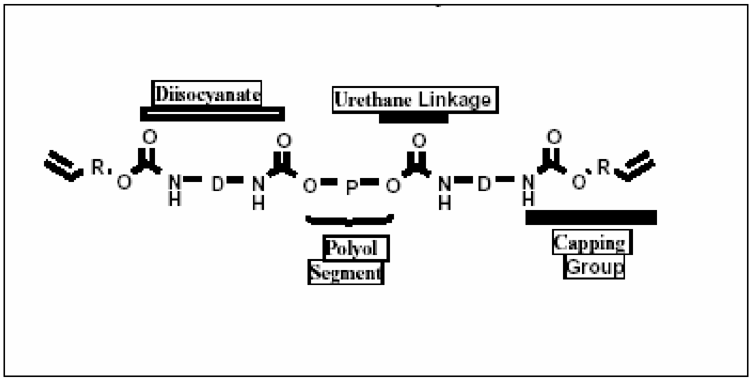
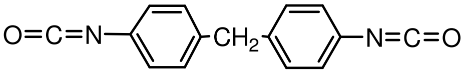
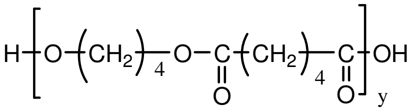
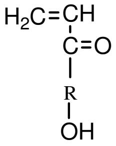


Figure 2.2: Urethane Acrylate Chemistry [7]

Table 2.1: Components of Urethane Acrylate Oligomer

 bis(4-isocyanatophenyl)methane	$O=C=N-(CH_2)_6-N=C=O$ hexamethylene diisocyanate
 $H-[O-(CH_2)_4-O-C(=O)-(CH_2)_4-C(=O)]_y-OH$ Polyesterol *	$H-(O-CH_2-CH_2)_x-OH$ Polyetherol *
 $H_2C=CH-C(=O)-R-OH$ Hydroxy functional acrylate	

---

* The molecular weights of the polyols vary between 250 to 2000 g/mol. [6]

Urethane acrylate oligomers are synthesized by reacting a diisocyanate with polyester or polyether polyol to yield an isocyanate terminated urethane. Subsequently, hydroxy terminated acrylates are reacted with the terminal isocyanate groups. This acrylation provides the unsaturation or the (C=C) group to the ends of the oligomer [5].

General urethane acrylate structure is like:

Acrylate —— Oligomer Backbone —— Acrylate

Figure 2.3: General urethane acrylate structure

The reactions are shown at Figure 2.4 and Figure 2.5 for synthesis of aliphatic and aromatic urethane acrylates, respectively.

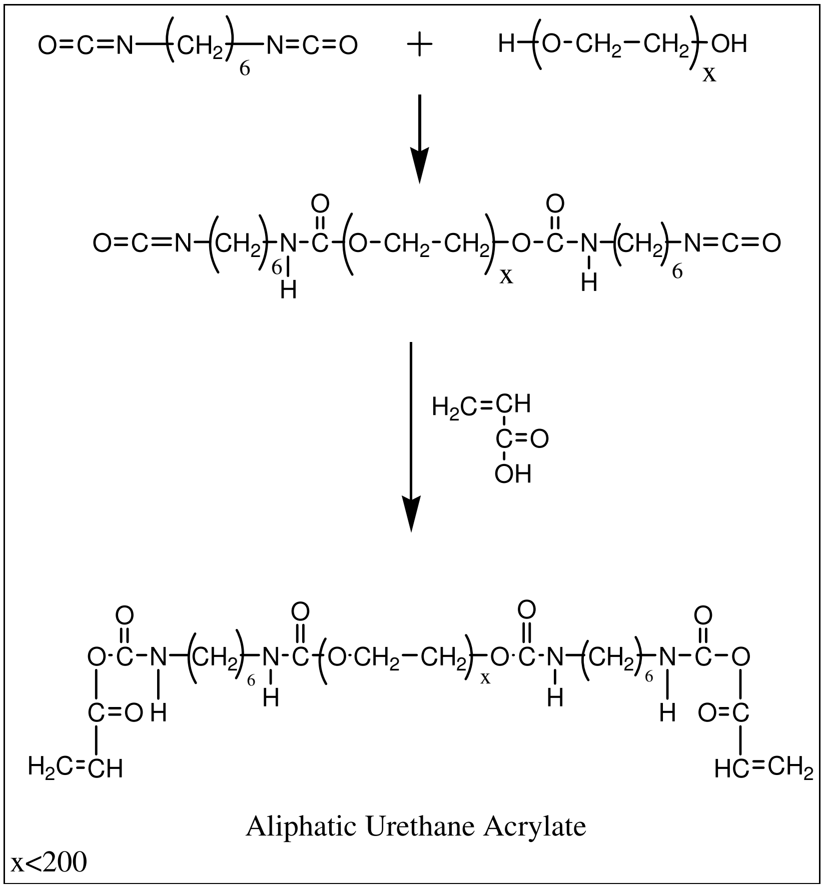


Figure 2.4: Aliphatic Urethane Acrylate Synthesis Scheme

As described previously urethane acrylates are synthesized by reacting a diisocyanate with a polyol and a hydroxy terminated acrylate.

They are divided into two categories: aliphatics and aromatics, derived from the structure of the diisocyanate used in their production [5]. Aliphatic diisocyanate based oligomer products are not highly susceptible to ultraviolet or thermal degradation.

They are generally more flexible and are recommended where weatherability is critical. Aromatic urethane acrylate oligomers, in addition to their lower cost, are generally lower in viscosity, harder, and slightly fastger curing. Like the aliphatics, they demonstrate good chemical resistance. However, they are more prone to yellow on extended UV exposure. As with the aliphatic urethane acrylates, a polyester backbone promotes greater flexibility. Beyond the choice of isocyanate, polyol backbone plays a pivotal role in determining the performance of the final oligomer. Polyols are generally classified as esters, ethers, or a combination of these two. The hardest urethane acrylates are the aromatics with ether backbones [5]. Polyol type and structure plays a pivotal role in determining the performance of the final oligomer. Among the three polyol categories - esters, ethers, or ester/ether combinations - many product alternatives are possible.Polyols can be polyethyleneglycol(PEG) or polyprophyleneglycol(PPG) used as polyether backbone, and 1,4 butanediol polyadipate as a polyester backbone. The oligomer backbone is terminated by two or more acrylate units, which serve as reactive sites for free-radical initiated polymerization.

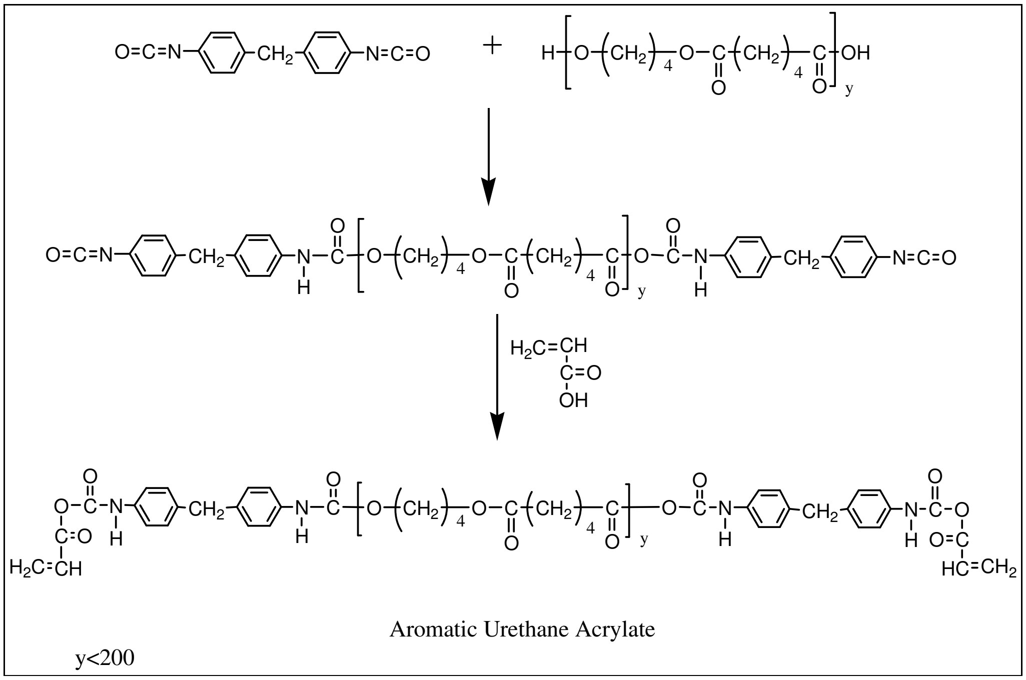


Figure 2.5: Aromatic Urethane Acrylate Synthesis Scheme

Choices among isocyanates, polyols, and acrylate termination units allow considerable latitude in the development of urethane acrylate oligomers.

Within the realm of diisocyanate structure, polyol type, and acrylate capping compound choices, virtually any combination may be achieved. Like most oligomers, the urethane acrylates are typically high in molecular weight and viscosity. Diluents, particularly multifunctional acrylate monomers, typically are used to reduce viscosity to manageable levels and to provide crosslinking. Additionally, the wide variety of available monomer types provide selective enhancement to adhesion, substrate wetting, flowout, cure rate, hardness, and other desired properties [5].

The ingredient monomer components, while reducing the viscosity of the mixture, also enhance the functional performance of the oligomer [20]. The chemical structure of the monomer will determine its ability to harden or flexibilize the cured material, promote adhesion to difficult substrates, or enhance some other desired property, such as water resistance.

Monofunctional monomers, which contain only one reactive group, react to become incorporated into the final coating material. On the other hand, multifunctional monomers contain multiple reactive sites. In addition to their role as diluents, these products are unique in their ability to create links between oligomer molecules and other monomers in the formulation. These crosslinks provide enhancements to hardness, toughness, strength, and relative solvent resistance. Because of the increased number of reactive sites, improved cure rate is a secondary benefit of multifunctional monomers [20]. Table 2.2 shows the comparison of aliphatic and aromatic UA's.

Table 2.2: Comparison of Aliphatic and Aromatic Urethane Acrylates

Oligomer Type	Performance Effects
Aliphatic Urethane Acrylate	Increase flexibility, toughness, weathering; Decrease yellowing
Aromatic Urethane Acrylate	Increase flexibility, toughness; Decrease cost (vs. Aliphatic)

Below, the items reveal the isocyanate and polyol chemistry of the uretan part of the oligomer play a big role in the performance properties of the urethane acrylate oligomers. The molecular weight, urethane content and functionality are also factors [5].

Influence of Raw Material and Composition;

- Diisocyanate Type and Structure → Mechanical Properties Weatherability
- Polyol Type and Structure → Hydrolytic Stability, Viscosity Reduction, Cure Speed
- Molecular Weight→ Solvent Resistance and Flexibility
- Urethane Content→ Adhesion
- Functionality→ Adhesion,Viscosity , Cure Speed, Hardness

The molecular weight of the polyol determines its hydrolytic stability. Lower molecular weight polyols, yields in general, urethane acrylate oligomers which are more hydrolytically stable. The molecular weight of the urethane acrylatge oligomer is both a function of the urethane and the polyol determines a variety of properties such as solvent and chemical resistance. Lower molecular weight urethanes tend to be more solvent resistant than their higher molecular weight counterparts. The Figure 2.6 shows the performance effects of components of urethane acrylate oligomers.

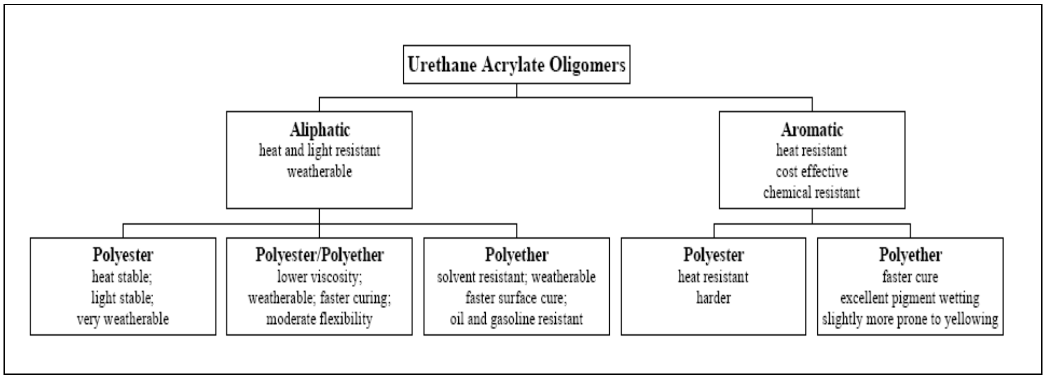


Figure 2.6: Component Effects for Urethane Acrylate Oligomers [5]

The dominant chemistry for UV curing is the radical polymerization of unsaturated monomers and oligomers. Monomers and oligomers containing acrylate unsaturation are the most commonly utilized due to their higher reactivity compared to methacrylate, allyl or vinyl unsaturation in UV initiated radical polymerization.

While specific formulations will vary greatly depending on end-use requirements, the majority will contain one or more of the following components:

- Multifunctional acrylate oligomers, which impart the basic properties of the cured coating.
- Multifunctional acrylate monomers, that have the major function of providing low coating viscosity, but will also modify film properties such as hardness, adhesion and chemical resistance.
- Monofunctional acrylate monomer(s), that also lower coating viscosity and reduce crosslinking in the cured film, reducing volumetric shrinkage for improved adhesion while increasing flexibility and impact resistance.

2.3 Acrylate Monomers

The acrylate monomers used in UV curing typically have from one to four acrylate groups and range in molecular weight from approximately 150 to 500. They are commonly light colored, non-volatile liquids with viscosities from five to 200 centipoise at 25°C. Acrylate monomers act as diluents for the acrylate oligomers in order to achieve coating viscosities suitable for typical application equipment.

Unlike solvents, the acrylate monomers co-polymerize with the acrylate oligomers to form an integral part of the cured coating, and can have significant effects on the coating performance. The functionality of the monomer has the most significant effect on properties of the cured coating.

Like the acrylate oligomers, the acrylate monomers within each type exhibit a considerable range of performance.Some monofunctional acrylate monomers will impart greater hardness to a coating than others, while some trifunctional acrylate monomers provide more flexibility relative to other triacrylate monomers [19].

2.4 Photopolymerization

Photopolymerization is defined as the reaction of monomers or macromers to produce polymeric structures by light-induced initiation (excitation of a photoinitiator) and subsequent polymerization.

Fundamental research and practical applications of photopolymerization have evolved significantly over the past few decades leading to a better understanding of the mechanisms of the reaction and to numerous industrial applications [8]. This technology is now commonly utilised to perform the ultrafast drying of protective coatings, varnishes, printing inks and adhesives, and to produce the high-definition images required in the manufacture of microcircuits and printing plates. Highly crosslinked polymers are readily synthesised by photoinitiated polymerisation of multifunctional monomers and telechelic oligomers [9].

UV-radiation curing has become a well-accepted technology which has found a large variety of industrial applications because of its distinct advantages.

Light-induced polymerization of multifunctional monomers is indeed a powerful method to achieve, selectively in the illuminated areas, a quasi-instantaneous transformation of a liquid resin into a solid polymer [23].

Radiation technology is widely applied in industrial fields as an important polymerization or cross-linking process [24]. Radiation curing is a production technique of fast transformation of specially formulated liquids into solids by electromagnetic wave irradiation. It has been an important technique in the coating, adhesives, and ink industry. Even though the main driving force for using radiation curing is environmental protection, the radiation process has benefits in productivity, profitability, manufacturing cost, etc. over the thermal processes. Primary radiation sources are infrared, microwave, radio frequency, UV, and electron-beam. The first three initiate thermal curing, whereas the last two initiate via electronic excitation and ionization. UV and electron beam are most commonly employed due to their fast and high curing abilities [8]. Ultraviolet Radiation (190-400nm) was used for photopolymerization in this study.

The light-induced polymerization of liquid multifunctional monomers and oligomers is one of the most efficient methods to produce quasi- instantly highly crosslinked polymer networks at ambient temperature [10]. Highly crosslinked polymers have been produced within few seconds by photoinitiated polymerization of multifunctional acrylic monomers and oligomers.

Photopolymerization requires three essential elements:

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

Besides its great speed, this technology (radiation curing) offers a number of advantages, such as solvent-free formulation, low energy consumption, ambient temperature operations and tailor-made properties of the photopolymer [11].

2.4.1 Radiation Curing

Radiation cure coatings cross-link by reactions initiated by radiation, rather than heat. Such coatings have the potential advantage of being indefinitely stable when stored in the absence of radiation, while after application, cross-linking occurs rapidly at ambient temperature on exposure to radiation. Rapid cure at ambient temperature is particularly significant for heat sensitive substrates, including paper, some plastics, and wood.

There are two classes of radiation cure coatings; one is UV cure coatings in which the initial step is excitation of a photoinitiator (or photosensitizer) by absorption of photons of UV-visible electromagnetic radiation and the second one is EB (electron beam) cure coatings in which the initial step is ionization and excitation of the coating resins by high energy electrons.

Crosslinking is initiated by reactive intermediates that are generated from the photoexcited photoinitiator in UV curing and from excited and ionized resins in EB curing. Infrared and microwave radiation are also used to cure coatings, but these systems are not included to this classification, since the radiation is converted to heat, they can be included to thermal curing systems [12].

2.4.1.1 UV Curing

In the first UV cure coatings, styrene solutions of unsaturated polyesters were used along with benzoin ether photoinitiators. However, styrene is sufficiently volatile that a significant amount evaporates between application and curing.

Furthermore, the rate of polymerization is relatively slow as compared to acrylate systems. However, the cost is low, and they continue to find some application.

Most current coatings use acrylated reactants. Acrylate, rather than methacrylate, esters are used, since acrylates cure more rapidly at room temperature; they are also less oxygen inhibited. Furthermore, polymerization of acrylates tends to terminate by combination, whereas methacrylate polymerization terminates largely by disproportionation. The extents of cross-linking, as well as higher molecular weights are favored, when termination of growing radicals occurs by combination.

In general, the vehicle consists of two types of acrylate esters: multifunctional acrylate-terminated oligomers and acrylate monomers. The monomers range from mono- to hexafunctional, most commonly mixtures of mono-, di-, and trifunctional acrylates. The monomers are also called reactive diluents. Multifunctional oligomer contributes to high rate of cross-linking, owing to its polyfunctionality and in large measure, controls the properties of the final coating due to the effect of the backbone structure on such properties as abrasion resistance, flexibility, and adhesion. Their viscosity is too high alone and monomers are required to reduce viscosity for application. Multifunctional acrylate monomers also give fast cross-linking owing to polyfunctionality, but have lower viscosities than an oligomer. Viscosity is lowered further by monofunctional acrylates, but the rate of cross-linking is reduced. The extent conversion of the double bonds is also affected by the choice of components; in general terms, extent conversion increases with an increase in monofunctional monomer, presumably because the small monomer molecules can diffuse through the film during the reaction.

Many multifunctional acrylate monomers have been used; examples are trimethylolpropane triacrylate, pentaerythritol triacrylate, 1,6-hexanediol diacrylate, and tripropyleneglycol diacrylate [12]. Care must be used in handling them because many are skin irritants and some are sensitizers. A range of monofunctional acrylates have been used. Those with lowest molecular weight tend to reduce viscosity most effectively, but may be too volatile.

Ethylhexyl acrylate has sufficiently low volatility. Ethoxyethoxyethyl acrylate, isobornyl acrylate, 2-carboxyethyl acrylate, and others are also used. Small amounts of acrylic acid as a comonomer promote adhesion.

2-Hydroxyethyl acrylate has low volatility, high reactivity, and imparts low viscosities, but the toxic hazard is too great in many applications. N-Vinylpyrrollidone (NVP) is an example of a nonacrylate monomer that copolymerizes with acrylates at speeds comparable to acrylate polymerization; NVP is particularly useful because the amide structure promotes adhesion to metal and reduces oxygen inhibition. But it introduces a possible toxic hazard. It has been found that monomers with carbamate, oxazolidine, or carbonate ester groups in addition to the acrylate functionality give faster curing and more complete conversion than simple acrylates [12].

Two classes of polymerization reactions are used in UV curing: free radical and cation initiated chain-growth polymerization. While there have been attempts to use photoreactions in which the radiation leads to generation of a reactive functional group, this approach is not useful for coatings. In such reactions, each photon absorbed can effect one cross-linking reaction. In chain reactions, absorption of a single photon can lead to formation of many cross-links.

A key requirement for UV curing is a UV source that produces high intensity UV radiation at low cost without generating excessive infrared radiation. The major sources in commercial use are medium pressure mercury vapor lamps. The radiation has continuous wavelength distribution with major peaks at 254, 313, 366, and 405 nm, among others. The rate of polymerization reactions is related to the concentration of initiating radicals or ions. It would, therefore, seem that the higher the initiator concentration, the faster the curing. As one increases from very low concentrations to somewhat higher concentrations, the rate of cure increases. However, there is an optimum concentration. The rate of cure in the lower part of the film decreases above this concentration. If the concentration is high enough, such a large fraction of the radiation is absorbed in the upper few micrometers of the film that little radiation reaches the lower layers. Since the half-life of free radicals is short, they must be generated within a few nanometers of the depth in the film where they are to initiate polymerization. Optimum photoinitiator concentration is dependent on film thickness: The greater the film thickness, the lower the optimum concentration [12].

Lower concentration is favorable from the standpoint of cost, since the photoinitiator is generally an expensive component. However, comparing the cure speeds of films of different thicknesses, each containing the optimum concentration of photoinitiator for its thickness, the time required to cure a thick film is longer than to cure a thin film. This follows since less radiation is absorbed in any volume element with increasing film thickness. In general, one should determine the concentration of photoinitiator just sufficient to give the required extent of cure at the surface; this concentration gives the maximum rate of cure for that film thickness of that system at the lowest possible cost.

UV curing is typically a process that transforms a multifunctional monomer into a crosslinked polymer by a chain reaction initiated by reactive species (free radicals or ions), which are generated by UV irradiation. Most monomers do not produce initiating species with sufficiently high yields when they are exposed to UV light, so that a photoinitiator must be added to the formulation. Once initiated, the chain reaction will develop very much like in a conventional thermal polymerisation, except for the much larger rates of initiation that can be reached by intense illumination.

The overall process is represented schematically in Figure 2.7.

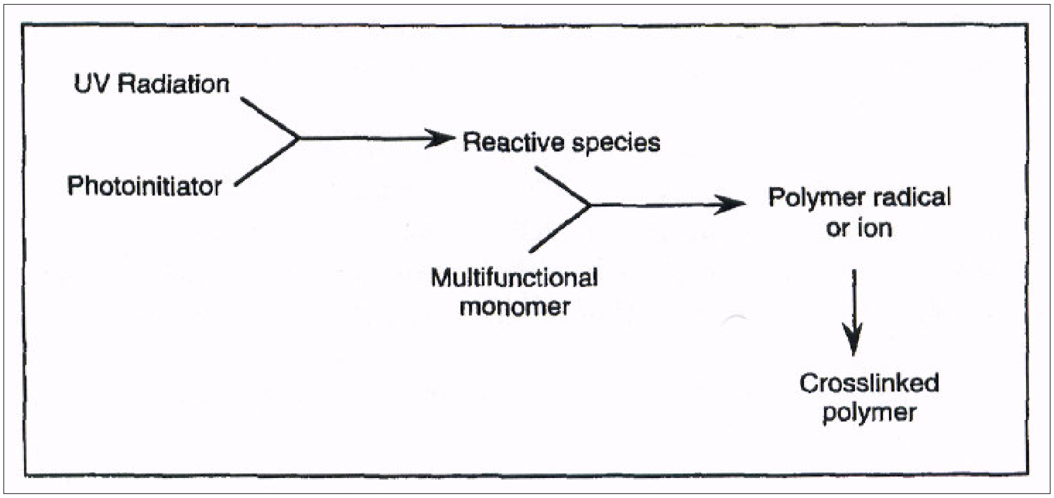


Figure 2.7: Photopolymerization by UV Radiation [9]

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

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

In this study, acrylate-based oligomers, which polymerise by a free radical mechanism, have been thoroughly investigated as they are by far the most widely used UV-curable systems, because of their great reactivity [9].

Cationic Initiated UV Curing

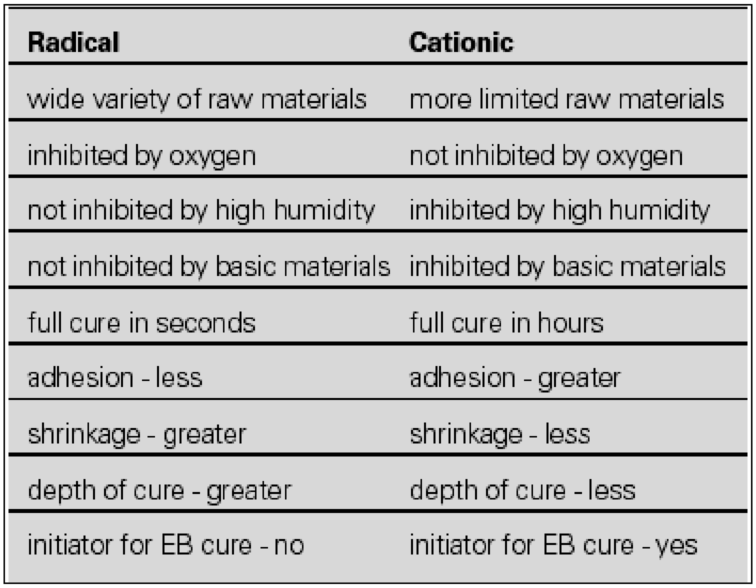
In cationic UV cure coatings strong acids are photogenerated to initiate chain growth polymerization. When the idea of using cationic polymerization for crosslinking coatings is mentioned it has been thought of infeasible. It is thought that cationic polymerization being carried out at very low temperatures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

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

Free Radical Initiated UV Curing

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

Free radicals are readily produced upon UV irradiation of aromatic carbonyl compounds, either by homolytic cleavage of C-C bonds, or by hydrogen abstraction from a hydrogen donor molecule [8]. Figure 2.8 shows the comparison of Radical and cationic UV cure systems.



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

Figure 2.8: Comparison of Radical and Cationic UV Cure Systems [19]

Photoinitiators:

Photoinitiators are chemicals that form energetic radical species when exposed to UV light. They are essential ingredients in UV-curable coatings in order to obtain polymerization. Depending on factors such as film thickness, UV-light source and particular coating performance requirements, the amount of photoinitiator in a UV-coating formulation can range from approximately 0.5 to 15%. Photoinitiator systems are available that meet the particular requirements for curing very thin(6μ) clear coatings, thin (25μ) pigmented coatings, and very thick (100μ) clear coatings [19].

Two classes of photoinitiators are used in UV free radical curing; those that undergo unimolecular bond cleavage and those that undergo bimolecular hydrogen abstraction from some other molecule [12]. Figure 2.9 shows those two type initiation processes.

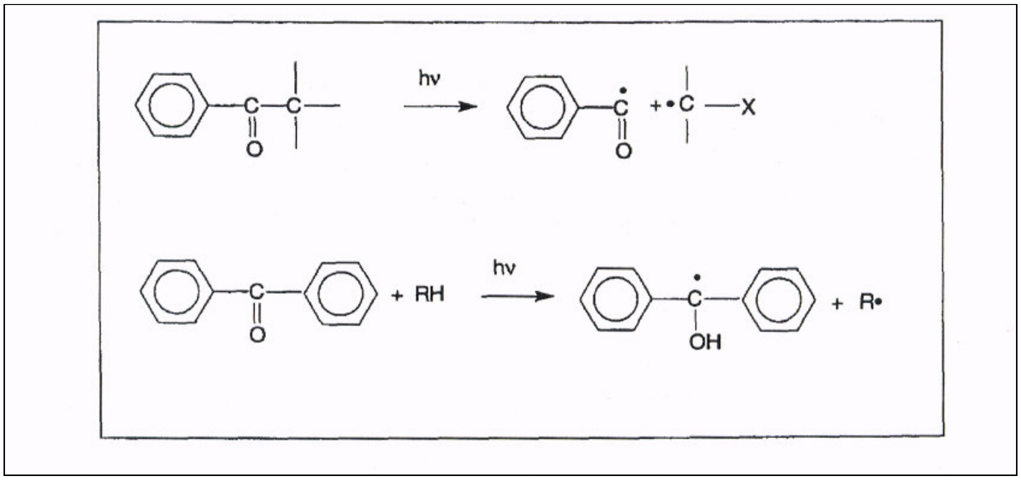


Figure 2.9: Two Types of Photoinitiation

The benzoyl radical was shown to be the major initiating species, while the other radical fragment may also contribute to the initiation. The ketyl radical generated upon photolysis of benzophenone is essentially inactive toward vinyl double bonds, so that initiation occurs here through the H-donor radical, usually an amino alkyl radical, since tertiary amines are typically employed as co-initiators.

In literature, a range of unimolecular photoinitiators has been studied [13]. The first ones used on a large scale commercially were ethers of benzoin. Benzoin ethers undergo cleavage to form benzoyl and benzyl ether radicals:

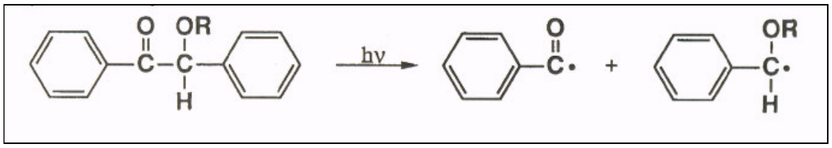


Figure 2.10: An example of Type I (bond cleavage) photoinitiation

Benxoyl ethers, hydroxyphenylketones and acylphosphineoxides are examples of photoinitiators which go bond cleavage for photopolymerization. Photoexcited benzophenone and related diarylketones, such as xanthone and thiox-anthones, do not cleave to give free radicals, but can abstract hydrogens from a hydrogen donor to yield free radicals that initiate polymerization. Thioxanthones, such as 2-isopropylthioxanthone, are used when their high absorption in the very near UV is desirable to permit absorption in the presence of pigments or dyes that absorb UV strongly in the shorter UV range. Widely used hydrogen donors are tertiary amines with hydrogens on carbon atoms.

An efficient photoinitiator must exhibit a large absorption in the emission range of the light source and generate initiating species with the highest possible quantum yields. A great number of photoinitiators have been developed for UV-curing applications. Their photolysis mechanisms and performances have been extensively studied [12].

There are three main classes of UV-curable systems that polymerise by free radical mechanism.

- Unsaturated Polyester/Styrene
- Thiol /Polyene
- Acrylate monomers/oligomers

In this study, acrylate functional monomers and oligomers are cured by UV radiation. Acrylates are known to be among the most reactive monomers polymerising by a free-radical mechanism. This feature, together with the remarkable chemical, optical and mechanical properties of the polymers obtained, account for the great commercial success of acrylate-based UV-curable oligomers. A diacrylate oligomer within a mixture of monomers irradiated in the presence of a photocleavable aromatic ketone, the basic process used in this study can be represented as shown in scheme in Figure 2.11.

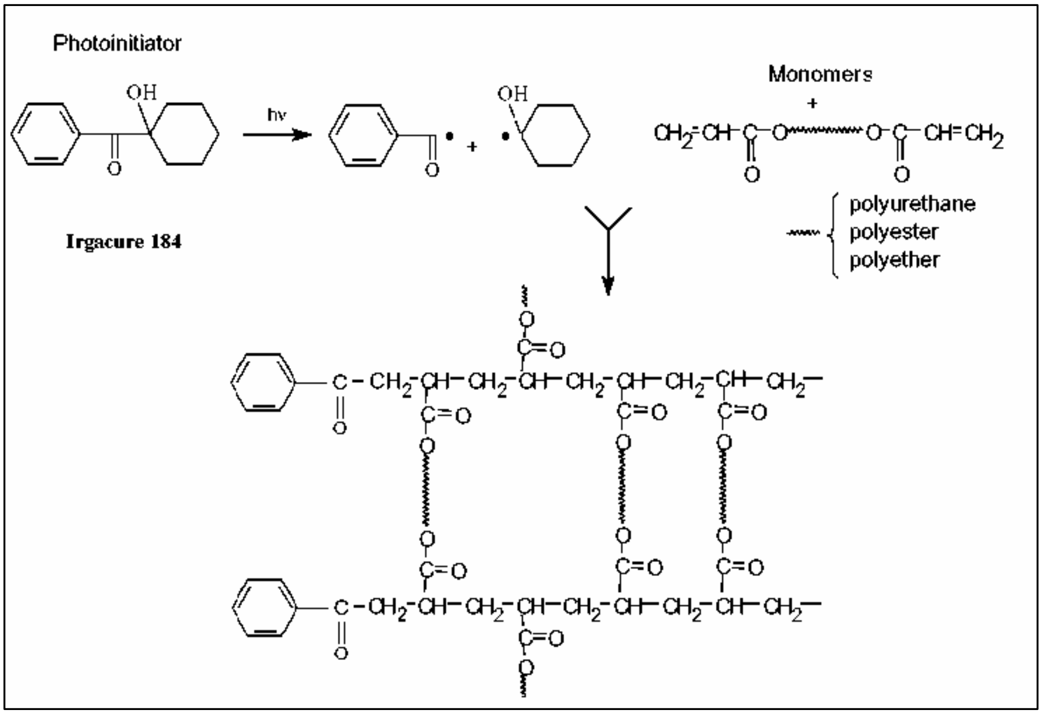


Figure 2.11: Free radical photopolymerization of urethane acrylate oligomers

As previously described, different types of structures can be used for the telechelic polymer or oligomer backbone, such as polyurethanes, polyesters, polyethers and polysiloxanes (Figure 2.11). The final properties of UV-cured acrylate polymers depend, primarly on the chemical structure of the functionalised oligomer. Low-modulus elastomers are generally obtained with aliphatic compounds, whereas hard and glassy materials are formed when aromatic stuctures are introduced into the polymer chain.

The great reactivity of acrylate monomers, together with the large choice of acrylate-functionalised oligomers, have afforded these radical-type systems a leading position in UV-curing applications. The high viscosity of the prepolymers often necessitates the addition of low molecular weight monomers, which will act as reactive diluents. Because of their high crosslink densities, such photocured polymers exhibit a great resistance to chemicals, heat and radiation, and show well-designed physical properties depending on the length and chemical structure of the crosslink segments.

Coatings based on urethane acrylate (UA) oligomers are widely used in industry. Purposeful formulation of coatings with desired properties and study of these properties are important tasks of applied polymer science [14].

2.5 Advantages, Disadvantages and Applications of Radiation Curing

The photoinitiated polymerisation of multifunctional monomers, or UV-radiation curing, has found a large number of applications in various industrial sectors.

For conventional thermal radical polymerization, chain initiation and propagation usually require a temperature higher than 40°C. However, since electromagnetic radiation provides highly efficient energy for photoinitiator excitation, the photoinitiation and the subsequent polymer chain propagation can proceed at lower temperatures (10~40°C) [8].

Very short cure times are possible at ambient temperature with package stable coatings. In the case of clear acrylate compositions, curing times required are fractions of a second. Since the curing can be done at ambient temperatures, the coatings are applicable to heat sensitive substrates such as paper, some plastics, and wood. Coatings can be formulated without solvent and, therefore, lead to minimal VOC emission.

The energy requirement is minimal. The major losses in energy encountered in thermal curing systems are not experienced. The cure is done at or near to ambient temperature, so no energy is required to heat the object being coated. (The IR radiation from the UV lamps does cause a modest temperature increase.) The heat loss from air flow through a baking oven required to keep the solvent concentration below the lower explosive limit is eliminated. The extent of this advantage is, of course, dependent on the cost of energy. The use of radiation curing in Europe and Japan has been greater than in the United States, at least in part because the cost of energy is higher in Europe and Japan than in the United States [12].

Capital cost for UV curing is low. This results primarily from the small size of the curing units as compared with ovens for baking. A UV cure coating only needs about 0.5 second exposure for curing. A line being run at a speed of 60 m min $^{-1}$ need be exposed to UV over a distance of only 0.5 meters. A UV curing unit with 4 lamps can do this in a total length of about 2 meters. In contrast, a thermal cure oven has to be a hundred or more meters long to provide time for curing at this speed.

In addition, there has to be space for flash off of at least some of the solvent from conventional coatings before the coated object enters the oven and space for it to cool down to handling temperature. The savings in building space can thus be large.

Half of the end users in a survey report "improved physical properties/product performance" as a major motivation for using radiation cure.

There are, however, limitations and disadvantages to radiation curing. It is most applicable to flat sheets or webs for which the distance to the UV source or the window of the EB unit can be approximately constant. Cylindrical, or nearly cylindrical objects, can be rotated in front of the radiation source and fibers can be pulled through a circle of sources, but irregularly shaped objects are not easy to expose uniformly.

In the case of UV curing, pigmentation can limit the thickness of films that can be cured. In the extreme case of carbon black pigmented films, the limit is about 2 µm. Electron beam cure coatings do not have this limitation because there is no gradient of initiation from top to bottom of the film. Owing to the effects of pigmentation on flow, the level of pigmentation is limited in both UV cure and EB cure coatings.

Furthermore, low gloss coatings cannot be applied. These limitations can be overcome by using solvent containing coatings, but this eliminates many of the advantages.

Shrinkage during curing can lead to adhesion problems on metal and some plastic substrates. When polymerization results from chain addition of free radicals to double bonds, there is a substantial decrease in volume, since the length of the carbon-carbon bonds formed is shorter than the intermolecular distance of monomer units. The degree of shrinkage is directly related to the number of double bonds reacted. In acrylic UVor EB cure coatings, the potential shrinkage is 5 to 10%. Since cure occurs in less than a second, there is not time for much of the volume shrinkage to take place before the free volume in the coating is so limited that movement becomes restricted. The stress from the restricted shrinkage applies a force to offset the adhesion forces holding the coating to a substrate so that less external force is required to remove the coating. Shrinkage can be minimized by using higher molecular weight oligomers or higher ratios of oligomer to low molecular weight reactive monomers, but these expedients increase viscosity and tend to increase cure time. Curing of epoxy systems by cationic photoinitiators leads to less shrinkage.

The decrease in volume resulting from the formation of polymers from monomers is partially offset by an increase in volume from the ring opening. Typical epoxy UV cure compositions shrink less than 3%. Adhesion of cationic cure coatings can be further enhanced by surface treatment of the substrate [12].

Porous substrates such as paper, CPS and wood give good adhesion, since the mechanical effect of penetrating into the surface of the substrate holds the coating on the substrate. However, there can be a curling problem with thin substrates as a result of the tension from shrinkage on one side of the substrate.

The photoinitiator in free radical initiated coatings is only partly consumed in curing, so substantial amounts are left in films. The photoinitiator can accelerate photodegradation of films exposed outdoors. Conventional UV stabilizers and antioxidants tend to reduce UV cure rates, which limits their usage. These constraints limit the use of UV cure coatings to interior applications. While there has been work done using precursors, including photoinitiators that convert to UV stabilizers on exposure, the results do not appear to be satisfactory.

Cationic coatings have the advantage that they do not generate free radicals when films are exposed outdoors. Electron beam cure coatings have the distinct advantage that there is no photoinitator in the system. However, even with EB curing, the coatings used must have excess unsaturation to cure on rapid schedules and residual unsaturation can adversely affect exterior durability. Also, there are trapped free radicals that can react with oxygen after the cure and generate peroxides.

Radiation cure coatings tend to be more expensive than conventional coatings so that commercial applications are primarily those where the advantages of UV cure permit unique advantages.

UV cure printing inks, particularly lithographic inks, are widely used. The viscosity of lithographic inks is relatively high, on the order of 5-10 Pa-s, so there is not a flow problem. The films are thin, so interference of pigment with curing can be offset by use of highly absorbing photoinitiators and/or high photoinitiator concentrations. Since the films are not continuous, adhesion or curling difficulties resulting from shrinkage are not a major problem.

The advantage of fast curing is large, it allows the webs to be wound up quickly without offsetting on the back of the substrate. In printing of tin plate and aluminum for cans, there is the advantage that the four colors can be printed in line by simply having a UV lamp after each printing station; operating costs are lower than with heat cure inks. Ink jet printing is another rapidly growing market for UV inks.

Clear coatings for paper, plastic film, and foil are probably the largest volume market for radiation cured coatings. The unpigmented coatings cure very fast at low temperatures.

An early commercial use of UV curing was in Europe for top coating wood furniture. A large part of European furniture is manufactured in flat sheets and assembled after coating. Furthermore, the finish on much European furniture is glossy. UV curing is ideal for such an application. The fast cure at low temperature is appropriate for wood. Early coatings were based on styrene-polyester resins, but acrylic coatings were later adopted because they cure more rapidly and emission of styrene is avoided. There has been relatively little use of UV cure top coats on wood furniture in the United States because a major fraction of U.S. furniture is assembled and then coated.

Furthermore, most U.S. furniture has a low gloss top coat that, as discussed previously, is difficult with solvent-free UV cure coatings. Wood kitchen cabinets and flooring are appropriate applications for UV cure coatings.

An important furniture application is filling of particle board. Particle board has a rough surface, and before use in furniture tops, it must be coated with filler and sanded smooth to give an even surface for the application of a base coat and printing. This was originally done with highly pigmented solvent-borne coatings applied at about 30% volume solids. However, the low solids require two or three coats to give sufficient film thickness to permit sanding to a smooth surface without cutting down into the substrate. With UV cure, the volume loss is only a few percent, so an adequate layer can be applied in one coat. This together with the fast cure means that UV cure fillers are less expensive to apply. The pigments used are clays and silica that absorb or scatter only minor amounts of UV. Aluminum trihydroxide absorbs still less UV and may be a particularly effective inert pigment.The high level of pigmentation leads to poor leveling, but it does not matter, since the surface is sanded [12].

Furthermore, the pigmentation results in less resin being at the surface so air inhibition is less of a problem. Originally, the fillers were styrene/polyester systems, but the higher speed of acrylics has led to their adoption despite their higher cost.

Another large scale application whose success results from the fast curing at low temperature possible with UV cure coatings is top coating of vinyl flooring. It is especially applicable to flooring with patterns made by expanded foams, since the foam pattern is heat sensitive. Acrylated urethane oligomer coatings have the high abrasion resistance needed in a floor covering; acrylated polyester coatings have superior stain resistance.

Abrasion resistant clear coatings for plastics have been developed. The poor abrasion resistance of clear plastics is a distinct disadvantage in applications, such as replacing glass in uses ranging from glazing to eyeglasses. Silicone-based coatings have been used for many years to improve the abrasion resistance. These coatings require long thermal cure schedules and have high VOC levels. Radiation cure coatings based on trialkoxysilyl-functional acrylate monomers and colloidal silica cure in seconds and have low VOC emission.

They have excellent adhesion to polycarbonates and other plastics and have abrasion resistance equal or superior to solvent-based coatings.

An application for cationic UV cure epoxy coatings is for coil coating on tin plate for the exterior side of can ends. The superior adhesion of epoxy coatings makes them preferable for this application, as compared to acrylate coatings. In some cases, a UV cure coating is applied on one side of the strip and UV cured. Then, a thermally cured epoxy coating is applied on the other side. When the strip is put through the oven to cure the thermally cured coating, the cross-linking of the UV cure coating is also advanced.

A large use of UV curing is for coating optical fibers for wave guides used in telecommunication cables. The process is carried out at high speeds in towers up to 25 meters tall. The glass fiber is pulled from a heat softened blank of glass and then coated through a die coater, that is, a reservoir with holes on each end through which the glass is pulled. The UV lamps are aligned parallel to the fiber as it comes out of the coater, with elliptical reflectors both behind the UV source and on the opposite side of the fiber from the source. The fiber is at the focal point of the pair of reflectors.

In this way, the coating is given very high dosages of UV, permitting cure speeds of the order of 20 m s" without an excessive bank of UV lamps.

Acrylated urethane oligomers have been used since abrasion resistance is a critical requirement. Two UV cure coatings are applied, a soft first coat and a harder outer coat.

UV curing is also the basis for important photoimaging processes used in the printing and electronic industries. In these applications, UV curable coatings on selected substrates are exposed through an image bearing transparency, such as a film negative. Cross-linking occurs selectively under the transparent regions. The unexposed regions are subsequently removed, commonly by washing out with aqueous or organic solvent. The resulting image transfer into the coated substrate is a critical step in making printing plates as well as printed circuit boards and integrated microcircuits (e.g., computer chips).

The ultraviolet light and electron beam curing technologies are growing industries. One hundred percent reactive inks, coatings and composites produce high quality finished products for the consumer market. Manufactured items may be tested, packaged and shipped in the same day. There are no pollutants given off into the atmosphere, nor is high energy required for the curing or drying of the inks/coatings. This growing technology allows the efficient manufacturing of coatings, inks, and adhesives, etc. with energy efficiency, no V.O.C.s, improved health and safety considerations and a cure-in-place technology [15].

Consequently, characteristic properties of the synthetic polymers can be modified to the desired applications simply by coating the appropriate constituents. Urethane acrylates are the highest performance oligomers offered in the radiation cure industry. Their wide range of performance properties has made them desirable products. Adhesives, electronics, coatings, inks, elastomers, and photopolymer performance can be enhanced with the use of these oligomers [5].

3. EXPERIMENTAL WORK

3.1 Materials

All materials are used as obtained without further purification.

3.1.1 Oligomers

Aliphatic Urethane Diacrylate Oligomer (Sartomer)

Diacrylate functionalized Aliphatic Urethane Acrylate (ALUA) oligomer which was prepared by polyaddition reaction of the appropriate amount of polyol (polyetherol or polyesterdiol), a hydroxy-functionalized acrylate, and aliphatic diisocyanate by standard procedures [5].

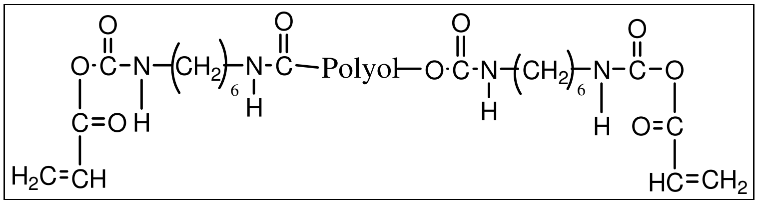


Figure 3.1: Aliphatic Urethane Diacrylate Oligomer

Aromatic Urethane Diacrylate Oligomer (Sartomer)

Diacrylate functionalized Aromatic Urethane Acrylate oligomer (ARUA) which was prepared by polyaddition reaction of the appropriate amount of polyol (polyetherol or polyesterdiol), a hydroxy-functionalized acrylate, and aromatic diisocyanate by standard procedures[5].

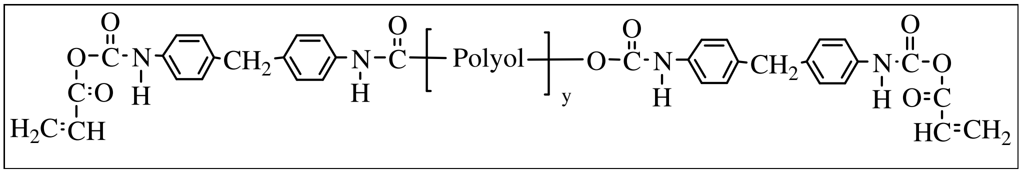
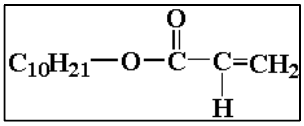


Figure 3.2: Aromatic Urethane Diacrylate Oligomer

3.1.2 Monomers

Isodecyl Acrylate (IDA) (Sartomer)

Isodecyl acrylate (IDA) is a monofunctional acrylic monomer which can be polymerised by free radicals. In particular it is used in U.V cured coatings, inks and adhesives.



$$C_{10}H_{21}-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{C}=CH_2$$

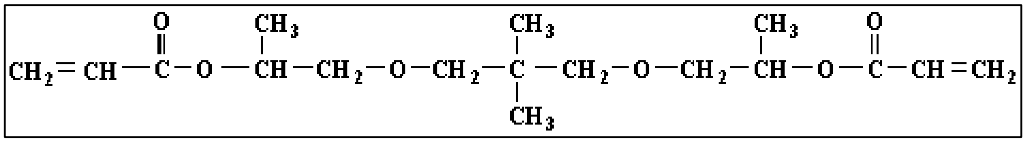
Figure 3.3: Isodecylacrylate

The following key properties are offered by isodecyl acrylate to formulations:

- ✓ Excellent solvency
- ✓ Low shrinkage > good adhesion
- ✓ Excellent water resistance
- ✓ Good flexibility

Propoxylated Neophentyl Glycol Diacrylate (NPGDA) (Sartomer)

Propoxylated Neophentyl Glycol Diacrylate (NPGDA) is a difunctional acrylic monomer. NPGDA is a very low viscosity oligoether acrylate which can be polymerised by free radicals. In particular it is used in U.V cured coatings, inks and adhesives.



$$CH_2=CH-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{CH_3}{|}}{CH}-CH_2-O-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-O-CH_2-\overset{\overset{CH_3}{|}}{CH}-O-\overset{\overset{O}{\|}}{C}-CH=CH_2$$

Figure 3.4: Propoxylated Neophentyl Glycol Diacrylate

The following key properties are offered by propoxylated NPGDA to formulations:

- ✓ Good solvency
- ✓ Good flexibility
- ✓ Good chemical resistance
- ✓ Excellent wetting properties

Propoxylated Glyceryl Triacrylate (GPTA) (Sartomer)

Propoxylated Glyceryl Triacrylate (GPTA) is a trifunctional acrylic monomer.

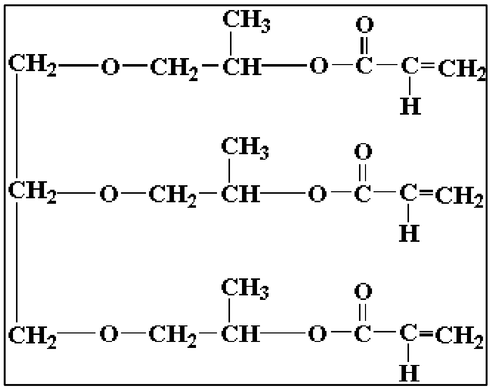


Figure 3.5: Propoxylated Neophentyl Glycol Diacrylate

GPTA monomer offers,

- ✓ Good flexibility
- ✓ Fast curing
- ✓ Low viscosity
- ✓ Good solvency
- ✓ Good reactivity
- ✓ Good chemical resistance
- ✓ Excellent hardness

Trimethylol Propane Triacrylate (TMPTA) (Sartomer)

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

Trimethylolpropane triacrylate (TMPTA), offers

- ✓ Low viscosity,
- ✓ Low volatility liquid monomer
- ✓ Offers fast cure response
- ✓ Low volatility during free-radical polymerization

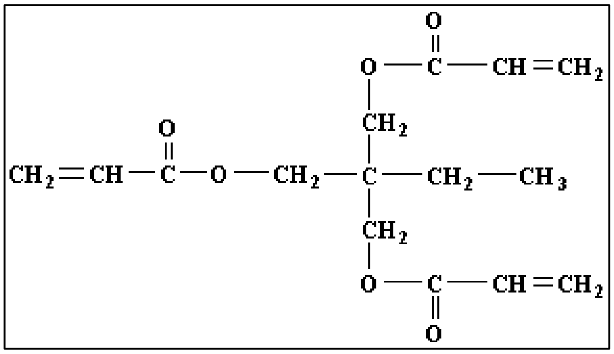
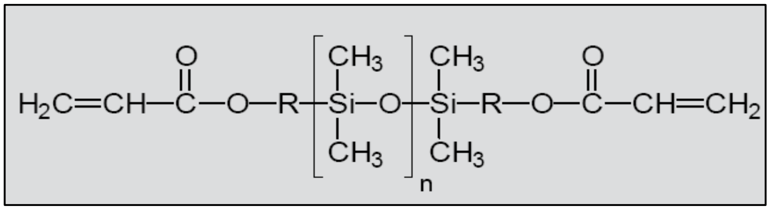


Figure 3.6: Trimethylolpropane triacrylate

3.1.3 Other Chemicals and Reagents

Acryloxy Organo Polysiloxane (Sartomer)

It is a linear acryloxyorgano-functional polysiloxane. Due to the acryloxy end groups, it can be used as a reactive component in suitable polymers. It provides;



$H_2C{=}CH{-}C({=}O){-}O{-}R{-}[Si(CH_3)_2{-}O]_n{-}Si(CH_3)_2{-}R{-}O{-}C({=}O){-}CH{=}CH_2$

Figure 3.7: Acryloxy Organo Polysiloxane

- ✓ Gloss
- ✓ Flexibility
- ✓ Hydrophobicity

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

1-Hydroxy-cyclohexyl-phenyl-ketone which is a alpha clevage type photoinitiator. It is white to off white solid photoinitiator that can be dissolved in liquid acrylic monomers.

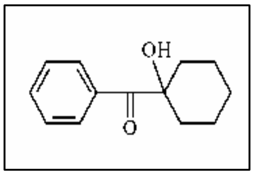


Figure 3.8: 1-Hydroxy-cyclohexyl-phenyl-ketone

3.2 Equipments

3.2.1 UV Curing Machine

A conveyor type UV curing machine (EMA) using UV lamps (254–313 nm,12 kW/m), donated with adjustable conveyor speeds was used for photoinitiated polymerization of formulations. EMA UV curing machine is shown at Figure 3.9.

Figure 3.9: EMA UV Cure Machine

3.2.2 Pendulum Hardness Tester

A König Pendulum Hardness (Gardner, BYK) tester was used to measure the film hardness of the UV-cured films. The method and equipment used in this study is described in Section 3.6.1.

3.2.3 Tensile Loading Machine

Tensile (uniaxially loading) tests for cured films were carried out and recorded with a horizontal tensile loading machine.

3.2.4 Spectrophotometer

Spectrophotometric analysis of UV cured treated and untreated coagulated polyurethane surfaces was performed with a Scinco(S-3100) instrument.

3.2.5 Bar Coater

The formulations were coated on aluminium plates and coagulated surfaces by a bar coater (Gardner,BYK) (25μ).

3.3 Preparation of Formulations

Two different formulations including urethane acrylate oligomers, reactive diluent monomers, additives and photoinitiator were developed.

3.3.1 Preparation of Aromatic Urethane Acrylate Formulation (ARUA)

Aromatic urethane acrylate oligomer formulation was prepared. ARUA composition is shown at Table 3.1.

Table 3.1: Aromatic Urethane Acrylate Formulation (ARUA)

Oligomer	Aromatic Urethane Diacrylate
Monofunctional Acrylic Monomer	Isodecyl Acrylate
Difunctional Acrylic Monomer	Propoxylated Neophentyl Glycol Diacrylate
Trifunctional Acrylate	Propoxylated Glyceryl Triacrylate
Polysiloxane	Acryloxy Functional Polysiloxane
Photoinitiator	1-Hydroxy-cyclohexyl-phenyl-ketone

3.3.2 Preparation of Aliphatic Urethane Acrylate formulation (ALUA)

Aliphatic urethane acrylate oligomer formulation was prepared; ALUA composition is given in Table 3.2

Table 3.2: Aliphatic Urethane Acrylate Formulation (ALUA)

Oligomer	Aliphatic Urethane Diacrylate
Monofunctional Acrylic Monomer	Isodecyl Acrylate
Trifunctional Acrylate	Propoxylated Glyceryl Triacrylate
Trifunctional Acrylate	Trimethylol Propane Triacrylate
Polysiloxane	Acryloxy Functional Polysiloxane
Photoinitiator	1-Hydroxy-cyclohexyl-phenyl-ketone

3.4 Application

The formulated solutions were cast onto Aluminium (Al) plates **(6X15 cm)** to obtain free films and coagulated polyurethane surfaces (CPS) **(6X15 cm)** using a bar coater. 4 Al Plate and 4 CPS substrates were coated for each of the formulations (ALUA and ARUA).

3.5 UV Radiation Curing of Coated Substrates

For photopolymerization via UV radiation, a conveyor type UV curing machine is used. Totally 16 samples are passed 8 times under the radiation source to ensure curing of the film. Samples are cured under UV light at different conveyor speeds of 0.1 m/min; 1.0 m/min; 2,0 m/min; 3,0 m/min.

3.6 Analysis

Following tests; Pendulum Hardness, Gel Content, Solvent Swelling Ratio, Water Uptake Ratio, Surface Reflectivity and Tensile Properties Tests are performed to monitor physical and mechanical properties of samples.

3.6.1 Pendulum Hardness Tests

König pendulum hardness method which is frequently encountered in practice is used for measuring the hardness of the samples. The device itself consists of a pendulum, to the support of which two agate balls are attached. The pendulum is placed on the coating with the two balls 5 mm in diameter and moved 6° away from the position of rest. After releasing the 200 g pendulum the oscillations are recorded by a counter. The measure of damping is the number of oscillations or the time in seconds which elapses until the amplitude of the pendulum has dropped from 6° to 3° [16]. Pendulum hardness (PH) of the UV-cured film was measured to determine the film hardness and the UV dose intensity at which the film is properly cured [21]. The test device is shown in Figure 3.10.

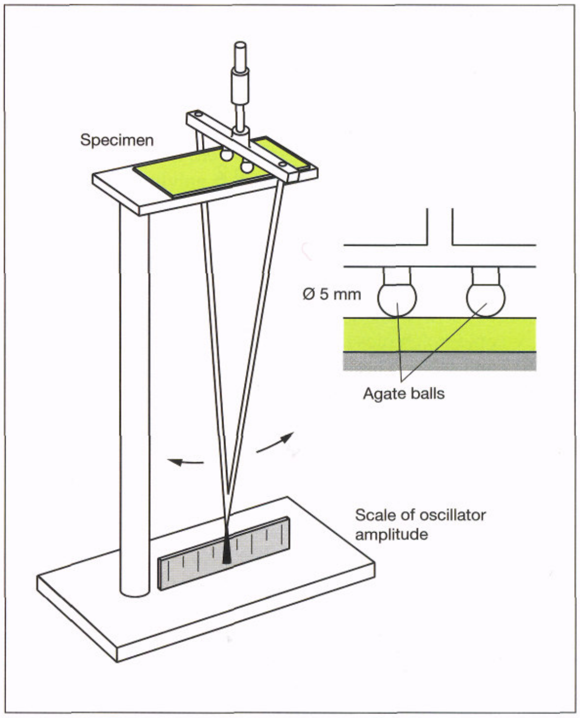


Figure 3.10: König pendulum hardness tester

The tests were applied while the cured film was still on the CPS and after cured film was peeled off Al plates. Test results are given in Table 4.1 and 4.2; related graphs are shown at Figure 4.1 and 4.2 for both ARUA and ALUA formulations, respectively.

3.6.2 Gel Content

The gel content is a representation of crosslinking density in the cured film as a whole, while film hardness represents the crosslinking density on the surface of the cured film [17]. A known weight of the free film; cured film peeled off the Al plate; was wrapped in a stainless-steel net that was put in a Soxhlet. Unreacted monomers were removed through extraction in hot benzene for 48 h in the Soxhlet. It would be difficult for benzene to remove large molecular compounds like polymers via the extraction process. The difference of weights of the cured film before and after the extraction determined the gel content [18]. The results are given in Table 4.3.

3.6.3 Swelling Ratio

As previously mentioned UV curing provides high conversions as a result high crosslink densities. At high crosslink densities solvent swelling can be used to determine extent of crosslinking. While crosslinked films do not dissolve in solvent, the solvent does dissolve in crosslinked film.

As crosslinks get closer together, croslinking density increases and the extent of swelling decreases [12]. The more a film is cured and crosslinked, the less ability it has to swell, because the swelling molecule, in that case, can hardly find enough functional group and space to swell the cured polymer through loose bonding or so [22]. Thus, as the crosslinking density (curing) increases, the swelling ratio is expected to decrease. A known weight of each extracted free film sample was soaked in acetone for 24 h at 25 °C. The weight difference of the swollen film with that of the dry extracted film yields the swelling ratio [17]. The results are given in Table 4.4.

3.6.4 Water Uptake

Water uptake is an important test for determining polymers water resistance. The extent of water uptake was determined by putting a drop of water on untreated and ARUA, ALUA treated CPS.

The wet time period of the water drop on samples was 5 minutes. The results were obtained from increased weight of the material due to water absorption during the period the water drop was allowed to stay on the surface. The results are depicted as water uptake (%) against treated and untreated samples in Table 4.5.

3.6.5 Surface Reflectivity

Traditional definition of gloss considers the light reflected at the surface of the coatings. The reflection of light varies depending on the smoothness of the surface so the illuminated environment is reproduced more or less efficiently.

As opposed to gloss, which is a sensory impression created by the reflection of light at the surface; color impression is the result of physiological effect due to interaction of the light within the coating with its constituents. If one assembles the various degrees of reflection R, depending on the wavelength λ, in order to create a curve, one obtains the reflection curve characteristic of a certain body color. When illuminated with identical light sources, two bodies with identical reflection curves have the same color physically speaking.

The reflection curve of a coating thus permits an objectively accurate description of the physical property of color without any subjective influences, as are bound to occur if the human eye perceives a color impression. As already indicated, the sensory impression complex resulting from light consists of the interactions of the light reflected in the surface (gloss) and the component penetrating and then scattered back diffusely (color). This reflectance R (λ) is measured with the aid of a spectrophotometer.

To monitor gloss factor International Commission of Illumination (CIE) recommends some different geometries of measuring probe for coatings [16]:

- Illumination at 45° / measurement at 0° (45/0)
- Illumination at 0° / measurement at 45° (0/45)

In this study, Illumination at 0° / measurement at 45° was studied with ALUA and ARUA treated CPS samples. The results are given in Table 4.6 and related graph is shown at Figure 4.3.

3.6.6 Tensile Properties

Tensile properties are important to the performance of radiation cured coatings as they directly impact the performance of the cured film. A load is applied to the film using a tensile testing instrument to determine properties such as modulus, elongation at break, and strength. Tensile is the greatest stress a coating can withstand prior to breaking [12].

Modulus is a measure of the stress required to elongate the film a given distance and elongation at break is the distance a film will stretch before breaking[7]. Tensile properties are very important in choosing a particular polymer for a specific application. Sometimes, a polymer of high tensile strength with moderate or low elongation, or vice versa, is desirable.

Thus, different formulations need to be developed while considering all these factors. As explained earlier, physical properties, including tensile properties, are closely related with the diluent monomers [18]. Several types of instruments are available for determining tensile properties. Horizontal tensile loading tester is used for tensile experiments. The sample is mounted between two jaws of the tester; care must be taken to ensure that the film is in line with the direction of pull.

The instrument can be run with a range of rates of jaw separation, but even the highest rates are slow compared to the rates of stress application found in many real situations. This problem can be partially overcome by running the tests at low temperatures. This method has the advantage that stress can be increased until the film fails, making possible determination of tensile strength, tensile modulus, and elongation-at-break [12].

The interrelationships of ideal elasticity can be described by Hooke's law between the tensile force F acting on a body in the case of elongation and the resultant deformation [12].

Tensile stress σ as an area-related force is directly proportional to elongation Δl in relation to initial length 1, the ε-value. The proportionality factor E in the appropriate stress-strain diagram is the modulus of elasticity by definition [16].

$$\sigma = F/A \qquad \textbf{(3.1)}$$

$$\sigma = E.\ \varepsilon \qquad \textbf{(3.2)}$$

$$\varepsilon = \Delta l\ /\ l \qquad \textbf{(3.3)}$$

Equation (3.1) , (3.2) and (3.3) are elastic modulus equations where,

F: Tensile force
A: Cross-sectional area
σ: Tensile stress
l: Initial length
Δl: Elongation
ε: Tensile strain
E: modulus of elasticity

The units of tests are for tensile stress is kg/mm^2, for tensile strain is unitless (mm/mm) and for elastic modulus is same as for tensile stress (kg/mm^2) [26].

Specimens for tensile testing are carefully cut in the shape of a dumbell as described EN ISO 527-3. Figure 3.3 shows the test specimen and its dimensions.

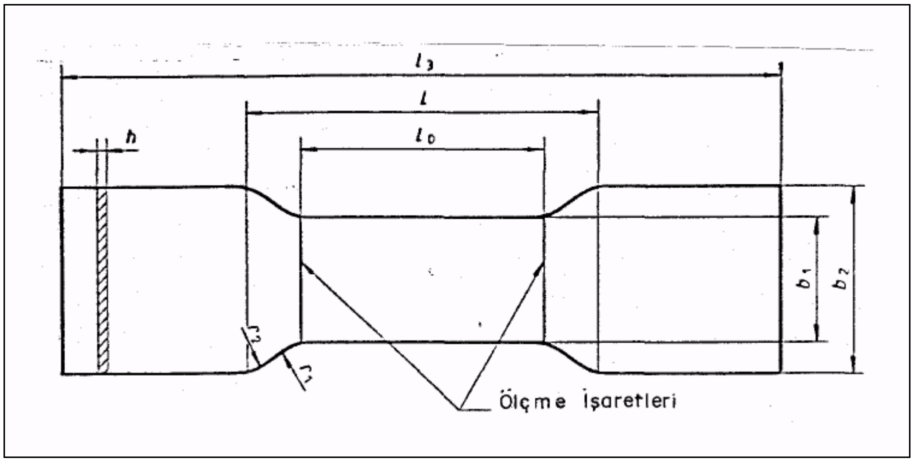


Figure 3.11: Tensile Loading Test Specimen (EN ISO 527-3)

Lengths of the specimen shown in Figure 3.11 are;

b_1: Narrow region width at parallel part: 25.4 mm + 0.1 mm

b_2: Width from edge to edge: 38mm + 0.5 mm

h: Thickness: < 1 mm

L_0: Length for measurement: 50 mm ± 0, 5 mm

L: Length between jaws: 73.4 mm + 5 mm

L_3: Total Length > 152 mm

r_1: Small Radius: 22 mm + 2 mm

r_2: Big Radius: 25.4 mm + 2 mm

Tensile test results are given in Table 4.7 and shown at Figure 4.4 and Figure 4.5 for ALUA and ARUA formulations, respectively.

,

4. RESULTS AND DISCUSSION

In this thesis, aromatic and aliphatic urethane acrylate oligomer formulations are prepared. Both formulations consist of high molecular weight viscous oligomer, mono and multi acrylic functional reactive diluents, polysiloxane and photoinitiator. Those two different formulations are coated on both Al plates and coagulated polyurethane (CPS) surfaces and cured by means of ultraviolet (UV) radiation. After curing with different conveyor speeds obtained samples are subjected to further physical and mechanical tests.

4.1 Pendulum Hardness Tests

König pendulum hardness tests are applied after ARUA and ALUA coated Al plate and CPS samples are UV cured with different conveyor speeds from 0.1 m/min to 3.0 m/min.

Table 4.1: ARUA Pendulum Hardness Results

Conveyor Speed (m/min)	Obtained Sample	Pendulum Hardness (könig)
3.0	Free film	22
2.0	Free film	23
1.0	Free film	24
0.1	Free film	26
3.0	Coated CPS	14
2.0	Coated CPS	16
1.0	Coated CPS	17
0.1	Coated CPS	18
	Untreated CPS	8

Tests were applied while the cured film was still on coated CPS and after cured film was peeled off Al plates.

Table 4.2 ALUA Pendulum Hardness Results

Conveyor Speed (m/min)	Obtained Sample	Pendulum Hardness (könig)
3.0	Free film	13
2.0	Free film	14
1.0	Free film	16
0.1	Free film	19
3.0	Coated CPS	9
2.0	Coated CPS	11
1.0	Coated CPS	12
0.1	Coated CPS	14
	Untreated CPS	8

The results are given at Table 4.1 and Table 4.2 and related graphs are shown at Figure 4.1 and Figure 4.2.

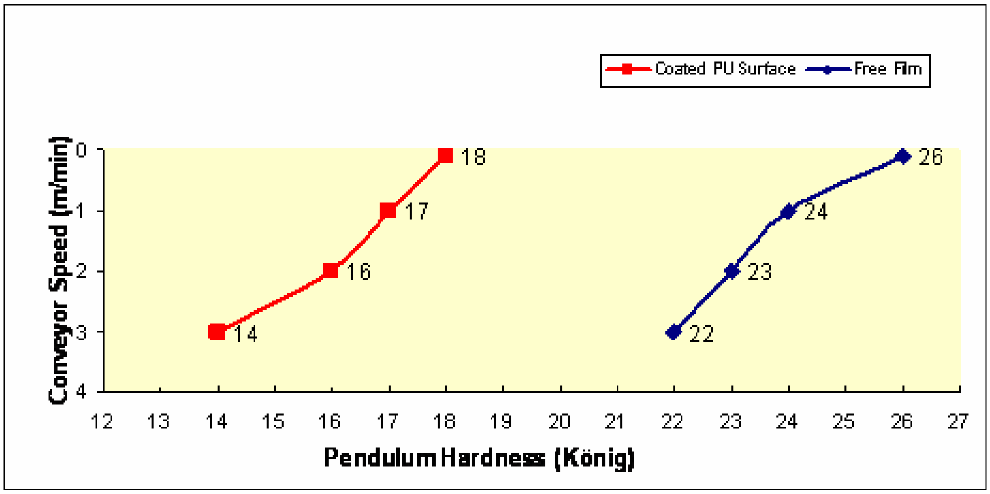


Figure 4.1 ARUA Pendulum Hardness Graph

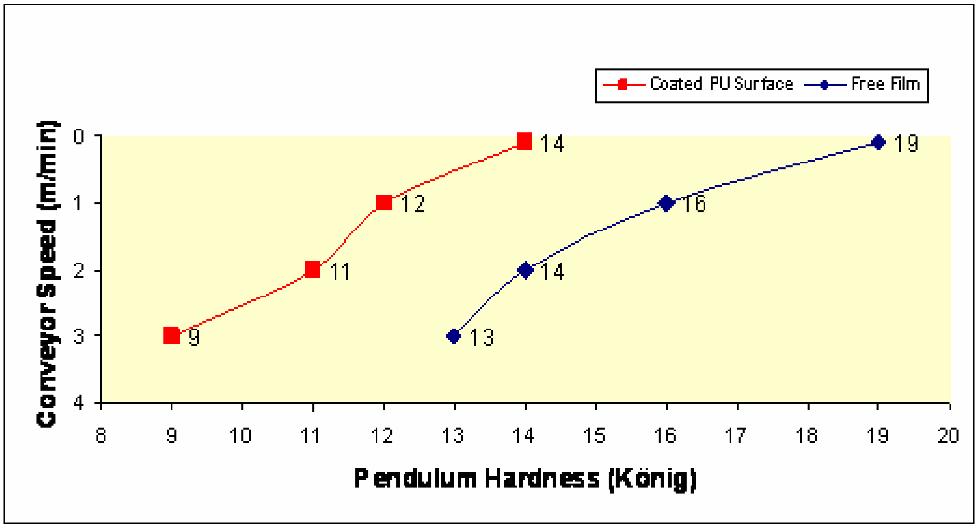


Figure 4.2 ALUA Pendulum Hardness Graph

As it is seen at Figure 4.1 and 4.2 for both ARUA and ALUA applications; pendulum hardnesses of samples have increased with decreasing conveyor speed which means as curing increases pendulum hardnesses of surfaces have inreased with both of the treatments.

4.2 Gel Content

The gel content is a representation of crosslinking density in the cured film as a whole, determined by soxhlet extraction as mentioned in section 3.6.2. The gel contents of the UV-cured free films prepared from ARUA and ALUA formulations are shown at Table 4.3.

Table 4.3 Gel Contents for ARUA and ALUA

Conveyor Speed (m/min)	3.0	2.0	1.0	0.1
Gel content of ARUA	95.7 %	95.8 %	95.9 %	96.0 %
Gel content of ALUA	98.6 %	98.8 %	98.9 %	99.0 %

Gel content results given in Table 4.3 confirms that in very short time polymerization rates are very high in UV curing in comparison to conventional polymerization. In addition to that gel content, crosslinking density, has increased slightly with decreasing conveyor speeds(longer cure time). Gel content results of ARUA formulations were lower than of ALUA. This can be due to free volume effect of chromophoric groups. In ARUA, aromatic groups prevent dense(frequent) crosslinking; while in ALUA crosslinking is denser.

4.3 Swelling Ratio

Solvent swelling can be used to determine extent of crosslinking. As crosslinking increases, croslinking density increases as a result the extent of swelling decreases. Swelling ratios of free films were determined by acetone solvent as described in Section 3.6.3. The resulting swelling ratios of free films given in Table 4.4 prove that with decreasing conveyor speed, solvent swelling (swell ratios) decreases. This can be due to crosslinking density increase with increasing curing time.

Table 4.4 Swelling ratios of ARUA and ALUA

Conveyor Speed (m/min)	3.0	2.0	1.0	0.1
Swell Ratio of ARUA Samples	50.8 %	46.0 %	43.5 %	34.4 %
Swell Ratio of ALUA Samples	30.2 %	27.3 %	23 %	21 %

Swell Ratios of ARUA Samples are higher in comparison to ALUA samples. This result is related to gel contents; crosslinking densities. The reason for this is probably ARUA; as it has aromatic groups (its crosslinking density lower); has much more free volume; as a result its solvent penetration is easier than ALUA; which has higher crosslinking densities.

4.4 Water Uptake

Water uptake test are performed to monitor water resistance of samples. Water absorption of untreated and treated CPS samples were determined as mentioned in Section 3.6.4. The results obtained are given in Table 4.5.

Table 4.5 Water Uptake (%) Ratios

SAMPLE	Water Uptake (%) in 5 min.
CPS (untreated)	10 %
ARUA treated (3.0)	0.03 %
ARUA treated (2.0)	0.05 %
ARUA treated (1.0)	0.07 %
ARUA treated (0.1)	0.04 %
ALUA treated (3.0)	0.03 %
ALUA treated (2.0)	0.02 %
ALUA treated (1.0)	0.04 %
ALUA treated (0.1)	0.02 %

Table 4.5 depicts ALUA and ARUA treated CPS samples at least 100 times more water resistant than untreated CPS sample.

4.5 Surface Reflectivity

Reflectance R(λ) values is measured with the aid of a spectrophotometer. The illumination was monochromatic white light. Reflectance values and wavelengths of ALUA and ARUA treated and untreated CPS samples are obtained from the spectrophotometer data. The results obtained are given in Table 4.6 and the graph indicating reflectance(%) values vs. wavelength is shown at Figure 4.3.

Table 4.6 Spectrophometer Data

Sample Name	R%(440 nm)	%R (465 nm)	%R (546 nm)	%R (590 nm)	%R (635 nm)
Untreated CPS	58.1	70.3	88.1	91.5	92.9
ALUA(3.0)	41.9	54.7	73.2	76.5	77.9
ALUA(2.0)	39.1	51.0	67.7	70.4	71.6
ALUA(1.0)	34.9	44.5	57.8	60.0	60.9
ALUA(0.1)	21.5	32.7	52.3	54.2	55.9
ARUA(3.0)	17.7	29.1	45.7	49.7	50.0
ARUA(2.0)	28.1	37.4	50.5	52.8	53.9
ARUA(1.0)	29.4	39.0	52.0	54.2	55.3
ARUA(0.1)	30.5	40.8	54.9	57.1	58.1

Table 4.6 and Figure 4.3 shows the reflactance results of ARUA and ALUA treated and untreated CPS samples. Here, the results are surface reflectivity values at the illumination of 440nm, 465nm,546nm,590nm,635nm wavelengths which means color violet, blue, green, yellow and red respectively.

As shown in Figure 4.3 reflectance (R %) values at same wavelengths have decreased with decreasing conveyor speeds for ALUA treated CPS samples; while values tend to increase with decreasing conveyor speeds for ARUA treated CPS samples. ARUA samples composed of aromatic groups, tend to degrade with increasing UV exposure, while ALUA don’t. This may be due to degradation of ARUA with increasing cure time, as sample was exposed to UV light longer time.

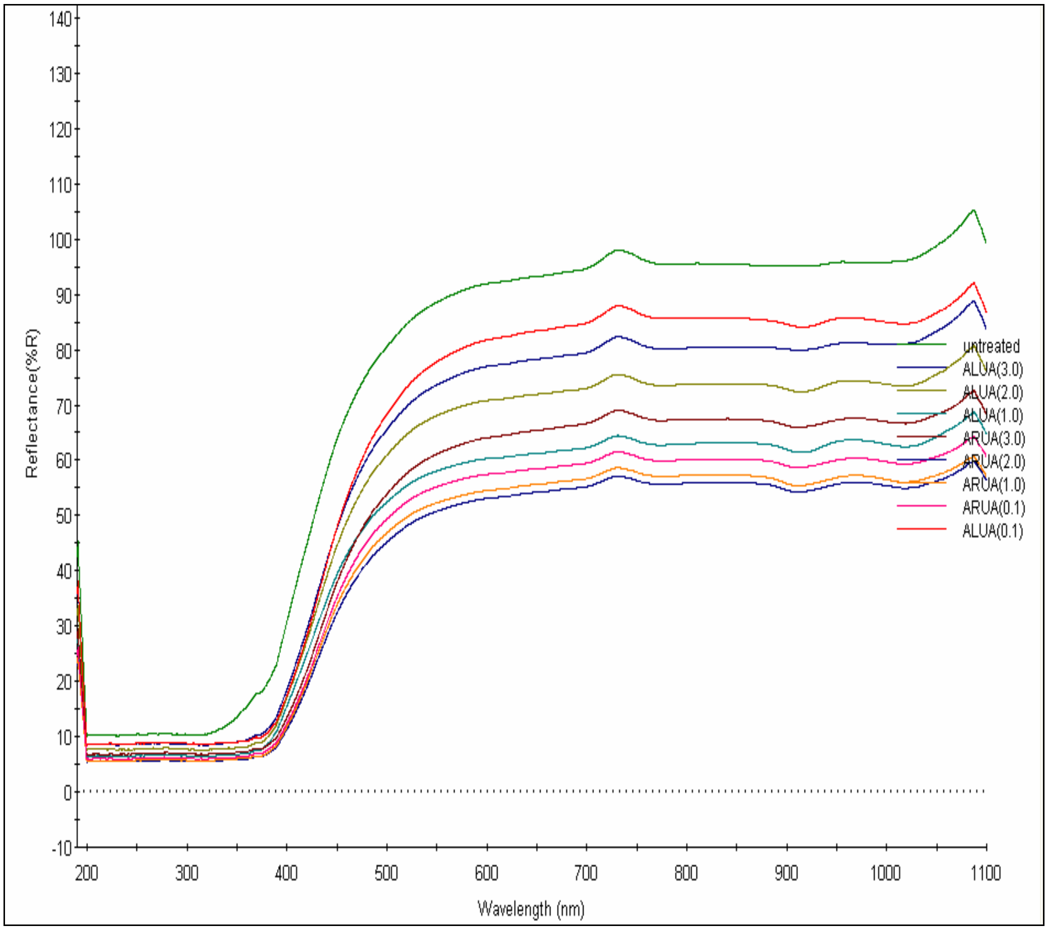


Figure 4.3 Reflectances of ALUA and ARUA Samples

4.6 Tensile Properties

Tensile properties are very important in selecting diverse applications of polymer and polymer-coated substrates [17]. Tensile properties may be utilized to provide data for research and development and engineering design as well as quality control and specification. Tensile properties may vary with specimen thickness, method of preparation, speed of testing, type of grips used and manner od measuring extension [29].

Table 4.7 Tensile Properties of untreated and treated Samples

Sample (CPS)	Tensile Strength (N/mm^2)	Max. Strain (%)	Elastic Modulus (N/mm^2)
ALUA(3.0)	11.7	23.3	40
ALUA(2.0)	13.1	16.6	79
ALUA(1.0)	11.4	13.3	90
ALUA(0.1)	11.0	13.3	88
ARUA(3.0)	9.4	16.6	55
ARUA(2.0)	12.6	20	71
ARUA(1.0)	7	23.3	82
ARUA(0.1)	9.7	13.3	70
Untreated Sample	7.9	33.3	23

Tensile test and results were determined as described in Section 3.6.6. The results are given in Table 4.7 and related graphs are shown in Figure 4.4 and Figure 4.5.

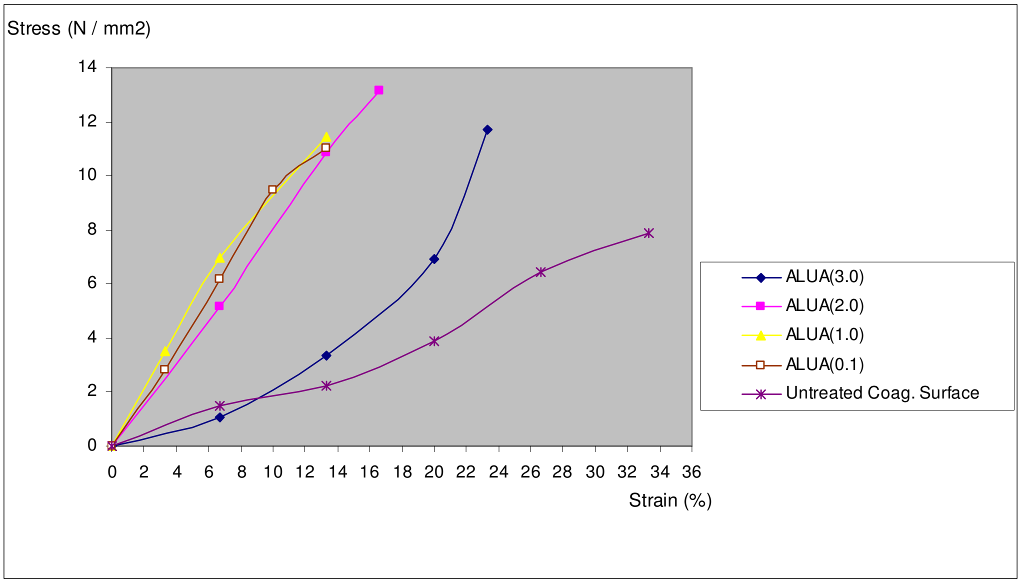


Figure 4.4 ALUA Treated CPS Samples Stress Strain Graph

Tensile test results in Figure 4.4 and Figure 4.5 show the tensile strength of all treated samples. Treated CPS samples tensile strengths increased in comparison to untreated CPS sample; meanwhile maximum strain(%) decreased. Both with ALUA and ARUA coating, the mechanical properties of CPS material is enhanced by treatment. On the other hand, it seems, with ALUA coating had attained better results in order to use this treated CPS material as a synthetic leather in shoe and luggage industry.

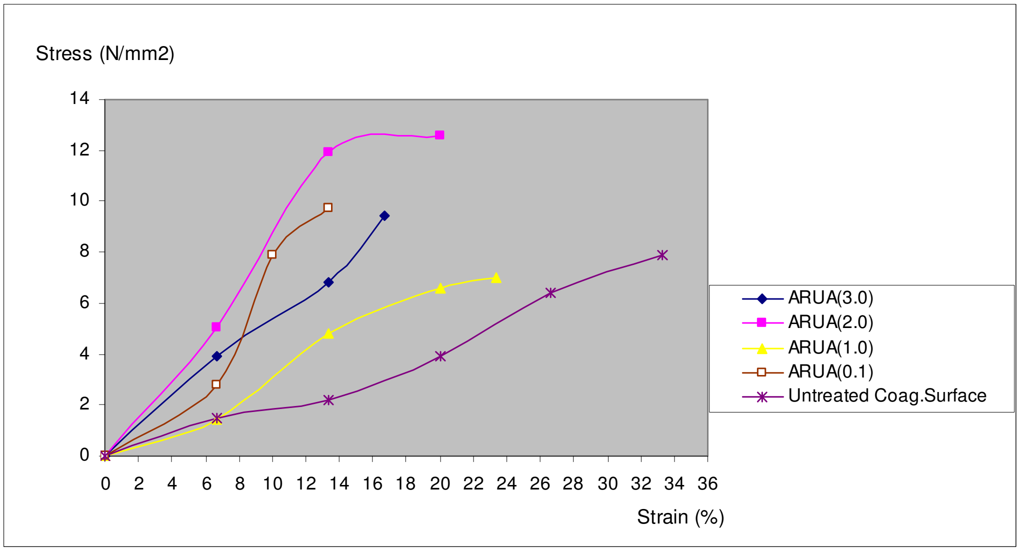


Figure 4.5 ARUA Treated CPS Samples Stress Strain Graph

5. CONCLUSIONS

Aromatic and Aliphatic Urethane Acrylate Oligomer based two formulations are prepared. Those formulations were applied on coagulated polyurethane surfaces and aluminium plates. Samples are cured with UV Radiation with different conveyor speeds.

As a second step, obtained ALUA and ARUA free films (films peeled off aluminium plates) and treated coagulated polyurethane surfaces were tested for their physical and mechanical properties.

Crosslinking densities of cured films have increased with increasing exposure time to UV light. As a result of this, pendulum hardnesses, gel contents, water resistance of treated samples have increased while their swelling ratios are satisfactorily decreased. Crosslinking densities, and gel contents of ALUA were higher than ARUA while pendulum hardnesses (at surface) and swell ratios are higher with ARUA coatings. This may be due to free volume effect of aromatic groups in ARUA coating.

Physical behaviours of treated CPS samples are determined by spectrophotometry. ARUA coated materials tend to degrade with longer UV exposure time. Tensile tests are applied to CPS samples. Elongation of treated samples have decreased in comparision to untreated CPS sample; while tensile stress at break and young’s modulus values have increased.

All the treated CPS samples have attained the enhanced strength**.** The best properties obtained, seems to be with the ALUA CPS sample UV cured at 8 pass at 2.0 m/min conveyor speed.

Consequently; by coating CPS with ALUA and ARUA formulations via UV Radiation, the material have been acquired desired mechanical properties.

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RESUME

Esra KIRAYLAR, was born in Edirne in 1981. She graduated from Edirne Science High School in 1999. The same year, after she admitted to Yıldız Technical University Chemical Engineering Department, she has been an AFS Exchange Student(1999-2000) in Stavanger, Norway. After one years study and cultural exchange in Norway, she returned to her my homeland Turkey to study chemical engineering. During her studies she has composed her chemical engineering passion with travelling abroad and she had her internship as an IAESTE Trainee in a resin plant in Valencia, Spain. In the plant where her curiosity about polymers has begun.

In 2004, she graduated as a Chemical Engineer. Two weeks after graduation, she was accepted as a M.Sc. student to the Polymer Science and Technology Programme of Istanbul Technical University in which she is about to graduate.

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She loves pets, internet, and movies. She is keen on travelling abroad, reading books, learning new languages, living in different societies, cultures. In addition she is into art; she writes her own poems and songs as a hobby.

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