Aluminum Pigmented Chromate- Free Metal Effect Coatings on Steel Substrates

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ABSTRACT

Metals such as iron and aluminum are used in industrial structures because of their mechanical properties including high strength and stiffness. These materials are very sensitive to corrosion due to aggressive environments, which cause energy and material loss. Making use of a protective film or coating is the most common route to protect metals from corrosion. A common coating used on metals is chromate coating due to its good protective and aesthetic qualities however; Cr (+6) is known and designated by EPA as one of the 17 high toxicity chemicals. It is known to be a human carcinogen and emits a toxic mist at elevated temperatures. Because of environmental and health perspective, alternative more environmentally friendly coating methods are under investigation. Sol-gel process is amongst the common methods for deposition of the coatings on metal surfaces. Such process has several advantages over those other methods such as low temperature and waste-free processing. In the current research sol-gel processing was used to deposit coatings on the steel substrates.

It is known that UV curing is becoming an accepted technique and offers a variety of advantages because of its uniqueness, therefore in the current study a series of UV-curable coating with aluminum pigments was prepared in order to replace the chromium coatings, since from the health and environmental perspective, chromium can be toxic and can have significant negative effect on human beings.

For this purpose, among the oligomers that can be applicable for UV-curing, aliphatic tri-functional oligomeric urethane methacrylate (ATOUA) was formulated from trimethylolpropane (TMP), isophrone diisocyanate (IPDI) and hydroxyethyl methacrylate (HEMA). Also, dibutyltin dilaurate (DBTDL) was incorporated to let the reaction to take place. As incorporated to let the reaction, the metallic shine effect was also achieved by formulating leafing and non-leafing aluminum pigments with ATOUA as binder with a proper dispersing agent, during the coating process.

In this study, ATOUA was reacted with 1,6 hexanediol diacrylate (HDDA) and trimethlol propane triacrylate, serving the function of a reactive diluent, benzophenone as phtoinitiator, N-methyl diethanolamine as co-initiator, aluminum pigments, wetting agent 1OEO), to produce UV-curable aluminum pigmented coatings. SEM analysis was also performed to monitor the surface morphology of the produced coatings. SEM images of the ATOUA polymers illustrated a crack free coating involving aluminum particles. Moreover, FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic measurements were employed to pinpoint the structural properties of the synthesized oligomers. Additional characteristics of the surface coatings such as chemical and mechanical properties have been investigated through the following tests: König hardness, cross cut adhesion, impact resistance, gloss, mandrel bend, cupping and salt spray. Furthermore, the DSC and TGA analysis were investigated. results clearly indicated that the cured films possess proper pendulum hardness and strong adhesion to the substrate. Moreover, coatings passed 1000 h of salt spray resistance test. Coatings have suitable abrasion resistance, gloss and flexibility and consequently can be applied in industrial sectors.

Keywords: UV Curable Coating, Aluminum Pigment, Organic- Inorganic Hybrid Film, Metal Effect Coating, Gloss, and Steel

ÖZ

Çeşitli çelik ve alüminyum alaşımları endüstriyel uygulamalarda yüksek mekanik dayanım ve esneme direnci gibi mekanik özellikleri nedeniyle kullanılmaktadır. Ancak bu metaller birçok ortamda korozyona uğramakta ve bu da enerji ve malzeme kayıplarına neden olmaktadır. Metalleri korozyondan korumak ve görünümlerini çekici kılmak amacıyla çeşitli kaplama yöntemleri geliştirilmiştir. Bu yöntemler arasında elektrolitik krom kaplama ve çeşitli boyama yöntemleri yaygındır. Ayrıca sol-jel yöntemi de düşük uygulama sıcaklığı ve çevre dostu bir işlem olması nedeniyle giderek önem kazanmakta olan bir kaplama yöntemidir. UV tepkimeli polimerleştirme de giderek yaygınlaşan bir yöntem olup yüksek etkinlik ve enerji verimliliği gibi çeşitli üstünlükler sunmaktadır. Krom kaplama teknolojisi ise sağladığı mükemmel parlak görünüme rağmen krom iyonlarının toksik etkisi nedeniyle endüstrinin vazgeçmekte olduğu bir teknoloji durumuna gelmiştir.

Bu çalışmada krom kaplamalar yerine geçebilecek alüminyum pigmentli metal etkili kaplamaların çelik yüzeyler üzerine uygulanması araştırılmıştır. Bu amaçla sol-jel ve UV tepkimeli polimerleştirme yöntemleri kullanılmış ve uygun kaplama malzemeleri geliştirilmiştir. Bu hedef doğrultusunda UV tepkimeli polimerleştirme yöntemine uygun olabilecek çeşitli oligomerler arasından alifatik üç işlevli oligomerik üretan metakrilat (ATOUA) geliştirilmiştir. ATOUA eldesinde trimetilpropan (TMP), izoforon diizosiyanat (IPDI) ve hidroksietil metakrilat (HEMA) kullanılmıştır. Ayrıca hızlandırıcı olarak dibütiltin dilaurat (DBTL) kullanılmıştır. Ayrıca yapraksı veya yapraksı olmayan alüminyum pigmentlerin kullanıldığı ATOUA tabanlı uygun kaplama bileşimleri geliştirilmiş ve uygun seyrelticiler belirlenmiştir. Sol-jel yöntemi ile elde edilen silika-Al pigment filmlerinde çatlama ve pigment boyutunun film kalınlığı ile uyuşmaması gibi sorunlarla karşılaşılmıştır.

UV tepkimeli Al pigmentli kaplamalar elde etmek için ATOUA, 1,6 hegzandiol diakrilat (HDDA), tepkimeli seyreltici trimetilolpropan triakrilat, fotobaşlatıcı olarak benzofenon, ek fotobaşlatıcı olarak N-metil dietanolamin, alüminyum pigmentler, ıslatıcı ve dağıtıcı olarak OA 1OEO ile tepkimeye sokulmuştur. Elde edilen kaplamaların taramalı electron mikroskop (SEM) görüntüleri Al içeren ya da içermeyen kaplamaların çatlak içermediğini göstermiştir. FTIR, ^{1}H-NMR ve ^{13}C-NMR spektroskopik analizleri sentezlenmiş olan oligomerlerin kimyasal yapısı hakkında bilgiler vermiştir. Ayrıca yüzey kaplamalarının kimyasal, fiziksel ve mekanik özellikleri çeşitli yöntemlerle incelenmiştir. Bu yöntemler König sertlik, çapraz kesikli yapışma, darbe dayanımı, parlaklık, mandrel bükme, batma/çökertme, ve tuz püskürtme, DSC ve TGA deneylerini içermektedir. Elde edilen sonuçlar, kaplamaların uygun darbe dayanımı, sertlik ve metale yapışma özelliklerine sahip olduğunu göstermiştir. Ayrıca kaplamalar 1000 saatlik tuz püskürtme deneyini başarı ile geçmiştir. Kaplamalar uygun aşınma dayanımı, parlaklık ve esnekliğe sahiptir ve endüstriyel uygulamalarda kullanılabilirler.

Anahtar Kelimeler: UV Tepkimeli Kaplama, Alüminyum Pigment, Organik-Inorganik Hibrit Film, Metal Etkili Kaplama

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Praise the Lord.

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INTRODUCTION

1.1Chromate Coatings

Considering the coating industry, one of the main concerns in the usage of chromium is its hazardous nature. Investigations indicated that chromium; particularly hexavalent chromium is detrimental to the health, therefore it needs to be replaced by benign organics, which are proven to be more environmentally friendly. Skin cancer and Dermatities are born through the chromated aluminum parts. Sever damages to mucous membranes and skin wounds called “chrome sore” occur due to ever-present chrome mist in chromium plating environments. Such hazardous health issues have limited the zeal to use the chromium in coating industries, leading to the loss of its popularity among all. Consequently, a broad range of research has been accomplished to develop more environmental friendly coatings since it is essential to remove chromium from industry in relation to its hazardous characteristics.

1.2Overview of the UV-Radiation Curing in the Coating Industry

Multifunctional oligomers polymerized via Ultra Violet light, which can be identified as UV-radiation curing, which is turning into of the most significant and attractive technologies, because of its industrial applications (1). On the whole, UV-curing offers a dozen of advantages over rivalry and conventional coatings. It is accepted as a fact that it can be beneficial through a number of reasons such as environmental compliance, tailor-made characteristics of the photo cured polymers, solvent-free formulations, lower energy consumption, and also providing a comprehensive and fast cure in order to satisfy the industrial requirements. Furthermore, conventional curing techniques can initiate major solvent evaporation resulting in environmental pollution. The most significant aspect of the UV-radiation is the coating industries. This technique has been used in a successful manner to maintain and protect the surface of various materials including glass, plastics, metals, and wood. UV-curable coatings can be employed to provide a variety of physical and mechanical properties for polymeric surfaces, including scratch resistance, anti-fogging, and chemical resistance.

UV-curable resins fall into two main classifications, based on the polymerization mechanism, i.e. the chain reaction can proceed by cationic or radical type. Generally, the applied resins consist of short polymeric chains, tipped with acrylic double bonds and are made of reactive urethane oligomers, phtoinitiators and reactive diluents. Also, choosing acrylates and telechelic polymers will enable us to adjust the desired properties of the cured polymer for special applications, more precisely.

1.3Chemistry and Application of Polyurethanes

Polyurethane (PU) is formed by reaction of an isocyanate with the hydroxyl-terminated polyester or polyether. It is important to mention that most polyurethane’s are useful because of their physical properties and their extent of applications is remarkable. One of the advantages of polyurethane is versatility and depending on the usage, the density and stiffness of the polyurethane can be adjusted to procure the intended properties. That the constituents of polyurethanes are compatible makes it a good candidate for a vast instances and applications. They have drawn much attention due to their tailor-made properties and can be applied as coatings, adhesives, sealants, elastomers, foam, and fibers.

Urethane-acrylate (UA) oligomers are the essential segment of the UV-curable coatings, thus PU’s are generally tipped with acrylic double bonds at the end of each chain. Generally, vinyl-containing molecules are employed to reduce the viscosity of the precursor. The precursor is then exposed to UV radiation, accompanied with the phtoinitiator.

1.4 Contributions of the Present Study to Science and Industry

- The main purpose of this research is to produce coatings that have adequate flexibility, gloss and abrasion resistance to develop a feasible, suitable and improved candidate for industrial coatings.
- A novel method is proposed to formulate aliphatic tri-functional oligomeric urethane methacrylate (ATOUA) with leafing and non-leafing aluminum pigment and produce UV curable coatings. The produced coatings demonstrate good mechanical properties including pendulum hardness and excellent adhesion between the coating and the substrate.
- The present study developed an industrially acceptable, non-hazardous and environmental friendly process for producing UV curable coatings.
- The proposed coating process has the following advantages in comparison with other coating processes: low capital investment, low emission, low energy consumption, low space consumption, and marginal substrate heating.

Chapter 2

LITERATURE REVIEW

2.1 Introduction

Coatings provide materials with sought-for properties, including the gloss and color. Making use of the organic coatings or paints on a substrate is highly recommended for its potentials to enhance appearance as well as protection against corrosion. Severe environmental conditions including heat, moisture, biological deterioration, radiation, solvents and the damage resulting from chemical or mechanical causes need protection. As a result, environmental concerns and economic competitiveness have led the coating industries to search for new approaches to make improvements in the overall effectiveness of the coatings of organic nature, taken the minimum volatile organic components (VOC) into account.

The quality of the coatings relies on the factors such as substrate features, the harshness of corrosive environment and the interfacial properties of the substrate and the coating. Corrosion is another natural damage that can impede the efficient operation of automotive components or metallic platforms and therefore coatings are applied to such surfaces to protect them from the corrosive effect of the surrounding medium. Common corrosion-resistant coatings are operated through the methods, which are mentioned below: To act as a physical insulation to isolate the metallic substrate from the environmental attack. Where as, the other one contains reactive materials (mainly pigments or inhibitors), which prevent from corrosion. For example, corrosion inhibitors such as cerium ions can be added to hybrid films. The inhibitor will be entrapped in hybrid films and release the Ce^{+3} to the damaged zones. Cerium ions were then formed an insoluble deposit on the surface, which hinders the pH increase. The pH increase accounts for the growth of metallic de-alloying. This investigation is in the direction of improving the technical performance and also minimizing the amount of VOC level, which has led the recent researches to adopt alternative coating systems. A major challenge in this arena is offering environmentally friendly coatings, which supply the required properties in ac cost-effective manner. Various technologies, including radiation curable, water-borne and powder coatings have occupied a stabilized place in the market because of attending to the aforementioned issues in an effective way. A number of researchers have been investigating methods that enhance the solid content of the resin, which is performed by employing low Mw polymer. The properties are attained in the curing process in the stage in which the crosslink networks are formed. It is observed that cross-linked thermoset coatings offer significant improvements in tensile strength, abrasion resistance, alkali resistance, solvent resistance and acid resistance, all of which look not superior in majority of the coatings of thermoplastic nature. Through the development of alternative, innovative and up-dated technologies in some features should be taken into account as mentioned below: formulation, application and film formation of the coating.

The earliest organic-inorganic hybrids were extracted from polymer and paint industries in which, the inorganic fillers or pigments were dispersed in the organic component (polymers, solvents, surfactants, etc.) for the purpose of enhancing the properties that are physical. Nevertheless, by improvement of soft organic chemistry in which mild synthesis circumstances permit a vast access to tailored hybrid networks. Therefore, great deals of research have been shifted toward improving the coating output (Chattopadhyay and Raju 2007).

2.2 Polyurethane

Polyurethanes, with a somehow short background, turned out to be a polymer combination which is used on a regular basis in our daily life and has a high potential in most of the fields of polymer applications, including, fibers, coatings, adhesives, thermo-rigids, foams, elastomers and so on. Polyurethanes have changed the quality of human life because of its use in every aspect of our daily life. There exist a variety of cases where the polyurethanes are appropriate to be applied, furniture, shoe soles, bedding, thermal insulation, car seats, and wood substitutes, among the other potential applications.

Polyurethanes are derived by reacting and oligomeric polyols which is a low Mw polymer having hydroxyl groups, and a diisocyanate. The polyols structure employed for synthesizing polyurethane affects physical properties, which form the final polymer. Additives like catalysts, blowing agents, chain extenders, etc. are usually added with respect to the initial reaction (Ionecu, 2005).

Polyurethanes are one of the versatile groups of polymers. They can be applied in foams (rigid, flexible, integral skinned), elastomers, coatings, etc. polyurethane elastomers consist of two kinds of segments, i.e. the soft segment besides the hard one.

There is a difference between the soft segment and hard segment. As such, while the soft segment represent low polarity resulting from its polyester or polyether diols or diamines, it’s established that the hard segment is formed through reacting between diisocyanate and diol chain extenders. Majority of polyurethanes are thermosetting polymers. Thermoset materials are plastic component that are in their final state and cannot be repeatedly softened by heating. A few examples of these materials can be epoxy and phenol-formaldehyde. Thermoplastic is another classification of polyurethanes. Thermoplastic elastomers are materials with thermo-reversible cross-links can be processed as thermoplastics and they exhibit elastic behavior similar to the chemically cross-linked conventional elastomers. It is worth reminding that the applied polyurethane in this study is thermoset polyurethane.

2.3Discovery of Polyurethanes

The first urethane was synthesized by Wurtz (1849). The original work focused on the duplication or improvement of synthetic polyamide fibers, which was followed by very systematic and intensive research work at IG Farbenindustrrie, in Germany. Dr. Otto Bayer (1937) synthesized the first polyurethane, by the reaction of a diisocyanate with polyester, which had two terminal hydroxyl groups. (Bayer, 1947).

As a matter of fact, Bayer (1937) invented a new approach for the synthesis of macromolecular compounds, i.e. the poly-addition reaction, as a special poly-condensation case, just different in product. In the classical poly-condensation reactions, the products are only poly-condensation polymer and a low molecular weight compound (water, alcohols and so on).

It is of paramount significance that poly-addition reactions product is merely a polymer. The technological importance lies in the purity and morphology of macromolecular compound. Over its lifelong of about 65 years, polyurethanes has had a stable growth, and its so appraised that the growth rate of the polyurethanes in the years to come will be promising, thanks to the advent of new markets in Eastern Europe, South America and Asia, (Kresta, 1998). Moreover, the polyurethane elastomers are used for industrial tires, pump and pipe linings, footwear, etc. Polyurethane coatings, adhesives, sealants and fibers manifest another group of polyurethanes of specific applications. The main applications of polyurethanes are illustrated below (Figure 1).

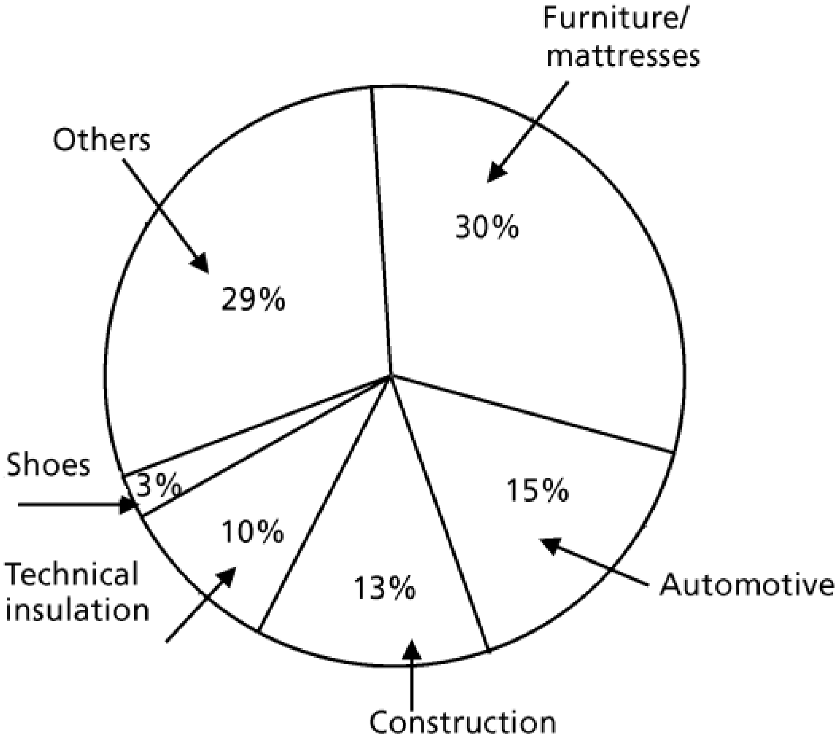


Figure 1: The Main Applications of Polyurethanes

2.4Advantages of Polyurethanes

Since polyurethane materials can be applicable for specific uses, including domestic (cushions and mattresses) and industrial applications (rollers), therefore the appropriate polyurethane for a particular need has to be opted. This polyurethane needs to be stable in chemical terms, not to mention that the process of producing such materials should be easy, having no hazard for the environment. It is also a point that chemical, mechanical and thermal properties of the polyurethane keep a profound effect on the application determination. By way of example, in food products, some particle amines cannot be used.

2.4.1 Fibers

The early efforts aimed at finding a replacement for nylon. The original developments by Dr. Bayer (1973) paved the way for the early patenting as well as fibers evolvement, in addition to foam evolvement. Amongst the general commercial fibers produced by polyurethane we can name Spandex and Perlon.

2.4.2 Films

To make films from polyurethane, there exist three major procedures, as follows:

- Bi-section spray-able: polyurethanes are employed for manufacturing polyurethanes chemical-resistant paints and coatings. It is possible to dilute polyurethanes by a solvent to simplify spraying of polyurethanes. As an attractive attribute, the fast curing has added to the significance of polyurethane in this segment of the market.

- Single Component: This system is contingent upon the reaction of the prepolymer and the environment humidity to constitute a solid polymer. CO_2 is emitted as a result of this reaction, either evaporating or being entrapped by fillers in the system. The aforementioned system is applied to produce single pack polyurethane paints and waterproof barriers.
- Latex: Polyurethane gives birth to latex, which turns into a film upon removal from the suspension. The system in question is utilized to produce thin-walled substances. The environmental concerns for VOC have called the attention of many scientists into this field.

2.4.3 Castables

The early business launch of Castable polyurethanes dates back to 1952, by DuPont (Hanford and Holmes, 1956), followed by BASF and Dow who offered a cheaper polyether alternative later in 1957. Changes and developments, neighbor to evolution, have taken place over the recent years so as to cure the systems and present isocyanates to make the optimal use of the various properties and capabilities. There exits a sea of applications for castable polyurethanes, varying from the military components to domestic roller blades.

2.4.4 Thermoplastics

This type of polyurethane is designed in a way to be process-able through conventional plastic machineries like injection molding or extruders. Thermoplastic polyurethanes may be employed in biomedical industry. Thermoplastic PUs would also be hired in the microcellular format in which the denseness can be abated. Tubing, automotive pieces, handles, and heels are just few applications by way of example.

2.4.5 Foams

The decision-makers of the second global fight, which hit the whole universe in the mid 2o century, made their minds to apply foamed polyurethanes in aero-plane combat devices. They have called the attention and caught the eyes since the inexpensive polyether polyols found their ways into the market. Foam polyurethanes production has been well examined. They are composed of even cell structures in 3D networks. The cells are of two types; open and closed, dictated by the intended application in place.

2.4.6 Millable

Millable urethanes, either sulfur cured or peroxide, undergo process through standard rubber-processing machinery. The former's varieties entail some chemicals added thereto to contribute sulfur curing. The millables include a diane group (-CH=CH-), ingredient to the polymer to facilitate cross-linking either by sulfur or peroxide. Still, the cross-linking level in millables is of limited cap.

2.5 Polyurethane Elastomers

Polyurethane elastomers have a broad range of applications owing to their unique combination of valuable physical and mechanical properties. Generally, these elastomers consist of crystalline hard segments as well as flexible soft segments. Generally, these elastomers consist of crystalline hard segments and phase separated flexible soft segment. As regards the hard segment, it must be said that this sort of segment is the direct output of the reaction between the diisocyante and low molecular weight diol chain extenders. But, when it comes to the soft segment we are faced with something, which is based on the polyether or polyester type aliphatic diols. This kind of segment is of low polarity, which isn't longer than the hard segment, providing a soft and flexible matrix. By the contrary, the hard segments are less in terms of length, extremely polar, which easily tend to aggregate. Thermodynamic incompatibility of the foregoing segments gives birth to phase separation, eventually places impacts on the mechanical and physical properties of the urethane elastomers (Lawrey & Barksby, 2003).

2.5.1 Main Polyurethane Constituents

The three substantial elements, making the elastomer, are demonstrated in details in the Table-1.

Table 1: The Substantial Polyurethane Elements

• Polyols	Polyether
	Polyester
• Diisocyanate	Aromatic
	Aliphatic
• Chain extenders	Diamines
	Hydroxyl compounds (glycols/water)
	Polyols
• Other Chemicals	

2.5.2 Diisocyanates

It known that the isocyanates form the bulk section of the rigid or hard segment of polyurethanes. The most rampant diisocyanates are as mentioned below: methylene diphenyl diisocyanate (MID), toluene diisocyanates (TDI), hexamethylene diisocyanates (HDI), and isophorone diisocyanate (IPDI), which are utilized, in the present paper, for the purpose of preparation of the polyurethane. Diisocyanates can be toxic and may affect the health of operators in manufacturing when they are monomeric. Toxicity is of two major influences: a. contact and b. inhalation that comes out of isocyanate moiety's vapor pressure. Three major isocyanates applied in the industry are mentioned below: 1,5-naphthalene diisocyanate (NDI), toluene diisocyanate (TDI), and 4,4' diphenylmethane diisocyanate (MDI).

2.5.3 Polyols

Generally speaking, the term "polyols" is employed in organic chemistry, to refer to low molecular weight organic substances, very clearly identified as molecular entities, having more than two hydroxyl groups, including glycerol, propylene glycol and sorbitol. This expression is substantially in connection with polyurethane fabrication, for the polymerization requirements; the polyols are linear with the Mw in the range of 400 and 7000.

2.5.4 Chain Extenders

Low Mw diols (e.g. ethylene diethylene glycol the same as glycol) are called chain extenders and are combined with polyurethane pre-polymer to produce polyurethanes.

Triols are employed in cases where crosslinking does work. The process conditions, as well as the needed properties decide what kind of chain extender should be opted. The hydroxyl compound, which is seen in majority of the cases appear to be diols. Substantially, diols enhance properties as well as the pace of the processing with TDI-terminated pre-polymers the same as diamines of MDI-based ones.

Isocyanate and chain extender molecule shape is decisive when it comes to facilitating hydrogen bonds creation. For the purpose of occurrence of hydrogen bonds it is essential that each molecule move towards the other. The foregoing two chains must be free of steric hindrances. Molecules of even numbered carbon permit hydrogen donor group (NH) to come close to electron donor group (C=O) in a much easier manner. In cases where the carbons are of odd number, the fit is inappropriate; the group, which can participate in the hydrogen bonding, is so limited. The experiments results proved that aliphatic diisocyanate melting point is the function of quantity of carbons on the main chain. Thus, The diisocyanates of odd number carbons demonstrates a lower melting point in comparison with diisocyanates of even-numbered carbons, (Wright and Cummins, 1969).

2.5.5 Other Chemicals

There exits numerous chemicals employed in polyurethanes that affects physical characteristics of the end product though not partaking in the chemical reactions whatsoever. Among such chemicals we may refer to catalysts, plasticizers, fillers, moisture scavengers and ultraviolet absorbers.

2.5.6 Catalysts

Catalyst is defined as a substance, when used in meager quantities; that makes the chemical reactions happen faster without undergoing any permanent changes. It is generally used to speed up a reaction. Contrarily, a catalyst slows down the reactions as well. Catalysts play a vital role to expedite the chain extension reactions of the polyurethanes. This substance, (i.e. the catalyst), is used by some specialized vendors in connection with polymer sector, varying from the amines to metal salts. Special reactions are influenced by catalysts. Polyurethane reactions in industry fall into three groups: 1) reaction resulted from amine interactions 2) reaction by diols (OH-NCO) interaction 3) reaction resulted from diols and isocyanates (NCO-OH) interactions. Adipic acid, tin-based salts (e.g. dibutyl tin dilaurate (DBTDL or dibutyl tin salt)), and bismuth are the most common catalyst that are used in the mentioned reactions, respectively.

2.5.7 Fillers

Polyurethanes do not generally take the fillers as reinforcement, because they wreck havoc on the mechanical properties, in a drastic manner, unlike the conventional elastomers. Ultrafine silica is incorporated in the form of thixotropic filler for trowelable polyurethanes. (These products are designed for the repair of existing elastomeric substrates such as urethane and rubber lining repairs).

2.5.8 Plasticizers

Plasticizers are divided into two types: a) reactive; and b) non-reactive. The latter, i.e. non-reactive plasticizers, fall under phthalate and ester groups. Diisooctyl phthalate (DIOP), tricresyl phosphate (TCP), and Benzoflex 9-88 are the most widely used typical plasticizers. Increasing the amount of plasticizers has a negative impact over the physical properties; therefore, plasticizers level should be monitored meticulously.

2.5.9 Moisture Scavengers

The existence of moisture in polyurethanes is a prime cause of performance loss in coatings. Moisture can react with isocyanate and produce CO_2, which results in bubbling issues. In some cases pigments and fillers can also procure absorbed moisture, which produces CO_2 gas. The produced carbon dioxide is then stored within the film surfaces, resulting into pinholes and micro bubbles which ultimately cause the loss of gloss in coatings. Consequently, oxazolidine-based moisture scavengers are highly effective for urethane coatings to eliminate CO_2 bubbles. They reduce the chances of residual moisture coming from solvents, polyols, prepolymer, plasticizers and pigments.

2.6 Pigments and Additives

The basic requirements of the ink and paint industry are quite alike: brilliance, lightness and hiding power. The main application and usage of the pigment is for aesthetic purposes. As a whole, the cured MDI- and TDI-based polyurethanes turn yellow, even upon short fraction of exposure time to UV light. As the resins color turns darker, light-colored or white pigments are not generally recommended to be used. Dispersing medium should be used to grind the untreated pigments for enhancing true and/or the full color of the intended pigment. As a rule, the dispersion phase uses a dry and non-absorbent non-reactive plasticizer. The pigment system is priced based on the heat stability and specific pigment light and its undertone strength. In cases where and when it is used in a system, which requires the food, and drug administration (FDA), as instances, or equivalent approval, the chemical nature of the pigment should also be taken into consideration. Chromium and cadmium-based pigments are often a cause of concern, which has led to the regulation to put restraints and limitations on the use of these pigments.

Prior to full production, the quality of pigments is tested, as a must. The pigments, which are not dispersed properly, will show up as swirls or lakes. Laky materials are dispersed in pre-polymer prior to the end heating. Swirl marks pinpoint the want of appropriate mixing, while a number of marks turn out to be very difficult to get rid of when facing the red-colored pigments. Pigments are poured through extended plastic nozzles. Plasticizers are used to control the viscosity of the mixture. In case of big size of pigments, tinting machines are available to dispense. These types of additives are responsible for carrying out numerous roles when it comes to polyurethane compounds. The non-reactive plasticisers, like the ester group as well as long-chained diols are the most rampant plasticizers in the industry, where the latter act as both plasticizers and combined curative.

2.6.1 Metal Pigments

The origin of metal pigments dates back to gold leaf manufacturing approximately to 1,000 B.C. Ancient Egyptians maintained the art of converting gold into very thin sheets to be used as decorative items, in line with ornamentation purposes. Nevertheless, regarding the excessive cost of gold, the use of metallic coatings to many objects was limited. As a result, bronze and copper were substituted for gold, while tin and silver were discovered to make silver shiny pigments. It took years to manufacture aluminum smelting, which made aluminum more available, at the easy access and reach of the users (Hall and Heroult, 1886).

Aluminum pigments can offer a metallic appearance. Since the environmental aspect of the coatings is becoming more important in the recent years, thus the paint and coat industry is focusing on developing systems, which can reduce the amount of volatile organic compounds (VOC). These pigments have two classification; leafing- and non-leafing.

2.6.2 Leafing Aluminium

Leafing aluminum is produced by adding stearic acid to the aluminum particles. These particles give a mirror-like appearance in the coating process. This type of aluminum can be used with transparent pigments to produce colored effects and because of the alignment of the pigments; they can prevent the penetration of water and offer chemical attack protection to the substrate.

2.6.3 Non-Leafing Aluminum

Non-leafing aluminum pigments can be applied to various systems. They can orient themselves randomly throughout the films. The advantage of this arrangement is to allow its use in coating systems in conjugation with other colored pigments. Moreover, the paints that contain non-leafing types can be colored with transparent or semi-transparent pigments.

2.7Basic Reaction of Urethanes

Urethane linkage serves as top significant combination of polyurethane in terms of chemical properties. Reacting a hydroxyl-terminated polyether or polyester with an isocyanate forms polyurethane. As an example, we may refer to the reaction of polypropylene glycol (PPG) and toluene diisocyanate to produce isocyanate-capped polypropylene glycol. During the 1950s, a novel technology was discovered, which was known as as "one-shot" process. In this method a capped polyol is produced which instantly reacts further to achieve its final form, which at the same time has isocyanate functionalities as end groups. The completion of the process is not materialized, unless these end groups proceed to show the proper reactions, as required. As a matter of fact, this reaction gives birth to pre-polymer. Prepolymer duplication in the laboratories is quite simple. The isocyanates are added gradually to the polyols, under magnetic stirring at room temperature, in which the mixture temperature should be monitored on a regular basis.

2.8 Industrial Coatings

A coating is a covering that is applied to the surface of an object, usually referred to as the substrate. In many cases coatings are applied to improve surface properties of the substrate, such as appearance, adhesion, wettability, corrosion resistance, wear resistance, and scratch resistance.

An industrial coating is a paint or coating defined by its protective, rather than its aesthetic properties, although it can provide both.

The most common use of industrial coatings is for corrosion control of steel structures such as offshore platforms, bridges and underground pipelines. Other functions include intumescent coatings for fire resistance. The most common polymers used in industrial coatings are polyurethane, epoxy and moisture-cure urethane.

In automotive industries from functional vantage point, coatings are divided into three main categories: topcoats, primers and sealers. The sealers are usually transparent or slightly colored, base coat, formulated for restraining capillary tube task in a permeable work-piece, like wood and masonry. These sealers provide a smooth foundation for primer, making possible a uniform film formation besides preventing the extractable substances of the substrate to enter primer and topcoats. The primer is deemed as the number one coating layer and guarantees a proper bonding between the coating and the work piece and provides a smooth base for the topcoats. The topcoats are the final layer of the coating, which represents aesthetically appealing decorative, and also supply the eventual protective barrier. Paints are basically architectural coatings that are employed to preserve and beautify the outer and insider appearance of the office and residential complexes. These types of coatings are normally utilized to the buildings to prevent humidity take-up, puffiness, and deterioration, besides supplying a long-lasting, elastic and ornamental layer. The suppliers offer paints (exterior/interior), as oil-based or water-based. Industrial coatings are often applied to metal substrates. Ferric substrates oxidize instantly, while they form an oxide layer that is not protective. An industrial coating is a coating that gives protective characteristics to the substrate. The most well known application of the industrial coatings is to protect the steel substrates from corrosion such as bridges and underground pipelines. Other applications include puffy coatings for fire resistance. The most common polymers used in coating industry are polyurethane and epoxy.

2.9Radiation Curing

In the late 1960s, there was little concern or even awareness about the extent of the solvent disposal into the environment, from the coating industry. As a consequence, more than 90% of the used industrial coatings were low solids in the nature, i.e. they usually had 10 to 20 % weight solids, excluding pigments or other materials, and the rest was just solvent. In the aforementioned period, industrial coating was characterized as either low solids or solvent-borne. Solvent-borne is a type of traditional coating in which the films were cured upon solvent evaporation. Some may think that solvent-borne coatings can be environmentally friendly but in the long run these coatings were also replaced with more proper coatings. All other choices for the conventional solvent borne coatings hold their own merits and demerits. High solids look basically very similar to solvent borne coatings. Therefore it was readily adoptable by conventional solvent-borne producers. Yet, they contained no more than thirty percent solvent. Therefore, they are to be restricted over time. Water-based systems are investigated aptly though they suffer from mal-performance, when disclosed to corrosive atmosphere, because of sensitivity to moisture. It comes out as a direct result of utilizing water compatible combinations for dissolving or dispersing. Additionally, curing these types of systems takes further energy and needs custom-made curing units.

The most efficient coating systems in terms of environment are UV curable and powder systems. These systems consist of 100% liquid and solid structures. There exist special imperfections for foregoing systems in connection with their performance. In the wake of the filmmaking interference of film formation and melting by cross-linking, these kinds of coatings demonstrate an orange-peel construction. UV curable systems have drawbacks, including oxygen inhibition reactions of the radical stimulated polymerization. Moreover, radiation-absorbing constituents, who are introduced in the formulations such as pigments, additives or radiation absorber, may result in cure problems. Economical, ecological, and performance are the major advantages of UV curable coatings. Merits and demerits of the upcoming coating systems are given in Table 2 (Wicks, Jones, and Pappas, 1994).

Table 1: Merits and Demerits of the Upcoming Coating

Coating	Advantages	Disadvantages
High Solid	Excellent properties Easy handling Familiarity of the users with solvent-based coatings	Still solvent containing Long curing time
Waterborne	Low V.O.C Widespread chemistries characteristics application methods	Poor chemical resistance Difficult to dry Foam
Powder	One hundred percent solid Environmentally friendly	Narrow process windows Orange peel structure High cost Time-consuming cure

UV/EB	100% liquidity Energy-efficient Little radiation Capital cost efficient Occupying little space Marginal substrate heat	Expensive raw substance Difficult curing surface Difficult cure of pigmented coatings Incurable shadow surfaces

The radiation curing procedure is primarily defined by the coat-targeted applications. Desired final output dictates the coated work piece. E.g. clear coat, papers cards varnish, colored or transparent clear coat and flexible and shielding coat. The role of coating, by way of example decoration, anti-scratching and corrosion resistance, comes to detect the required thickness and the desired property requirements. The intended characteristics such as excessive gloss, color effect, scratch resistance, flexibility and hardness need to be presented through the chemical formulation, including base resins, diluents and photo initiators and other additives.

Moreover, an apt collection of the constituents should be performed so as to come up with an efficient cure procedure. By way of example, in coating having pigment or radiation stabilizers the spectral absorbance of photo initiator needs to be fine-tuned with a spectral range for example, in which the pigment and radiation absorbers are relatively crystal-clear. The Adjusting and matching the UV source properties with the chemistry of the coating result in a cost-efficient cure procedure.

Radiation curing of the coatings, inks, adhesives and sealants is a direct and effective method in transforming the liquid, which produces a polymerized and cross-linked mass, with functional or decorative capabilities. In this process subsequent to the energy absorption by the phtoinitiator molecule, UV photons or electrons become electronically excited or ionized and the specially formulated resin then transforms to a solid and useful product.

The radiation, which is used in the coating industry, is an ultraviolet radiation (UV) or electron beam (EB) energy by electronic ionization, which results in a non-thermal curing, whereas microwave and radio frequency initiate thermal curing.

In industrial radiation curing applications the electrons having energy range of 100-300 k eV or UV photos with energies in the range of 2.2-7.0 eV are applied. Through electro-statis1 collaboration, the energy of electrons is passed to the reactive liquid. The process results in excitation, ionization, and ultimately the generation of reactive varieties.

Generally, the UV curing technology is the photo-initiated fast transition of a liquid resin into a solid film in a fraction of seconds. The initial species may be cation, anion or radical. The immense substantial part of radiation curable coatings is centered over the radical making photo-initiators, (Mehnert, 1998). These special phtoinitiators are applied to absorb the photons, energy and generate radicals. The first conversion from the liquid into solid occurs as radical or cationic polymerization followed by cross-linking. A schematic representation of radical formation, polymerization and cross-linking is illustrated in Figure 2.

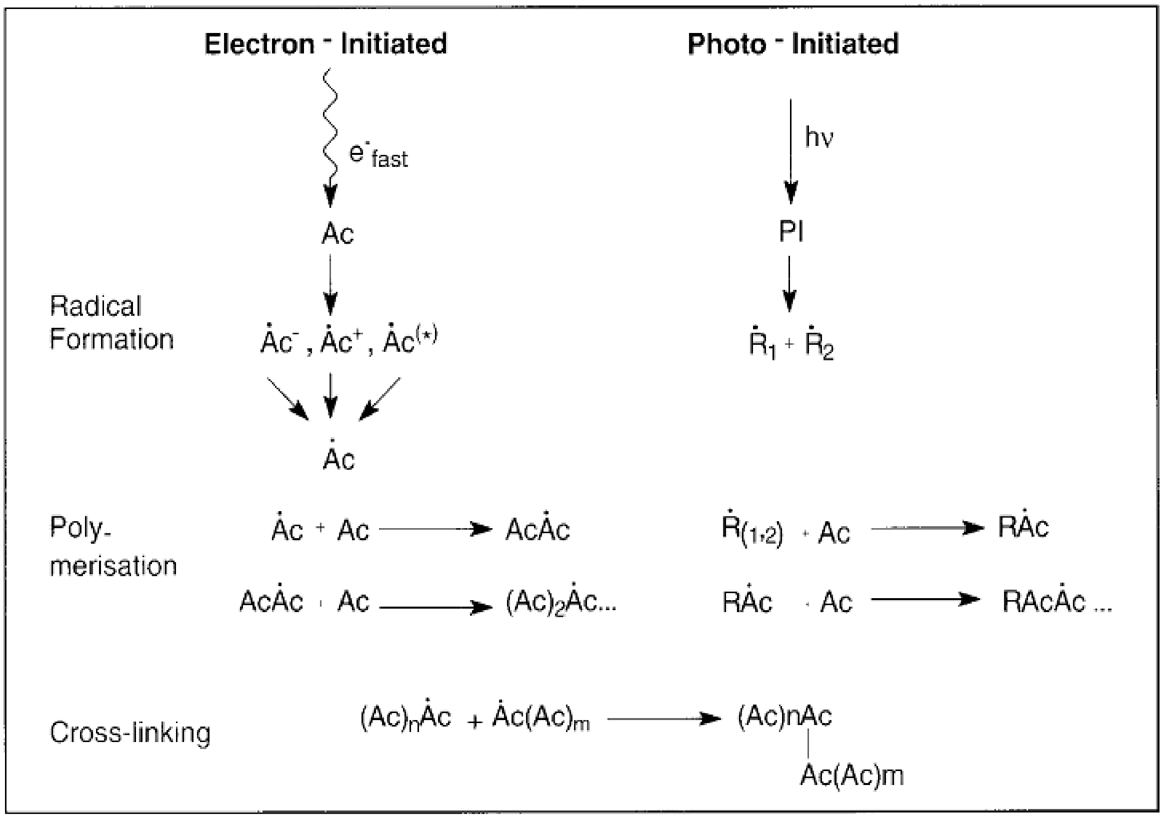


Figure 2: Radical Formation, Polymerization and Cross-Linking in Acrylates (R= Radical, Ac= Acrylate, PI= Photoinitiators)

As a result of the curing process, a solid polymer network is formed from a 100% reactive liquid. This means that liquid radiation curable systems do not contain any components, which do not take part in the polymer formation. In radiation curable formulations, volatile organic solvents are avoided; they are solvent-free and consist of 100% reactive monomers and oligomers (Hoyle, 1990).

2.10 Applied Chemical Systems for Radiation Curing

The initial substances to generate radiation curable coatings include low Mw resins, particularly, in the scope of 300-5000 g/mo. Resin types are drastically polymerizable, unsaturated polyesters, acrylate terminated molecules, such as polyether, polyepoxid, polyurethane, polyester, epoxides and vinyl ethers. Table 2 illustrates a summary of different kinds of UV curable resins. By a considerable difference, the resins used frequently are the radical polymerization acrylates and unsaturated polyesters. Thiolene systems look insensitive to oxygen inhibition, so far few applications they have (Allen and Edge, 1993).

Table 2: Resin Kinds for Ultra Violet Curing Systems

Radical	Cationic	Phtoinitiator free
Acrylates Epoxy acrylates Polyester acrylate Urethane acrylates Acrylated polyacrylates	Epoxides Bisphenol A-diglycidyl-ether 3,4-Epoxycyclohexylmethyl-3,4-Epoxycyclohexane carboxylate **(**ECC**)**	Donor-acceptor system Malemide-acceptors N-ethyl-MI N-phenyl-MI

2.10.1 Acrylates and Methacrylate Systems

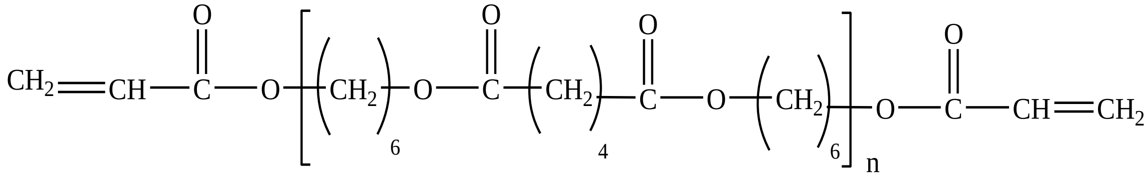
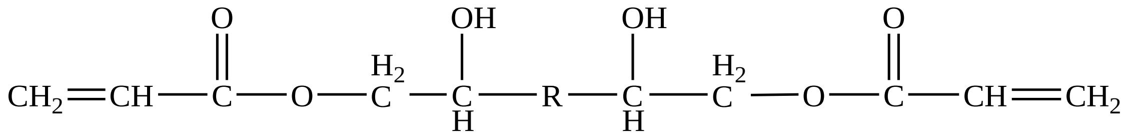
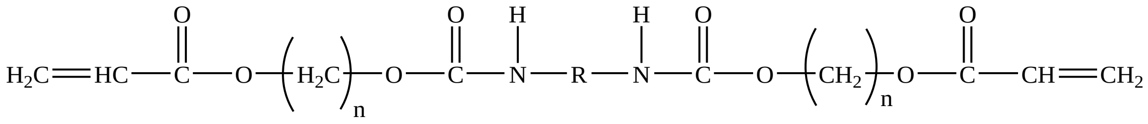
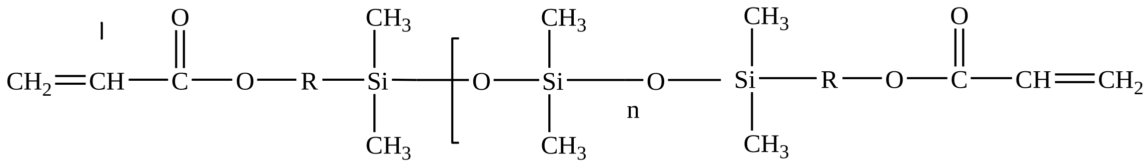
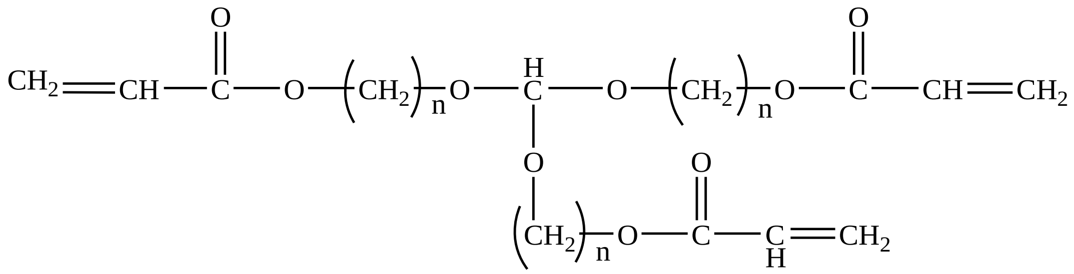
The well-known electron beam or radiation curable systems entail the acrylate unsaturated H_2C=CR-COOR (R=H: acrylate, R+CH3: metacrylate). Methacrylates are less reactive in comparison with the acrylate and are applied in particular situations. Radicals enlighten polymerization of acrylates. Radical polymerization includes Chain growth, cross-linking and termination. During this process the acrylate double bonds will be consumed. Thus, it is presumed that the degree of conversion can be criteria for evaluating the degree of cure. After a certain amount of time the extent of double bond conversion can be evaluated through time-resolved infrared spectroscopy or stationary methods. High reactivity and adjustable viscosity are two most crucial performance characteristics that have to be met by solvent free radiation curable acrylate formulations. On one hand, the formulations which contain only monomers results in bad adhesion to the substrate, brittleness and a high content of extractable materials which are not acceptable. On the other hand, acrylate oligomers are available which usually have higher viscosity and lower reactivity than acrylate monomers but are to meet a broad range of coating property requirements. Thus, radiation curable formulations normally contain both monomers as reactive thinners and oligomers as binders. Multifunctional acrylate monomers based on various polyols such as TMPTA, TPGDA, HDDA, PETA, etc. (Table 3) have been used since the 70's. Such monomers demonstrate good diluency in combination with high cure speed and low volatility. However, such materials can cause irritation to skin and therefore there is an ongoing tendency toward the development of these monomers.

Table 3: Bifunctional and Polyfunctional Acrylates

Tripropylene glycol diacrylate	TPGDA
1,6-hexanediol diacrylate	HDDA
Dipropylene glycol diacrylate	DPGDA
Trimethylolpropane triacrylate	TMPTA
Trimethylolpropane ethoxytriacrylate	TMO (EO) TA
Trimethylolpropane propoxytriacrylate	TMO (PO) TA
Pentaerythritol triacrylate	PETA
Glyceryl propoxytriacrylate	GPTA

Epoxy, polyester, urethane and silicon acrylates are the main type of acrylic oligomers. Epoxy, polyester, urethane and silicon acrylates are the main type of acrylic oligomers. The chemical structures of some oligomers are illustrated in Table 4. Also, aromatic and aliphatic epoxy acrylates have a wide range of applications in radiation curable oligomers, despite the fact that they have to be thinned with monomers. Epoxy acrylates can be a proper acrylic oligomer for wood finishing and hard coatings, since they are highly reactive and are able to produce chemically resistant coatings.

Table 4: Acrylate Oligomers

Polyester acrylates  $CH_2{=}CH{-}C(=O){-}O{-}[(CH_2)_6{-}O{-}C(=O){-}(CH_2)_4{-}C(=O){-}O{-}(CH_2)_6]_n{-}O{-}C(=O){-}CH{=}CH_2$
Epoxy acrylates  $CH_2{=}CH{-}C(=O){-}O{-}CH_2{-}CH(OH){-}R{-}CH(OH){-}CH_2{-}O{-}C(=O){-}CH{=}CH_2$
Polyurethane acrylates  $H_2C{=}HC{-}C(=O){-}O{-}(H_2C)_n{-}O{-}C(=O){-}NH{-}R{-}NH{-}C(=O){-}O{-}(CH_2)_n{-}O{-}C(=O){-}CH{=}CH_2$
Silicon acrylates  $CH_2{=}CH{-}C(=O){-}O{-}R{-}Si(CH_3)_2{-}[O{-}Si(CH_3)_2]_n{-}O{-}Si(CH_3)_2{-}R{-}O{-}C(=O){-}CH{=}CH_2$
Polyether acrylates  $CH_2{=}CH{-}C(=O){-}O{-}(CH_2)_n{-}O{-}CH[O{-}(CH_2)_n{-}O{-}C(=O){-}CH{=}CH_2]{-}O{-}(CH_2)_n{-}O{-}C(=O){-}CH{=}CH_2$

Urethane acrylates offers a broad range of properties such as good adhesion to surfaces, abrasion resistance, flexibility, toughness and chemical resistance when aromatic or aliphatic derivatives of the urethane acrylates are selected properly. Urethane acrylates are created through the reaction of isocyanate and hydroxyl functional acrylate monomers. The use of polyols and polyesters into these acrylates, leads to a diversity of modified structures.

Generally, polyester acrylates resins are not viscous, which invite pint-sized or no monomers. They can be produced through the reaction of hydroxyl group of polyester and acrylic acid. Polyester acrylates are applicable in varnishes and lithography. Solid urethane or polyesther acrylates are the key component of UV-curable powders. Incorporated with proper unsaturated polyesthers, powders are made of low film flow temperatures and permit differentiating film creation from curing; such technique for woods and plastic is becoming feasible (Wittig and Gohmann, 1993).

Polyether acrylates are synthesized by esterifying polytherols with acrylic acid. They can reach lower viscosities in comparison with polyesther acrylates and do not require reactive thinners. Silicone acrylates are acrylated oraganopolysiloxanes. As the most important class of silicone acrylates the backbone consists of polydimethylsiloxane units. This silicon backbone is responsible for flexibility and resistance to heat and radiation degradation. Good release characteristics are related to the low intermolecular interactions that are induced by methyl group. Reactivity, degree of cure and release force is adjustable over a wide range by variation of the acrylate functionality and the steric arrangement of the reactive groups within the polymer chain.

2.10.2 Cationic Systems

Cationic polymerization of substances containing oxirane functionality such as aliphatic and cycloaliphatic epoxides as well as glyvidyl ethers can be initiated by photogenerated Lewis acids (Crivello, 1984). Yet cationic UV curing is limited to epoxides. Vinyl ethers can likewise be polymerized by cationic polymerization and turn into an interconnecting polymer arrangement if mixed with epoxides. The addition of vinyl ethers increases the cure speed of epoxides and decreases viscosity. Multifunctional polyols are usually used in cationic radiation curing system as chain transfer agents, expediting the cure process, adjusting the crosslink denseness, and influencing the coating elasticity. Vinyl ether, glycidyl ethers, epoxysilicones, and epoxides are the main constituents, which are applied in cationic system.

Cationic radiation curing formulations that are meant for coatings show a broad range of features, like impact resistance, chemical resistance, hardness, good adhesion, and abrasion resistance. Ambient humidity, amines or other bases can affect this process negatively.

2.10.3 Maleate/Vinyl Ether Systems

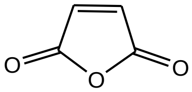
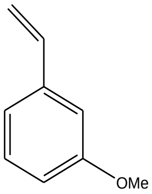
Maleate/Vinyl ether (MA/VE) UV curing systems have been commercially used in the past (Noren, Tortello and Vandeberg, 1990). They contain only oligomeric components. The main benefit of this system is low volatile organic compound concentration. Contrarily, the cure speed is generally low compared to the acrylate formulations. When radicals are created, e.g. from classic radical phtoinitiators, cyclopolymerization happens through an electron donor-acceptor compound.

The present MA/VE systems are predominantly applied to timber coatings in roll and spray applications. They may serve the function of binders for UV curable powder coatings. The binders contain two polymers: unsaturated polyester containing maleic and fumaric acid functionalities, and polyurethane with vinly ether unsaturation.

2.10.4 Donor Acceptor Complexes

If an unsaturated molecule that contains excessive electron charge at the double bond like vinyl ethers, mixes with electron deficient unsaturation (maleic anhydrides maleimides, maleates or fumarates), the donor-acceptor complex can be formed. This complex can be produced after the UV irradiation. Maleic anhydride and Methoxy styrene are two acceptors and donors, respectively. The structures of these substances are shown in Table 5 (Johnson et al., 1994).

Table 5: Donor Acceptor Pairs

Acceptors	Donors
Maleic anhydride 	Methoxy styrene 

2.10.5 Unsaturated Polyesters

Unsaturated polyesters refer to the initial commercially UV curable systems, which are at hand. Unsaturated polyesters are produced by condensation of organic glycol and diacids. In the condensation reaction phthallic, maleic anhydrate and 1,2-propylene glycols are used to prepare unsaturated polyesters.

2.10.6 Thiol-ene Systems

Thiol-ene systems are composed of a mixture of polythiols and olefinic compounds. The addition of thiols to the olefinic double bond can occur by radicals or ions. Polythiols have volatile emissions, thus their applications are very restricted.

2.11 PU Coating Classifications

ASTM devises classified six dissimilar polyurethane coating types in the ASTM D 16 Standard (Dieterich, Grigat, and Hahn, 1993). Most solvent-less and high solids polyurethane coatings for high performance application and corrosion protection are formulated through the plural element format of the ASTM D 16 type V.

2.11.1 Thermoplastic PU Coatings

Thermoplastic PU elastomers (TPUs) were the initial uniform elastomeric products that are usually employed for the processing of the thermoplastics. The basic reaction of the polyurethane chemistry is between a compound that contains a hydroxyl group and an isocyanate:

$$\underset{\text{Isocyanate}}{R{-}N{=}C{=}O} + \underset{\text{Alcohol}}{R'{-}OH} \rightleftharpoons \underset{\text{Ester of a carbamic acid}}{R{-}NH{-}CO{-}OR'}$$

Generally, Thermoplastic PUs are produced from extended polyols with common Mw in the scope of 600-4000, chain extenders with Mw in the scope of 61-400 and a polyisocyanate. Choosing constituents of the reaction mixture and their proportions influences on the characteristics of the end product, which can be in the range of hard to soft materials.

Thermoplastic PU can be defined as the linear basic block co-polymer of $(SH)_n$ type. In such formula, H is the hard segment (HS) and S is soft segment. In the finishing material the observed phase separation is because of the diversity of properties of S and H segments. This phase separation takes place because of the thermodynamic immiscibility or intrinsical incompatibility among the soft and hard segments. The main constituents of the HSs are polar material. These constituents convert carbonyl to amino hydrogen bonds and therefore the tendency to form a bunch or mass hooked on ordered hard zones (Seymour, Cooper, 1974). The hard segment acts as filler particle together with cross-linker to hinder the movement of Ss chains (Cooper and Tobolsky, 1966).

The original work of Schollenberger (1959) in addition to Cooper and (1966) confirmed the fact that segmented polyurethanes consists of high T_g or T_m. These two temperatures derive the points at which a specific elastomer goes through transition in its physical properties. The degree of the soft and hard segments phase separation plays an important function in pinpointing the solid-state characteristics of multiblock coatings.

Properties of thermoplastic polyurethane coatings are a function of, lengths of soft and Hard segments, composition of S and H segments, length of S and H segments and the sequence of length distribution, anomalous linkages (branching, crosslinking), biochemical type of the polymers composed units, Mw and the morphology of the solid state. Soft macro glycol segments are beyond their T_g and ensure easygoing segmental at room temperature and therefore pass on the material its elastomeric characteristics or rubber like performance. But then, H segments are beneath their T_g or T_m. Thus they pass on the permanent deformation, hysteresis, high modulus, everlasting deformation, and tensile strength and deliver dimensional solidity (Koutsky, Hien, and Cooper, 1970).

Treating circumstances and compositional variables including the soft and hard segments structures (Sanchez, Papon, and Villenave, 2000), Evenness of diisocyanate, type of chain extender (diol or diamine), quantity of carbons in linear low Mwt chain extender (Sung, Smith, and Sung, 1980), the type polyester or polyether and chain length of soft segments (Wang and Cooper, 1983), crystallizability of the segment (Aitken and Jeffs, 1977), thermal history of the PUs (Seymour and Cooper, 1973) and the method of synthesis (Sanchez, Papon, and Villenave, 2000), are recognized to influence the extent of phase separation, phase mixing, hard and oft segment organization and consequent polyurethane coating properties.

2.11.2 Thermoset PU Coatings

The substantial disadvantage of thermoplastic polyurethane coatings is their modest endurance concerning mechanical strains and high temperature distortion. In general, the acceptable mechanical properties of the polyurethane coatings disappear above the temperature of 80 ^{0}C and thermal degradation occurs above the temperature of 200 ^{0}C (Masiulanis and Zielinski, 1985). The existence of crosslink in thermoset coatings improves the tensile strength, mar and scratch resistance. In order to improve the final performance and operational temperature range, the presentation of chemical crosslinker in the polyurethane arrangement was investigated. In the urethane elastomer through the reaction of terminal isocyanate groups with urethane groups, allophanate linkage will be formed. Crosslinking was correspondingly attained and coordinated by replacement of a tri-functional hydroxyl compounds on behalf of the normal glycol chain extender.

Moreover, the concentration of the crosslinking can be increased through the improvement of the functionality in polyether or polyester SS. Coatings may incorporate triols or higher functional polyols (Smith and Magnusson, 1961), isocyanate with functionalities greater than two (Desai, Thakore and Sarawade, 2000), NCO/OH ratios greater than one (Paulmer, Shah, and Patni, 1991) or a combination of both (Kothandaraman, Venkatarao, and Thanoo, 1990). Also, peroxides and tri-functional CEs have been employed for the chemical modification of the extent of hard segment adhesion using chemical crosslinks (Smith and Magnusson, 1961). The introduction of cross-linker to the hard segment, soft segment or chain extender would decrease the mobility of hard segments and trigger a steric hindrance which decreases the power of hard segments to form H-bonding (Chiou and Schoen, 2002). Cross-linked PUs have demonstrated a huge prospective in the coatings district according to their high T_g, ease of synthesis and processing, capability to form high quality films and decent solvent resistance. Generally, higher crosslinking increases the phase mixing (Dounis and Wilkes, 1997). For instance, Thomas et al (1994) changed the crosslinking level by altering the functionality of the polyol. Thomas and co-workers proposed that an increase in the polyol functionality could increase the phase mixing. Consequently, so as to enhance the assets of segmented polyurethane for higher performance application, a measured quantity of cross-linker is required.

2.12 UV-Curable Coating Applications

It is demonstrated that radiation curing offers multiple industrial applications, which have several advantages including, high quality, performance and productivity. The conventional applications for radiation curable systems are in sectors in which temperature-responsive substrates undergo coating process. As example for the foregoing case we may refer to the substances such as paper, timber and plastics the same as imaging applications, including electronics and printing plates, (Pfeiffer et al, 1997) (Table 6).

Table 6: Classical Applications of Radiation Curable Coatings

Industry	Application
Coatings	Wood (Parquet flooring, furniture, baseboards, doors, …) Paper (Postcards, high gloss flyers, cosmetic packaging, …) Plastics (PVC-flooring, headlight lenses, CDs') Glass fibers
Electronics	Photoresists Printed circuit boards
Adhesives	Pressure sensitive adhesives

Coatings can be functional or decorative or even both. Functional coatings can improve the surface by protecting it from scratch or providing various properties such as adhesion. Coatings can be applied to a metallic surface, to protect the metal against environmental attack. Depositing an adherent protective coating onto the metal surface usually attains metal protection. Metallic corrosion is produced through chemical interactions among environment and the metal substrate, that convert the metal to a thermodynamically preferred compound, such as an oxide, hydroxide or sulfide, depending on the environmental species. In general, anti-corrosion technology uses techniques described below: a) Alloying metals bearing component, which strengthen the surface using a corrosion-resistant constituent or layer; 2) adding a water-based inhibitor that absorb on metal surface, while hindering metal oxidizing reactions; 3) deposition of protective coatings (Betova et al., 2002). There exist various procedures for the depositing coating on substrate; involving chemical vapor deposition (CVD), physical vapor deposition (PVD), electrochemical deposition (ED), sol gel route and plasma spraying. Making use of protecting film or coating is a common method to prevent corrosion in metals. Here the procedure that allows achievement of the aimed characteristics, (Buchheit et al., 1997).

2.13 Overview of Sol-gel Coating

Ebelmen (1842) initially introduced sol gel method to synthesize uranium oxide. In this method, the aging and heating took around one year to preclude crack formation that made it problematic for broader applications (Ebelmen and Ann, 1842). The conventional sol-gel process was then transformed into new ceramic oxides synthesis method, which consequently drew the attentions towards the sol-gel silicate powders (Roy, 1956). Also, the process of producing silica through the hydrolysis of triethyl orthosilicate (TEOS) joined by cationic surfactants was investigated (Chiola, Ritsko, and Vanderpool, 1971). TEOS based sol-gel films were used on cathode ray tubes by a spin coating process. These films provided additional optical functionality such as anti-reflective properties or a color. Since coatings can protect surfaces from corrosion, the sol-gel coatings are focused on hybrid organic-inorganic coatings in order to get higher critical thickness than with inorganic ones. Organic-inorganic hybrid systems are produced from the structural organic compounds integration, such as methyltriethoxisilane (MTES) in the precursor solutions, thus incorporating organic groups in SiO_2 coatings.

A few years later, synthesis of organic-inorganic hybrid (OIHMs) by sol-gel process, was started (Wilkes, Orler and Huang, 1985). Since then, the sol–gel method attracted growing interest, particularly in polymer, organic-inorganic chemistry field (Brinker & Scherer, 1990). As mentioned before, there are number of methods to deposit coating on metals and sol-gel technique has several advantages over other methods which are described as follows;

Sol-gel processes are substantially centered over hydrolysis and condensation reactions of metal alkoxides M (OR) $_n$ that leads to an environmentally safe and non-hazardous method for preparing coatings. It also employs constituents not discharging pollutants to final products. One of the major factors considered in industrial processes is the temperature of synthesis. Generally the temperature of sol–gel processing is close to room temperature. Thus, the sol-gel technology can be developed as an alternative to make ready inorganic materials like ceramics and glasses and ceramics at lower temperatures, although subsequent annealing may be required at higher temperatures. Thanks to lower process temperatures, thermal volatilization and dilapidation of the trapped species will be minimized (Wright and Sommerdijk, 2001).

2.13.1 Preparation of Sol-gel Coatings

Sol-gel procedure covers creation of oxide network through condensation reactions reflected by molecular precursors media (Brinker & Scherer, 1990). Mainly, sol-gel coatings can be prepared via two approaches: The organic method and inorganic method. In general, the organic method has drawn more attention compared to the inorganic method. The organic sol-gel process commences with a solution of monomeric metal or begins with any solution with monomeric metal or metalloid alkoxides precursors M (OR) n in the beverage or the rest of low Mw organic solvents. In this formula M stands for an ingredient effective in generation of network, including Si/Ti/Al and so forth. Again, R refers to an alkyl group (C_xH_{2x+1}). On the other hand, the inorganic procedure covers network completion of networks by the way of colloidal suspension as well as the gel process.

All in all, gelation takes place through 4 phases; 1: Hydrolysis, 2: Condensation and polymerization of monomer 3: Particle evolution, 4: Agglomeration of the polymer construction after which comes network evolution extending within the whole medium which results in condensation and therefore gel formation. As a matter of fact, hydrolysis and condensation occur simultaneously and produce low molecular weight by-products, for instance water (Figure 3). Once the drying is completed, such diminutive particles get pushed away where network contracts in sync with increase of thickness. Reactants molar proportion, pH, temperature, solvent configuration can act as influential factors in such processes.

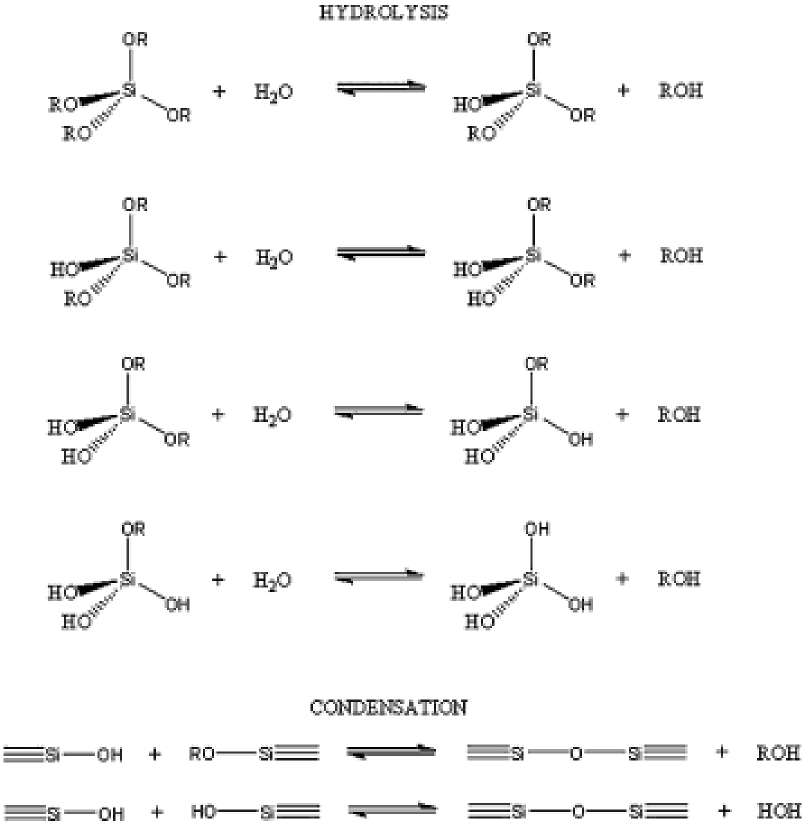


Figure 3: Hydrolysis and Condensation Involved in Making Sol-gel Derived Silica Materials

The two most common approaches of coat of gelation process over metal substance are dip & spin coat process. Subsequent to the coating deposition (in both methods), significant amount shrinkage happens, while intramural stress build up as a result of evaporation of solvents and water. Considering such internal stress, cracks are certain to appear once the film generation fails to be checked duly. Contingent over the microstructures, the amount and viable application of prepared coatings, parameters related to curing and heating treatment must be carefully adjusted.

Other methods for sol-gel film deposition include spraying and ultrasonically pulverized spraying, which emerged recently (Parkhill, Knobbe and Doley, 2001) and may serve the function of chief applications of sol-gel within the years to come.

Other methods for sol-gel film deposition include spraying and ultrasonically pulverized spraying, which emerged recently (Parkhill, Knobbe and Doley, 2001) and could be the major applications of sol-gel in the years to come.

2.13.2 Dip Coating Process

Dip coat stands among the well-known approaches to create thin films. In this process, the substance goes through and gets dipped into the coating solution; thereafter it is taken away from the solution in some constant pace (Figure 4). Coating thickness decreases with slower abandonment promptness. The stiffness is achieved through balancing some forces in stagnation point. A high-paced abandonment gathers and preserves further fluid towards substrate earlier than it can pour back over solution. The fluid viscosity and the surface tension also influence the thickness of the coating layer.

While dip coating is thoroughly efficient for making high superiority similar coatings, it also necessitates accurate controller besides pure surroundings (Scriven, 1988). The applied coating stands damp in a time being till solvent vaporizes. Heated drying can accelerate this process. Additionally, various processes involving classical thermal, UV, or IR procedures, according to the coating formulation, can cure coatings.

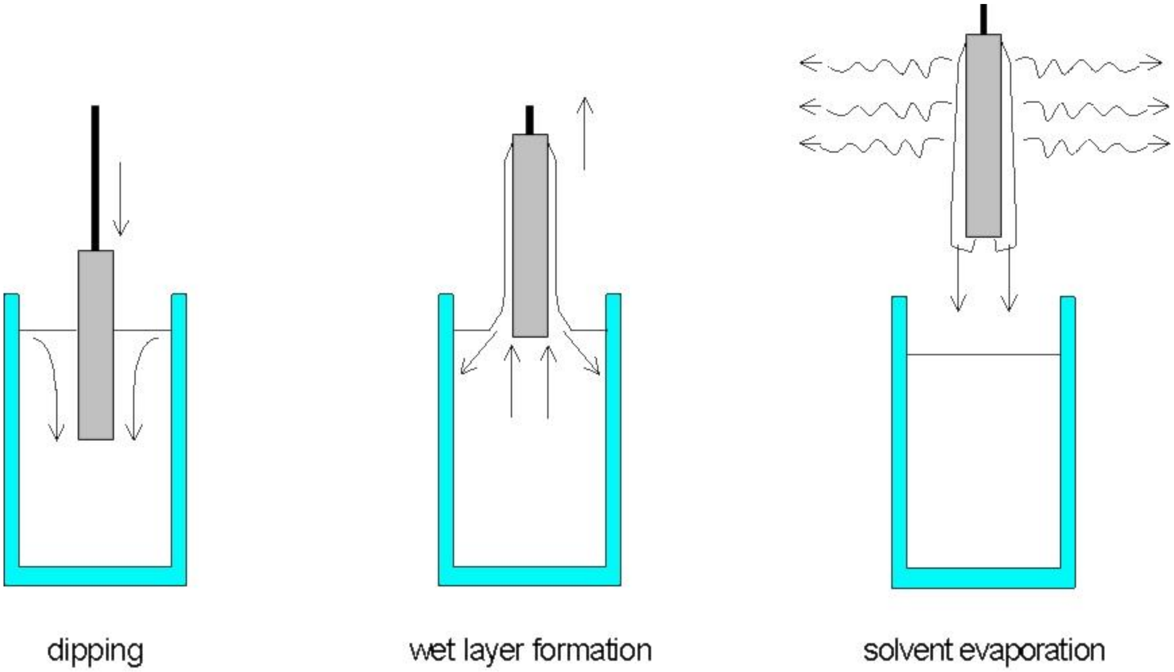


Figure 4: Stages of the Dip Coating: Dipping the Substrate, Wet Layer Formation and Gelation of the Layer by Solvent Evaporation

2.13.3 Spin Coating Process

Spin coating is a technique used to employ thin films on substrates. In spin coating the substrate is placed horizontally on a rotating platform. The substrate commences to spin very fast and the coating solution is poured onto it. The rapid rotation shoots off most of the solutions, leaving a thin layer of uniform coating. The coating thickness is accurately controlled by the angular velocity of the substrate: Slow rotation results in a thicker layer. Advantages of spin coating include uniform layer over the whole surface of the curved parts, lenses with varying curvatures can be coated uniformly with minimum thickness variation or edge effects. Nevertheless, spin coating is only applicable on one part at a time, in contradiction with dip coating in which numerous parts can be coated together. The spin coating process is divided into 4 phases as illustrated under Figure 5. Deposition, spin up, and spin off take place successively. Evaporation phase happends within the whole event as the number mean method for thinning before the close of the procedure.

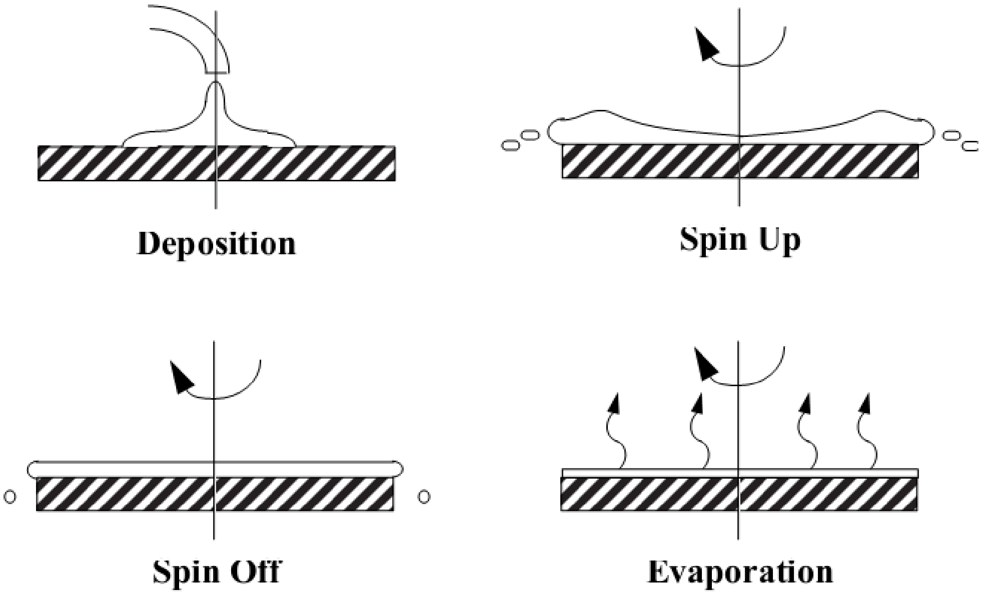


Figure 5: Spin Coating Process; The Four Stages of the Spin Coating Process

The deposition process incorporates dispensing a big quantity of fluid onto a stationary substance. The fluid gets deposited with one nozzle in the middle of substance or over some scheduled track. The speed of the substrate is increased in spin up stage so that it can perform at the highest pace. While rotational forces get transmitted in the up direction in fluid, a wave front is generated, moving to the direction of substrate edge by centrifugal force. The spin off stage is the stage, in which the overload solvent is thrown off the work piece surface as it revolves at pace in the range of 2000-8000 rpm. Centrifugal forces substantially thin the fluid till sufficient solvents are evaporated to enrich viscosity to an extent at which the flow stops. The spin off phase happens in a mater of ten seconds, following spin up, (Carcano, Ceriani and Soglio, 1993).

2.14 An Overview of Previous UV-Curable Coatings

In this section a summarized history of UV-cured coatings are presented. The table illustrates various attempts for preparing UV-cured films, which inspired us to use the aliphatic tri-functional oligomeric urethane methacrylate in synthesizing the UV-curable aluminum pigmented coatings.

Table 7: Overview of the Accomplished Studies

The investigated cases	Researchers	Year
UV-cured polyurethane acrylate (PUAs) based on PCL and TMXDI were prepared. The influence of the percentage of the reactive diluent on the viscosity was also studied.	B. Nabeth, J. F. Gerard J. P. Pacsault	1996
UV-curable polyurethane acrylates for poly (viny1 chloride) (PVC) floor coating were prepared using non-yellowing polyisocyanates.	Chang- Sik HA Soon-Joon JUNG Eunc-Seob KIM Won-soo KIM Sang--Jin LEE	1996
UV radiation curing has been used to produce weathering resistant protective coatings, high-resolution relief images, glass laminates and nanocomposite materials	Christian Decker	2002

The UV-curable urethane acrylates based on 2-hydroxylethyl methacrylate (HEMA)-terminated PU for lithographic and coating applications was attended to.	K.H. Hsieh C.H. Kuo C.A. Dai W.C. Chen T.C. Peng G.H. Ho	2003
The influence of the isocyanate type of acrylated urethane oligomer, and the additives (HALS, UVA and TiO2), on the weathering of UV-cured films was dealt with.	Byoung-Hoo Lee Hyun-Joong Kim	2005
Three PU-type polymeric phtoinitiators containing side-chain, benzophenone and coinitiator amine were synthesized via polycondensation of DATBP, different diisocyanates and MDEA.	Jun Wei Hongyu Wang Xuesong Jiang Jie Yin	2007

Chapter 3

Experimental

3.1Materials

The required materials for synthesis of ATOUA are listed in Table.9. All reagents are commercially available.

Table 8: Materials and Manufactures

Hydroxyethyl methacrylate (HEMA)	Merck, Germany
Isophorone diisocyanate (IPDI)	Merck, Germany
Trimethylolpropane (TMP)	Merck, Germany
Acetone	Merck, Germany
Dibutyltin dilaurate (DBTDL)	Aldrich, Germany
Benzophenone	Merck, Germany
N-methyl diethanolamine (NMDEA)	Merck, Germany
Hexandiol diacrylate (HDDA)	Aldrich, Germany
Trimethylolpropane triacrylate (TMPTA)	Aldrich, Germany
Aluminum pigments (Leafing and non-Leafing)	Eckart, Germany

3.2Methods

3.2.1 Synthesis of Tri-Functional Urethane Methacrylate

The first experiment in this study is the synthesis of aliphatic tri-functional urethane methacrylate (ATOUA) and for this purpose tri-functional urethane methacrylate was prepared in three steps.

, 0.1 mol (13.4g) of trimethylolpropane, DBTDL (as catalyst) and acetone (50ml) were charged into a reactor to synthesize the reactive monomer with three NCO terminal groups. Then isophorone diisocyanate was drop wise added into the mixture and subjected to magnetic steering for 2h under magnetic stirring. In the next step, aliphatic tri-functional oligomeric urethane methacrylate (ATOUA) was synthesized by adding 0.3 mol (39g) of hydroxyl ethyl methacrylate and tri-functional reactive macromonomer in 55 ^{o}C for 1h. Eventually, acetone was removed by vacuum in 60 ^{o}C for 1h.

3.2.2 Formulation of UV-Curable Aluminium Pigmented Coating

In these experiments, aluminum pigments (both leafing and non-leafing) were formulated with the ATOUA organic-inorganic hybrid film as binder with suitable dispersing agent in order to prepare collection of radiation-curable coatings in the presence of benzophenone and N-methyl diethanol amine as phtoinitiator and co-initiator, respectively. Also, trimethylol propane triacrylate (TMPTA) and 1,6-hexanediol diacrylate (HDDA) were added to the mixture as reactive diluents. In order to yield an aluminum pigment loading of 0.6 wt. %, film formulations were calculated and are shown in Table 10.

Table 10: Formulation of UV-Curable Aluminum Pigmented Coatings

Component	Parts by weight
ATOUA	59%
Leafing aluminum pigment	0.6%
HDDA	20%
TMPTA	10%
Wetting and dispersing agent (OA 1OEO)	5%
N-methy diethanolamine	5%
Benzophenone	5%

3.2.3 UV Irradiation Set-Up

An ever-increasing sector in paint and coating industry is UV (radiation) processing to dry or cure a coating on timber, metal or plastic goods. In a radiation cure coating procedure, the UV light spectrum emitted through an ultraviolet source interacts with exceptional coating chemistries to produce a high quality, lasting coating. In a great deal of functions, UV curing can reach the coating quicker and consequently, at a less cost in comparison with other coating techniques. During the radiation curing process the samples were placed in air and exposed to a mercury lamp. This lamp emits ultraviolet light with highest intensity at a wavelength of 365 nm. ATOUA formulations were first applied on a steel substrate and then subjected to ultraviolet radiation of medium-pressure 1KW mercury lamp at 10 centimeters distance for 2 minutes to obtain cured films. Also, in the aim of applying the ATOUA formulations onto the steel substrates, suitable pretreatment of these substrates is required. Thus the pretreatment of the steel substrates was carried out using a bar applicator. The UV irradiation set-up is illustrated in Figure 6.

Figure 6: Example of UV Irradiation Set-up

3.2.4 Substrate Pre-treatments

3.2.4.1 Phosphate Conversion

In general, phosphate coatings are applied on the surface of the basis metal to transform this surface into a non-metallic crystalline coating. In this process first a diluent solution of phosphoric acid and phosphate salts was prepared. Then the substrate will be immersed in the solution and chemically reacted with the surface to form a layer of insoluble, crystalline phosphates and upon sealing of the surface from chemical solution, the reaction ceases.

Phosphate conversion is the built-in and inalienable section of majority of finishing procedures, ensuring the functions mentioned bellow: absorbing lubricants, increasing chemical attack endurance, enhancing aesthetics, promoting adhesion and providing mar resistance and/or facilitating cold formation. Phosphate conversion can be applied on various substrates such as aluminum, zinc, silver and tin.

3.2.4.2 Electro Deposition Painting (ED)

Electrodeposition (ED) is becoming a well-accepted technique for protective or decorative coatings and continues to be extensively employed in number of industries like automotive industry. The main aim behind the process is providing the substrate with a high weathering resistance, even at very low thickness. In this process the metal substrate immersed in an aqueous bath solution and coated with charged organic primer (positive or negative ions), and then uses an electric field to electrophoresis the paint on the metal surface. The surface was then goes to water and drying process to ensure paint stays over metal surface. Deposits are generated to meet a range of designer demands, such as; giving the substrate a high weathering resistance even at very low thicknesses.

In this experiment, cold-rolled steel panels were selected since they are applicable in automotive components. Panels were phosphated firstly and then electro deposited with a thickness of approximately 30 microns and the applied epoxy-based electro deposition paint was purchased from PPG industries.

3.2.5 Characterisation of the Product

3.2.5.1 Chemical Structure and Morphology

In the current study, a Perkin-Elmer spectrometer was employed to obtain Fourier transform infrared spectroscopy (FTIR) spectrum and confirm the chemical composition of the synthesized oligomer. FTIR characterization was performed in nitrogen-protected chamber at room temperature. ^{1}HNMR and ^{13}C-NMR spectrum were recorded with 500 MHZ Bruker spectrometer in CDC13 solvent. The morphology of the coatings was then assessed via scanning electron microscopy (SEM) utilizing a LEO-SEM model 44i.

3.2.5.2 Thermal Properties of UV-Cured ATOUA

In the current study, TGA and DSC analysis was hired to investigate the cured coatings thermal characteristics. TGA is a thermal analysis for fast assessment of the thermal steadiness in various substances. Alteration in chemical and physical characteristics properties of materials is measured as a function of temperature gain, or as a function of time, which also demonstrates the decomposition of polymers at different temperatures. Differential scanning calorimetry (DSC) is one of the commonly employed methods that check the heat flow.

Thermal degradation of the cured samples was evaluated by a Perkin-Elmer Pyris-6 thermo gravimetric analyzer from room temperature to 600 centigrade under nitrogen atmosphere at a heating rate of 10 centigrade per min and the weight loss/temperature graphs were also recorded. In the aim of observing the crystallization behavior of the cured films, DSC analysis was conducted using a Perkin-Elmer DSC Pyris Diamond model device. Samples were analyzed under N_2 ambiance from room temperature to 200 ^{o}C at a scale of ten ^{o}C /min. Mechanical and Physical Test Methods

3.2.5.2.1 Pendulum Hardness Test

Pendulum hardness test was employed to examine shallow stiffness of the cured films so as to see the impacts of different types of pigment orientation on the hardness of the coating. In this test, the testing device comprises one pendulum, unrestricted to sway on 2 balls, which rest on a coated substrate. In the pendulum hardness test, the principle is according to the faster decrease of amplitude of the pendulum's oscillation in case of a smoother coating. The harshness of coating is assessed through the number of fluctuations of pendulum in the specific limited amplitude derived by accurate photo sensors. The sways reflected by pendulum is archived by an electronic counter. Actually the hardness test is qualitative test method for comparing the surface hardness of kinds of coatings. The pendulum hardness of ATOUA coating gradually decreased with the introduction of pigments in the coating formulation. The inevitable reduction of coating pendulum hardness through the introduction of pigments is because of the addition of the pigments into the coating formulation, which adds to the elasticity and the resilience of the ATOUA coating that is pointed as an abated hardness of the coating. Hardness of the coated surface was evaluated by Konig pendulum hardness tester Elcometer model 3040.

Figure 7: Konig Pendulum Hardness Tester

3.2.5.2.2 MEK Solvent Rub Test

One of the mechanical properties essential for coating to perform successfully its protective role, solvent resistance to methyl ethyl ketone (MEK) was evaluated through scrubbing coatings with MEK 200 times. MEK test was carried out to anticipate the capability of the coating to stand against cracking initiated by quick distortion. All samples passed this test (ASTM D 5402-06).

3.2.5.2.3 Impact Resistance Test

In this test, an unchanging load indenter was permitted to drop on the coated substrate by a directed tube and the distorted coating surface was visually observed and reviewed by the use of magnification lens for cracks made because of fast impact. This test was employed in intrusion form operating an intended with a semicircular head and a thickness of 0.625 inch and a 2 1b (1.58 cm, 907.18 g) load test (ASTM: D 2794).

3.2.5.2.4 Cross Cut Test

The adhesion of a coating on a substrate is a crucial mechanical property together with the corrosion protection. Crosscut test is a rapid and simple technique, which is usually used to establish whether the adhesion of a coating to a substrate is at an adequate level. In this test a lattice pattern or X-cut was used to evaluate the endurance of the coating to split-up from substrate. The pattern cuts through the coating and pierces into substrate.

An adhesive tape applied to the sample and pulled off. Adhesion was examined by a crosscut test where a lattice pattern saw scratch into the coating by a cutting blade. Then, glue tape was put over the lattice pattern, tightly scrubbed by fingertip and detached upon 15 minutes.

The quantity of detached cubes by glue tape was then matched with the quantity of remained cubes on the coated substrates (ASTM-D3359).

3.2.5.2.5 Salt Spray Test

Coatings offer corrosion resistance to metallic surfaces and thus this quality has to be examined through a salt spray test. This test is an expedited and repeatable corrosion test, which mimics a corrosion attack to coated substrate on order to anticipate its suitability in use as a protective layer. The amount of the corrosion is assessed after a while. The duration of the test depends on the corrosion resistance of the coating. In this method, samples were placed in a testing chamber. Thereafter, a salted solution, a solution of 5% sodium chloride is atomized by a nozzle, which produces an intense corrosive environment. In the study in question, coatings were tested under 1000h salt spray test (Figure 8) and the coatings showed superior corrosion resistance and all samples passed the test (ASTM D2059/D2059M).

Figure8: Salt Spray Test

3.2.5.2.6 Mandrel Bending Test

In this test coated substrates are bent over a conical or cylindrical mandrel and properties like cracks, color change, adhesion, etc. of the coated substrates are evaluated. Findings, produced by decreasing mandrel sizes, indicated the degree of elasticity of the coating. Flexibility of the coated substrates was also evaluated at an angle of 180^o on conical mandrel (Elcometer Co.) according to ASTM D4145-83. The employed conical mandrel in the present study is shown in Figure 9.

Figure 9: Mandrel Bending Test

3.2.5.2.7 Gloss

Gloss is a degree of the capability of a coating to mirror a ray light at a specific angle (for instance 60 centigrade) without spreading. Gloss is an optical feature that describes surface capability to mirror light into the specular direction without scattering it. The appearance of gloss depends on a number if parameters including surface conditions and illumination angle. As it was mentioned before, gloss is an important quality in coatings and thus in the current project, a gloss meter (Figure 10) was utilized to measure the angular gloss in the coated films. Gloss is measured by guiding a uniform intensity light beam at a fixed angle and then by the measuring the mount of reflected light at the same angle. BYK-Gardner Micro-Tri Glossmeter is employed to measure the angular gloss in the coated film and evaluate the angular gloss of the coatings (ASTM D523).

Figure 10: Gloss Test

Three measurement angles are specified to cover the majority of the industrial coatings applications (Table 9). The angle is selected for a particular application based on the anticipated gloss range.

Table 9: Gloss Measurements for Industrial Applications

Gloss range	60^o Value	Angle
High Gloss	>70 GU	20^o
Medium Gloss	10-70 GU	60^o
Low Gloss	<10 GU	85^o

*GU= Gloss Unit

3.2.5.2.8 Cupping Test

The cupping test measures the ductility of the coating, which is utilized to measure the ability of coated substrate to bear plastic deformation in stretch forming. The test consists of forming an indentation by a punch, which has a spherical end against a coated substrate that is clamped between a blank holder and a die, until a crack is propagated. Then the depth of the cup is measured (ASTM D2749-93).

3.2.6 Sol-gel Coatings with Metallic Effect

It is worth mentioning that various experiments have been carried which enabled us to find the optimum condition for producing aliphatic tri-functional oligomeric urethane methacrylate (that is used for UV-curable aluminum pigmented coatings) successfully. In the next part we only mention a short summary of the attempted trials. At First, several attempts have been made for synthesizing crack-free sol-gel films and after several experiments we produce coating with no cracking. Then organic-inorganic hybrid films were synthesized using aluminum, titanium oxide and mica as pigments and it was concluded that Al was the best pigment in such formulations. Also, the results of the various applied formulations will be presented in the result and discussion section.

3.2.6.1 Preparation of the Sol-gel Coating

Sol-gel processing can be used to produce the organic/inorganic hybrid films. Sol-gel films are made through deposition of sols onto a substrate. Various methods are employed for the deposition of the sols, including spin- and dip coating. In the current experiment, all samples were ultrasonically cleaned in acetone for 5 minutes prior to the dip and spin coating process. Tetra-orthosilicate (TEOS, 98%), water and 2 drops of Hydro chloric acid (pH=1.5) were mixed under magnetic stirring for 24 hours to let the sol to hydrolyze and ethanol was used as a solvent. The cleaned samples were then spin coated at speed of 5000 rpm for 120 seconds. Subsequent to the dip coating or spin coating, the substrates were heat treated at 600^{o}C for 1 h. The resultant SEM images will be shown in results and discussion part.

In order to overcome the observed cracking, methyltriethoxisilane (MTES) was used as an alternative instead of TEOS to increase the organic residue. iso-propyl alcohol (IPA) was also used instead of ethanol. All samples were heat treated at 600^{o}C for 1 h.

In another effort for improving the coating quality, a dispersant was introduced to the gel. A dispersing agent is of two groups: non-surface active substance and surface-active. This dispersant will be introduced into suspension, often a collide, to facilitate detachment of subdivisions and to avoid setting or clumping. In the current research the dispersant was an anionic acrylic-PEG copolymer (Mw=1000), which is a comb surfactant.

In another effort, the same experiment was repeated using a silicon-polyether copolymer (SP25) two drops in 10g resin. Introducing the SP25 to the gel has a positive effect on the coatings.

3.2.6.2 Synthesis of Urethane Trimethacrylate (UTMA)

Urethane trimetacrylate was prepared by 1,8-diamino-4-aminomethyloctane (Chemos GmbH, Germany), dichloromethane (CH_2Cl_2), triethyl amine (TEA), and trichloromethyl chloroformate. All materials were used as received from Merck without further purification. A solution of 1,8-diamino-4-aminomethyloctane (17.33gram; 0.1mol) and triethyl amine (60.6 gram; 0.6mol) in dichloromethane (100mL) was supplemented drop by drop to a solution of trichloromethyl chloroformate (35.61gr; 0.18mol) in dicloromate (100 mL) at 0 centigrade over a period of 30 minutes under magnetic steering. The ice bath was detached from solution and mixture stirred for a more 60 minutes in 40 centigrade prior to the vaporization of the volatiles in vacuum. Then triethyl ammonium chloride filtered in organic stage. The solvent was detached in vacuum to produce 1,8-diisocyanato-4-(isocyanatomethyl) octane in liquid phase (23.1gram; 92 percent). Finally, urethane trimethacrylate (UTMA) was synthesized by the reaction of 1,8-diisocyanato-4-(isocyanatomethyl) octane (12. 5g; 0.05 mol) and HEMA (23. 4g; 0.18 mol) in the presence of 0.3g of DBTDL (as a catalyst).

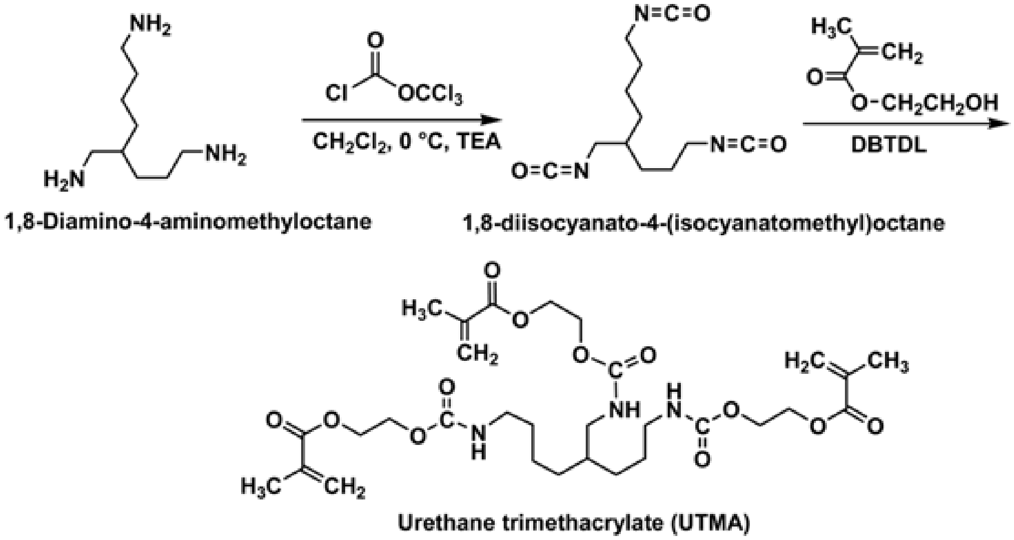


Figure 3 Synthesis of Urethane Tri-Methacrylate (UTMA)

3.2.6.3 Preparation of the Organic-Inorganic Hybrid Film Based on UTMA

Polyurethane acrylates are broadly employed as oligomers for radiation curable coatings, which render excellent mechanical and physical properties, such as adhesion on substrates, impact strength and flexibility. Organic-inorganic hybrid films can be prepared by sol-gel method. In the present study, urethane trimethacrylate (UTMA), SP25 (3 drops), aluminum pigments (1g) were ultrasonicated for 10 minutes and then placed in the oven. Aluminum pigment was chosen to formulate with the hybrid film since it has various properties including high strength, low thermal conductivity and good electrical insulation. However, results suggested that Aluminum is a better choice in comparison with TiO_2 and mica. TiO_2 is the commonly used white pigment due to very extreme refractive index and its brightness, suggested by only a few other materials surpass it. Mica is a group of silicate sheet. The crystalline configuration of the mica produces a layer that is able to break into slim sheets generally triggering leafing in rocks. Mica is chemically inactive, dielectric, elastic, hydrophilic, flexible, insulating, lightweight, platy, refractive, reflective, resilient and range in opacity from opaque to transparent. Mica is stable when subjected to moisture, light, electricity, and high temps. It has huge electrical characteristics as an insulator and as a dielectric, and can stand an electrostatic field as scattering least energy as heat; it may also be divided extremely slim (0.025 to 0.125 mm or thinner) , sustaining its electrical characteristics.

3.2.7 Synthesis of Tri-Functional Urethane Methacrylate

Synthesis steps of tri-functional urethane methacrylate were explained at the experimental part of this thesis. In this section a schematic of these steps are illustrated.

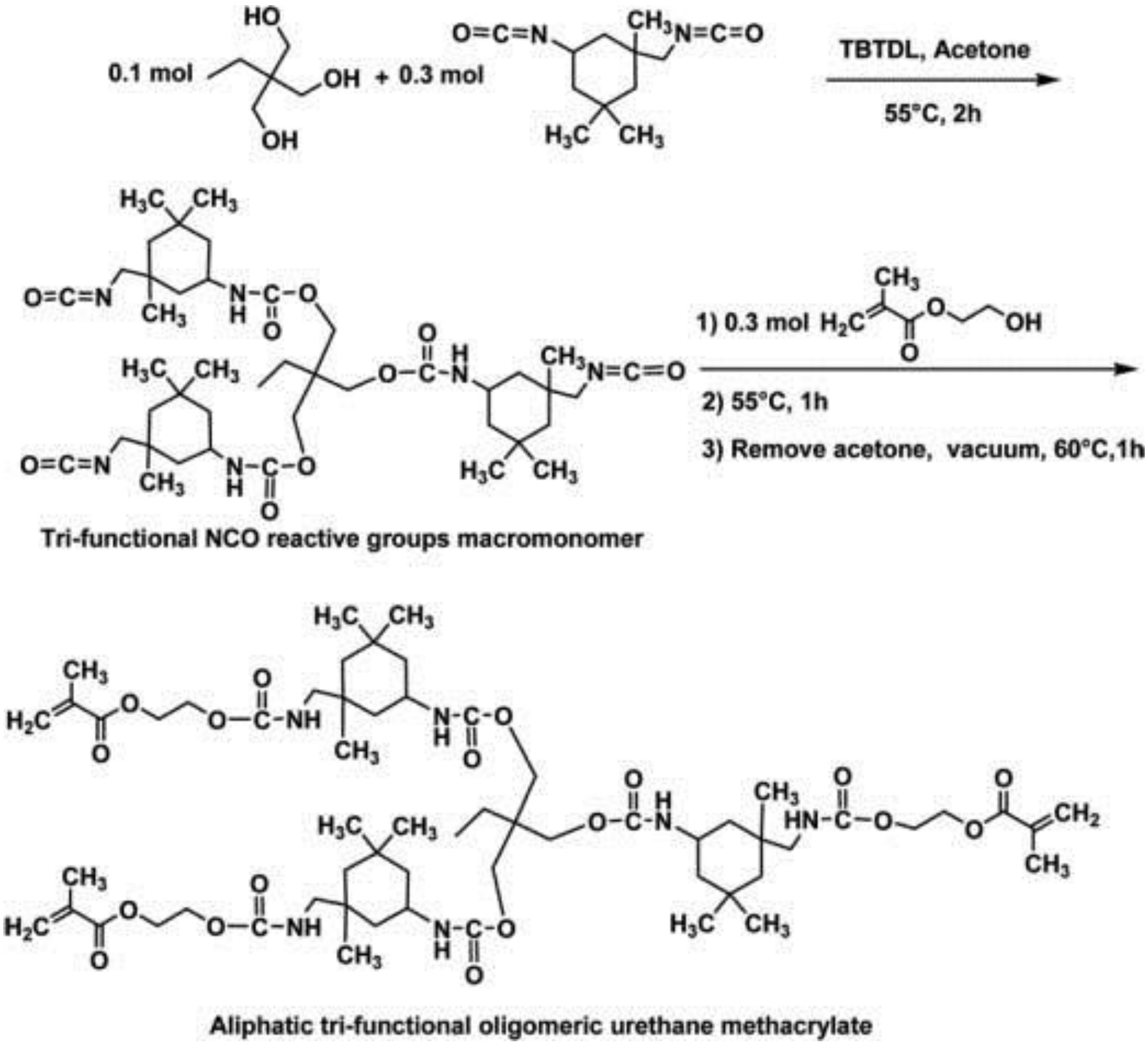


Figure 12: Synthesis of Aliphatic Tri-functional Oligomeric Urethane Methacrylate

Chapter 4

RESULTS AND DISCUSSION

4.1 Aluminium Pigmented Chromate- free Metal Effect Coatings on Steel Substrates

Stainless steel and steel substrates are extensively employed in various industrial areas for mechanical and corrosion characteristics. Still, they cultivate to decompose when exposed to corrosive environment. As a result, steel substrates should be protected from corrosion by means of sol-gel coatings or other methods. It should be mentioned that steel and aluminum substrates are preferred for the coating process because of their great adhesion. Coating adhesion to the substrate is of great importance for a complete mechanical characterization of the surface.

It is worth mentioning that various experiments have been carried out which enabled us to find the optimum condition for producing aliphatic tri-functional oligomeric methacrylate (that is used for UV-curable aluminum pigmented coatings) successfully. next part deals with a short summary of attempted trials. At first, several attempts have been made for synthesizing crack-free sol-gel films and after several experiments we produced coatings with no cracking. Then organic-inorganic hybrid films were synthesized using aluminum, titanium oxide and mica as pigments and it was concluded that Al was the best pigment in such formulations. Also, the results of the various applied formulations will be presented in this section.

4.2SEM Results of the Prepared Sol-gel

Sol-gel processing was explained in the experimental part and in this section. SEM images of these sol-gel films that were prepared by coating method are shown below.

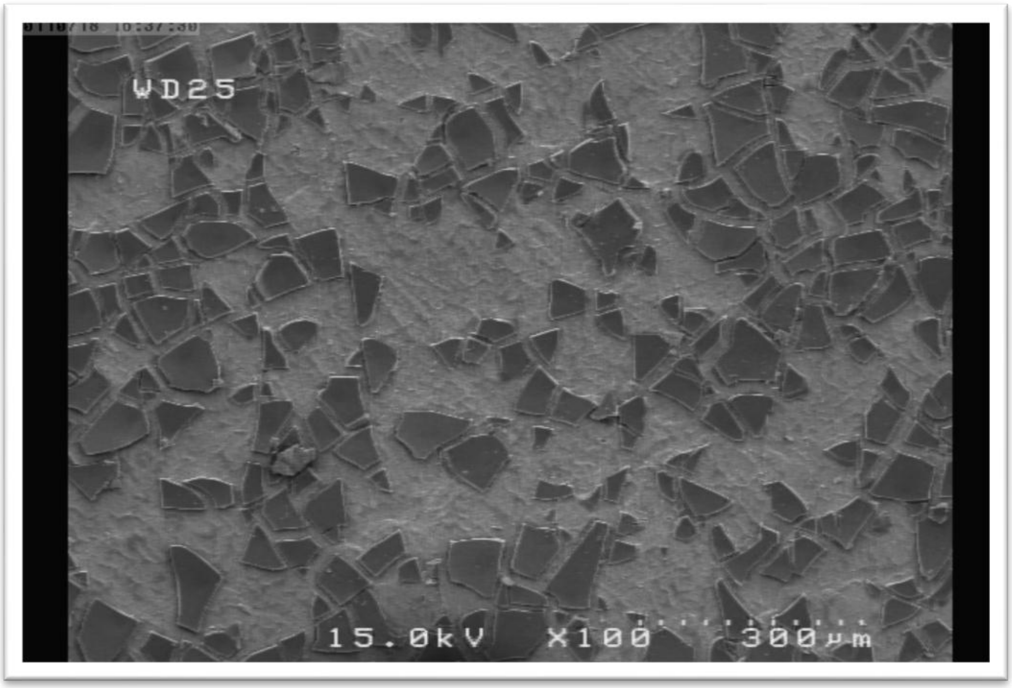


Figure 13: Scanning Electron Microscopy Images of Sol-gel Coating

SEM image illustrate the coating has lots of cracks.

In another effort for improving the coating quality, a dispersant was introduced to the gel. The SEM micrographs of the samples showed that polyethylene glycol (PEG) has a positive influence on the coating quality (Figure 14).

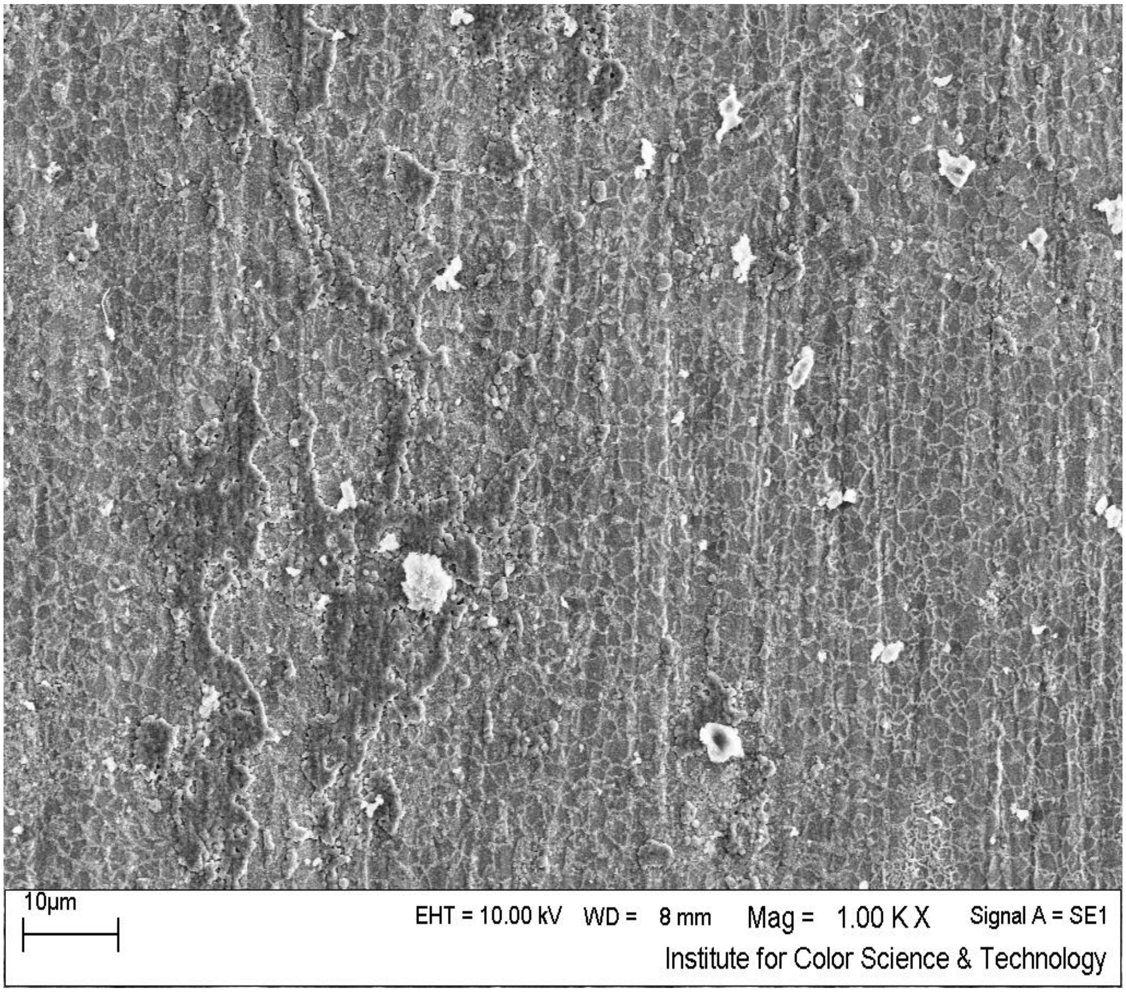


Figure 4: SEM Images Shows the Effect of the Organic Residue Increase to Overcome Cracking

As mentioned in the experimental part another effort was made with a silicon-polyether copolymer (SP25). As shown in SEM images, introducing SP25 to gel has a positive effect on coating quality (Figure 15).

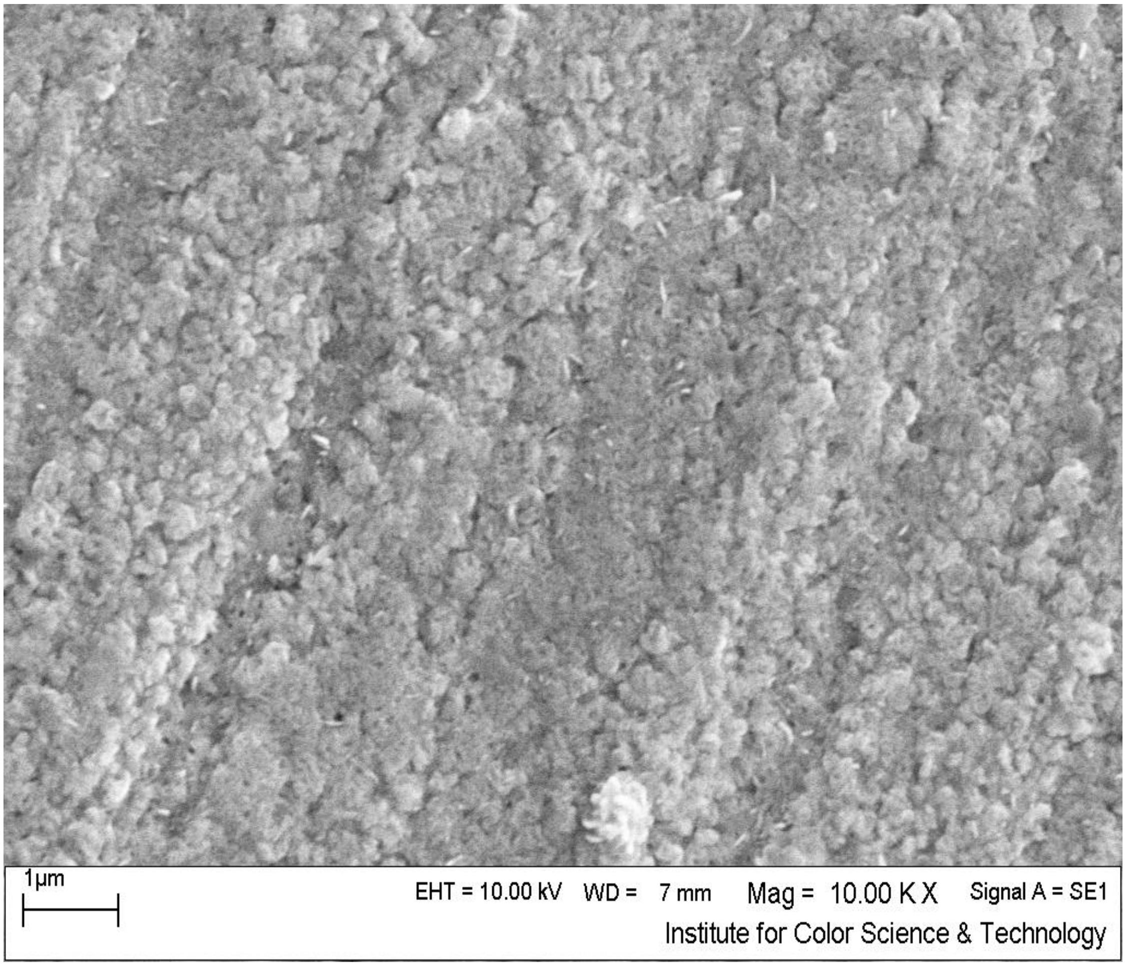


Figure 5: SEM Micrographs of the Samples Showing the Influence of Dispersant to Overcome Cracking

Subsequent to the preparation of the silica sol-gel, pigments were added to the sol-gel coating formula. It can be seen that all the employed methods were not a complete success, since by introducing the pigments into silica sol-gel, pigments did not stick to the coatings, available pigment sizes were larger than the coating thickness, and more importantly the coatings were not crack free.

4.3Spectroscopic Analysis of the Product

4.3.1 FTIR Analysis for ATOUA

IR spectra of ATOUA polymers are illustrated in Figure 16. We may observe that the peak at 3359 cm^{-1} concerning N-H stretching vibration of urethane. The C-H groups of HEMA illustrate an absorption peak at 3025 cm^{-1}. The mixture of IPDI+HEMA spectrum shows a sharp peak in 2929 and 2957 cm^{-1}, which refers to the C-H stretching vibrations of CH3, CH2, and CH in the alkyl chain. Pure IPDI spectrum shows a sharp absorption band for NCO groups at 2250 cm^{-1}. It is noticeable that NCO stretching vibration of IPDI in 2250 cm^{-1} has vanished; for thorough blockage of IPDI. C-H bending vibration of CH is appeared in 1366 and 1386 cm^{-1}. C=O stretching vibrations of ester HEMA and urethane demonstrate a broad band in 1721 cm^{-1}. Moreover, the C=C groups of HEMA show an absorption peak at 1637 cm^{-1}. The peak at 1533 cm^{-1} represents N-H bending vibration of urethane. C-H bending vibration of CH2 is observable within 1409 and 1461 cm^{-1}. The absorption peak at 1301 is correlated to C-N stretching vibration of urethane. C-O stretching vibration of ester HEMA indicates an absorption peak at 1169 cm^{-1}. C-O stretching vibration of urethane can bee seen at 1042 cm^{-1}.

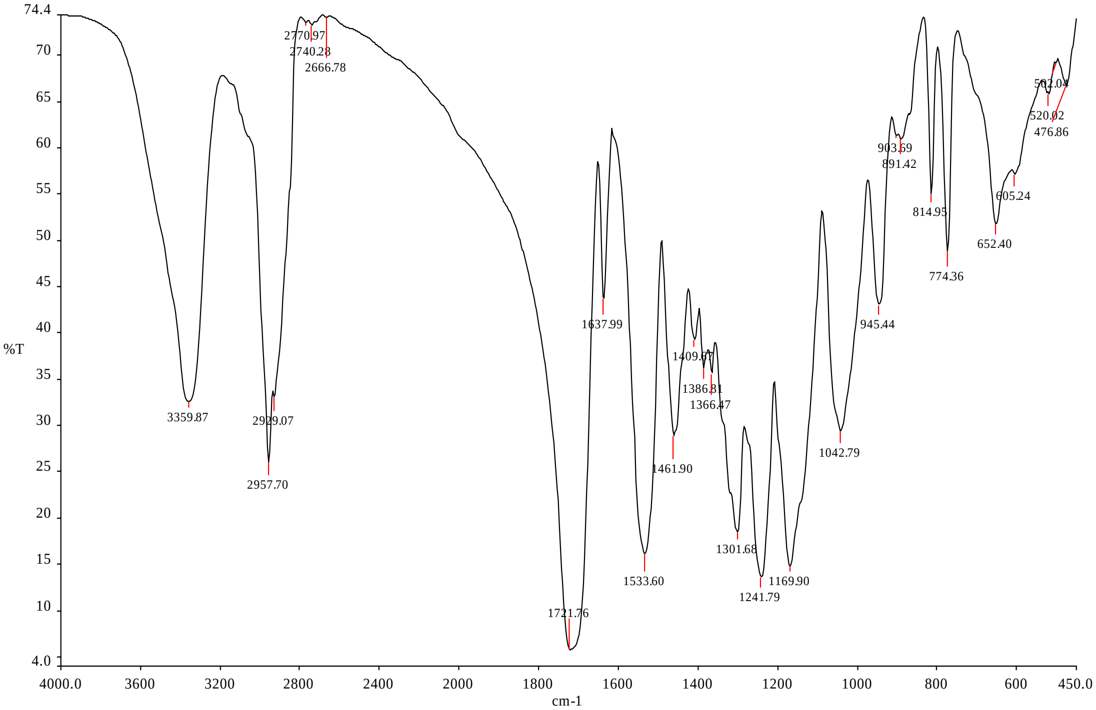


Figure 6 FTIR Spectrum of ATOUA

4.3.2 ^{1}H-NMR and ^{13}C-NMR Analysis

In this section the structure of UTMA is studied by ^{1}H-NMR and ^{13}C-NMR spectra.

4.3.2.1 ^{1}H-NMR Spectra

The structure of the synthesized ATOUA is shown in figure 17.

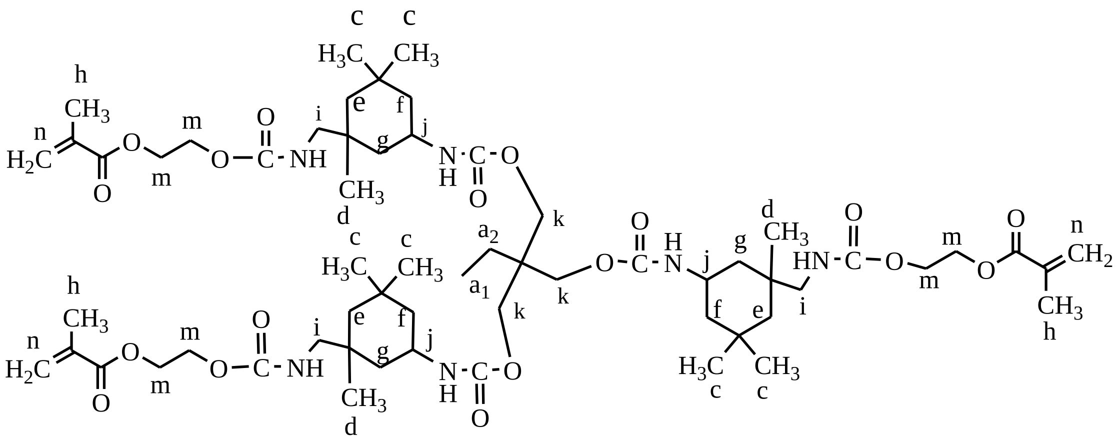


Figure 7: Structure of ATOUA

^{1}H-NMR spectra demonstrate the structure of the synthesized product. The protons of methyl (CH_3) in ATOUA, which are related to the HEMA, appeared at 2 ppm. Protons of saturated OCH_2 in HEMA appeared at 4.4 ppm. Moreover, protons of unsaturated methylene (CH_2) in HEMA are appeared at 5.7 and 6.2 ppm.

In the IPDI ring, methyl (CH_3) groups are observed at 0.9 and 1 ppm. Protons of methylene (CH_2) are also appeared at 1.8, 1.5 and 1.3 ppm, respectively. CH_2-NHCO and methylene (CH) of IPDI are appeared at 3 and 3,4 ppm, respectively. NH group of urethane is seen at 5.1 ppm in form of a broad peak.

In TMPT, protons of CH_2-NHCO are appeared at 4,1 ppm. Protons of CH_2 and CH_3 are observed at 0.8 ppm. Finally, other protons are shown in ^{1}H-NMR spectra (Figure 18).

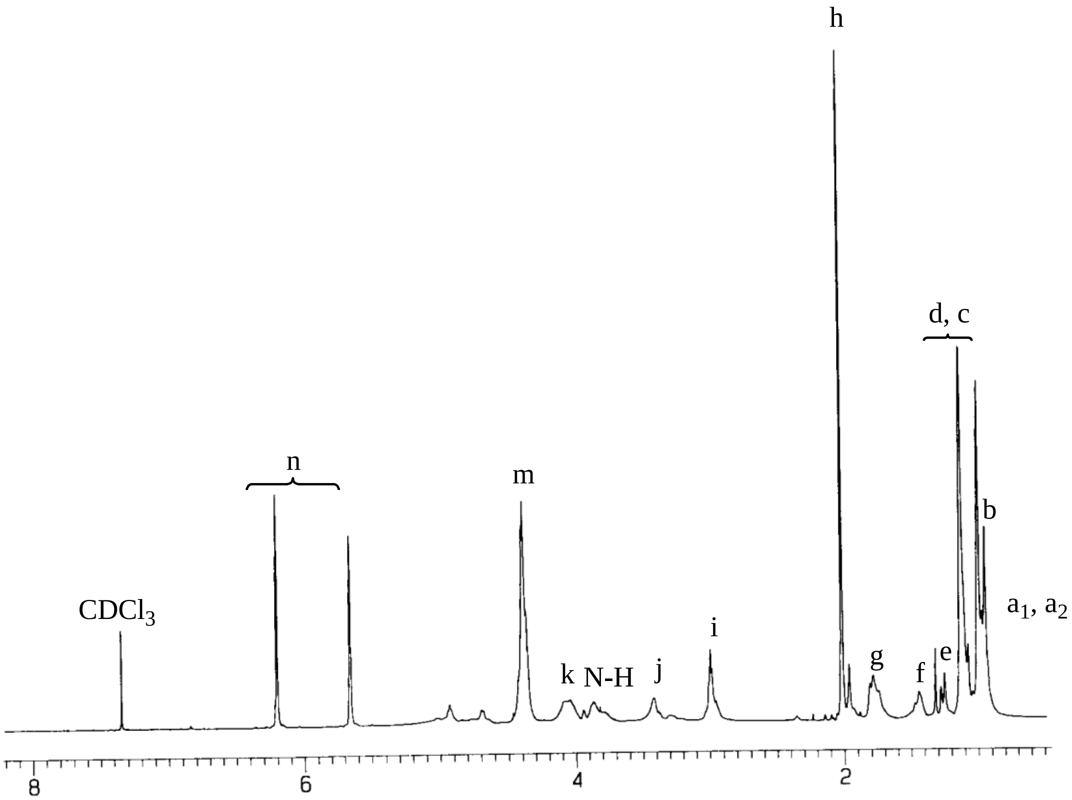


Figure 8: ^{1}H-NMR Spectra of ATOUA

4.4.2.2 ^{13}C-NMR Spectra

Schematic structure of ATOUA for 13C-NMR analysis is illustrated in figure 19. ^{13}C-NMR spectrum demonstrates the structure of the synthesized product. CH_3 and unsaturated CH_2 of HEMA were appeared at 18.6, 125, and 136 ppm, respectively. Carbonyl group and saturated CH_2 of HEMA were also observed at 168 and 62 ppm, respectively.

In IPDI, methyl groups (CH_3) were seen at 23 and 26 ppm. The connected CH_2 to the urethane band observed at 45 ppm. CH_2 groups in the inner ring of IPDI were observed at 30, 31 and 35, respectively.

In TMPT, the connected CH_2 to urethane band appeared at 55 ppm. Also, other carbons of ATOUA are shown in ^{13}C NMR spectrum (Figure19).

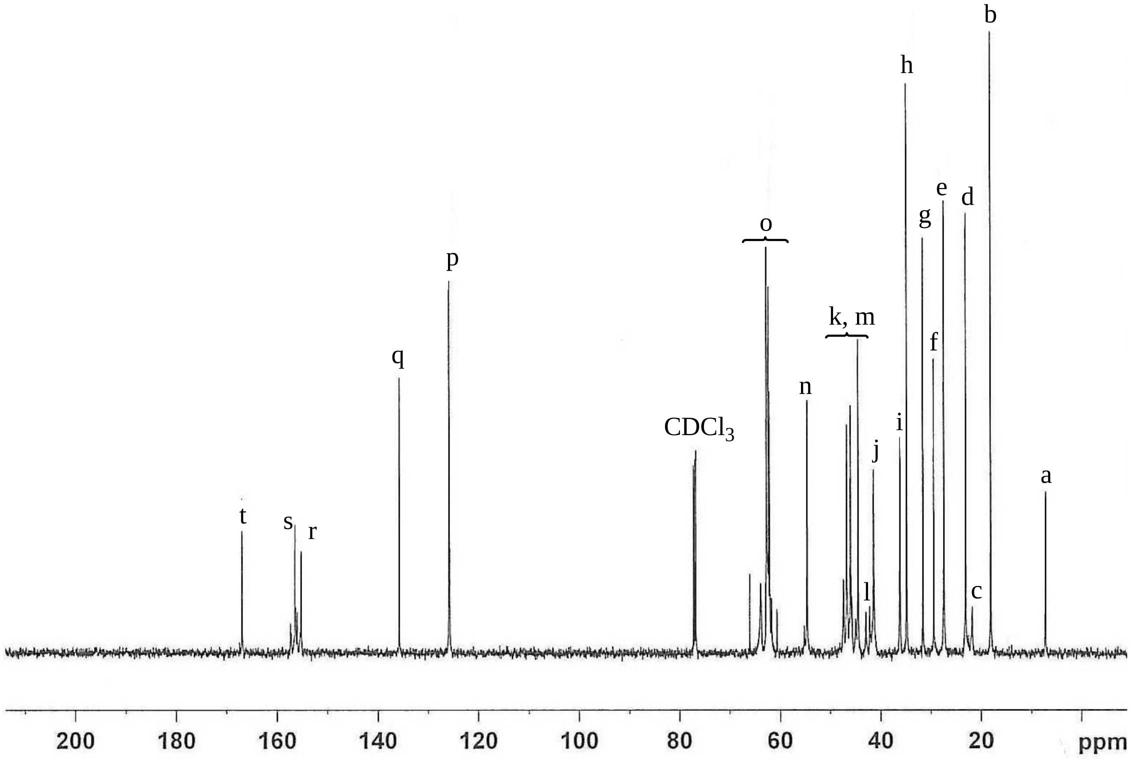
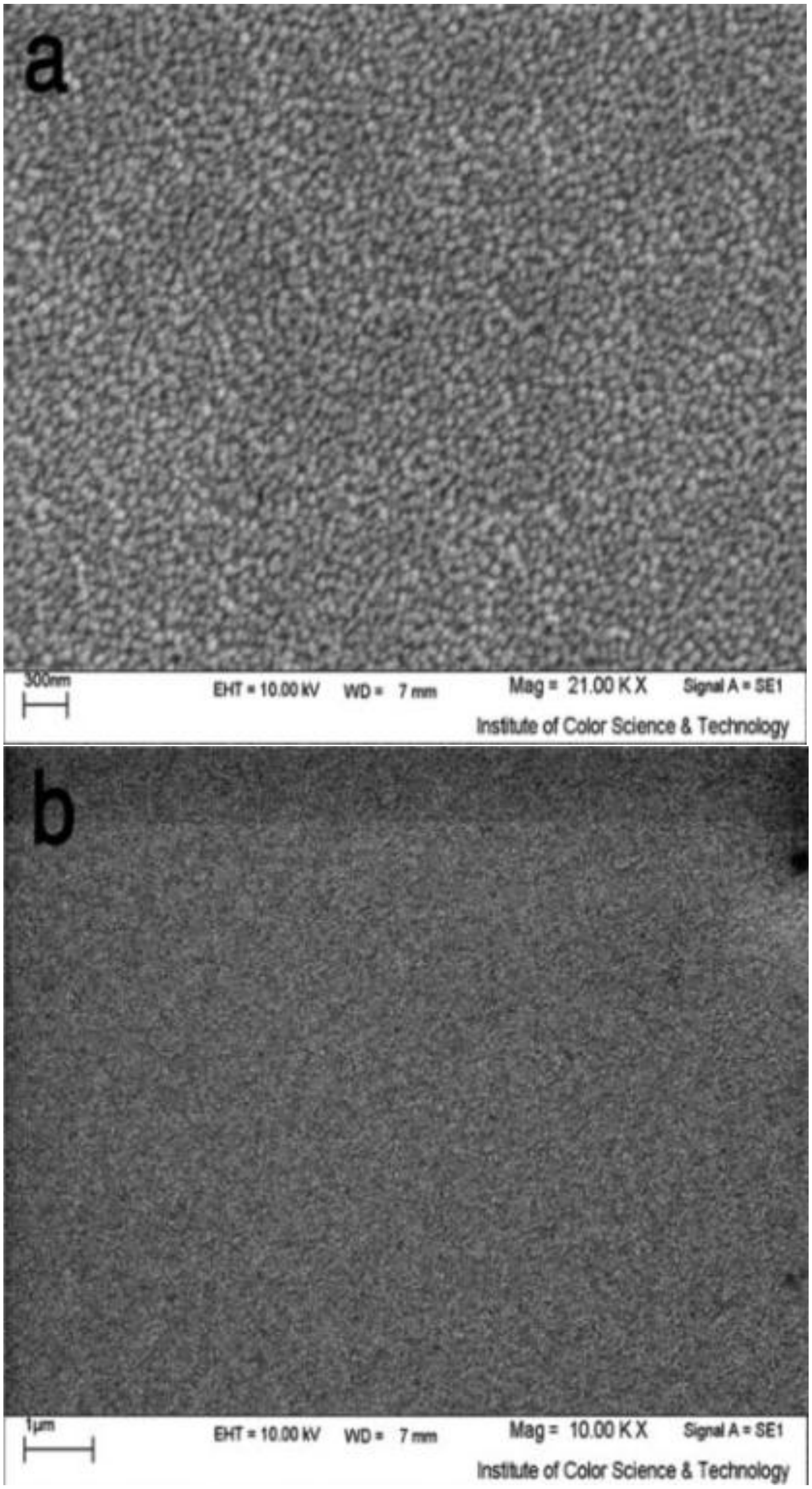


Figure9: ^{13}C-NMR of ATOUA

4.4Morphology

In this investigation, SEM analysis employed to garner data about homogeneity of the coating on the metals. SEM is used to visually appraise the dispersion of aluminum pigments and the surface morphology of the coating. Scanning electron micrographs demonstrate a crack free coating involving aluminum particles, which are evenly dispersed in ATOUA matrix. Figure 20 demonstrates the SEM images of ATOUA with leafing and non-leafing aluminum pigments and ATOUA with no aluminum pigments.



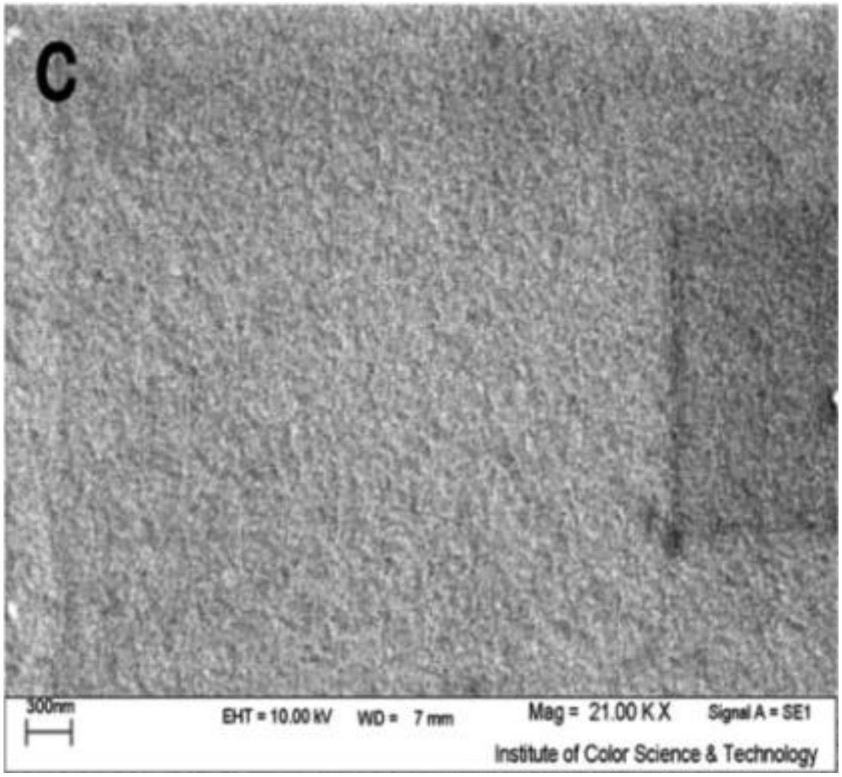


Figure 20: SEM of a ATOUA with Non-leafing Aluminum, b) ATOUA with Leafing Aluminum and c) ATOUA with no Aluminum Pigments

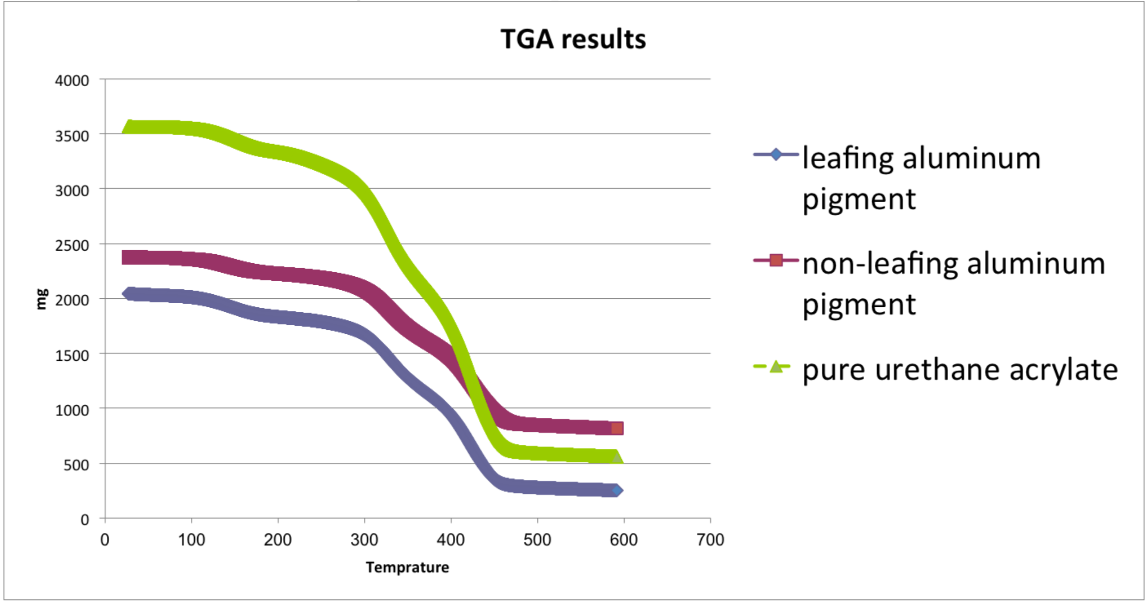
If we carefully investigate the micrographs, there is no pore in the coating and the structure is solid.

4.5Thermal Behaviour of ATOUA

4.5.1 Thermogravimetry Analysis (TGA) and Differential Thermogravimetric Analysis (DTG)

Figure 21 and 22 illustrates the thermogravimetry analysis (TGA) and differential thermogravimetric analysis (DTG) plots of the UV-cured ATOUA from 30ºC to 600 ºC. Thermal decomposition of the coatings started from 300 to 450◦C and almost 75% decomposition took place between these two temperatures. The cured film shows a 5% weight loss at 188◦C and a 10% weight loss at 211◦C. The degradation can be divided into three stages. The first stage of the degradation occurs in the tempera- ture range of 180 to 345◦C and the maximum rate of weight loss occurs at 325◦C. The low degradation temperature is due to the less stable polyurethane which can be decomposed from alcohol and isocyanate groups (4). The second stage of degradation takes place in the temperature range of 345 to 450◦C, which may be due to the residual material. The last stage is observed between 450 to 600◦C, in which the product is further decomposed to form nitro- gen and carbon volatiles. Samples containing either leafing or non-leafing aluminum pigments exhibit similar weight loss patterns. Pure ATOUA exhibits more weight loss than samples containing aluminum pigment, which is expected because aluminum pigments do not decompose in this temperature range.

Figure 21: TGA spectrums of ATOUA



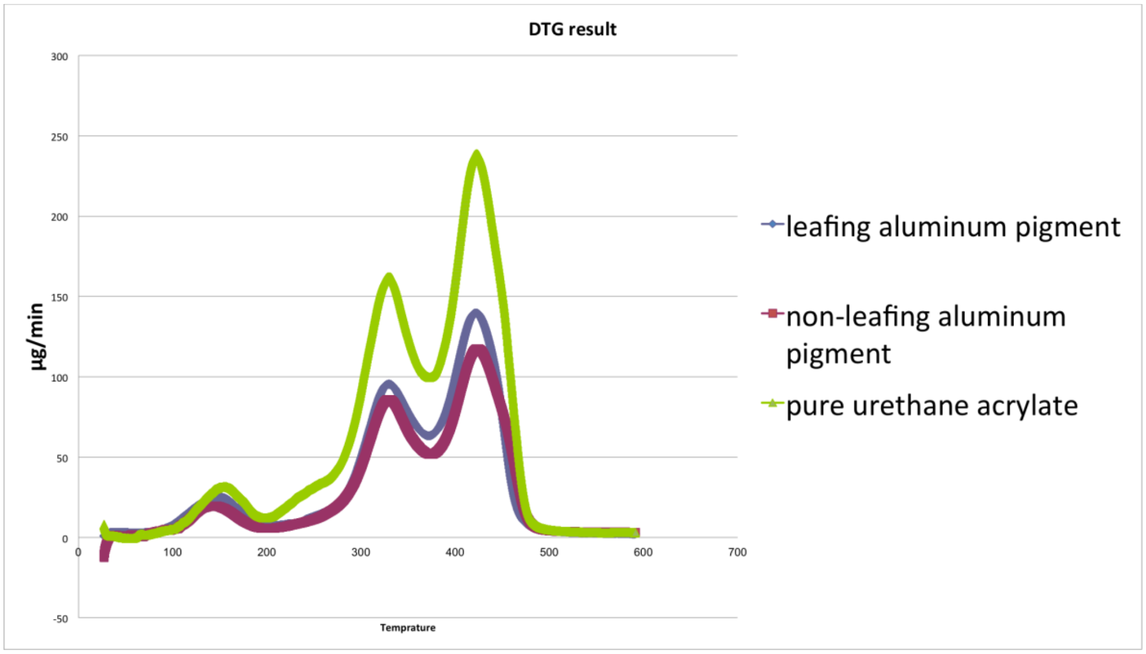


Figure 10: DTG spectrums of ATOUA

4.5.2 Differential Scanning Calorimetry (DSC)

According to The DSC thermograms of ATOUA films (Figure 17), the films that contain aluminum pigments (a) show higher endotherm peaks in comparison with the films that contain leafing aluminum pigments (b). This can be due to the different pigment orientations (leafing and non-leafing) in the films that result in different rates of heat flow in the films.

Also it can be observed from the thermograms that films containing aluminum pigments show higher endotherm peaks than films without aluminum pigments. Metallic pigments cause higher endotherm peaks, since they increase the rate of heat transfer due to their high thermal conductivity.

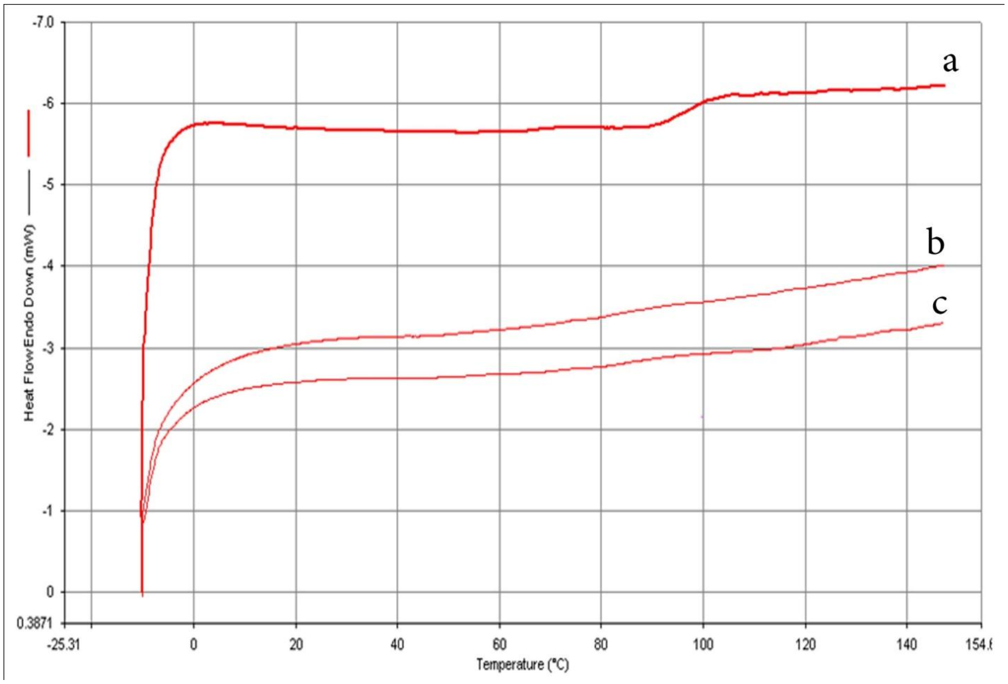


Figure 11: a) DSC thermograms of ATOUA + Non-leafing Aluminum Pigment, b) DSC of ATOUA + leafing Aluminum Pigment, c) DSC of Pure ATOUA

4.6 Metallic Coating Characteristics

Metallic coatings can be deposited onto a surface by the action the electric current. These coatings can provide a layer that changes the surface properties of the coated object. To appraise coating capability as a protective surface with metallic shine, a series of tests were performed on the coatings and the results are given in table.

Gloss is an important performance property in the synthesized films, which is employed to cover decorative and aesthetic issues. In our experiments, cured coatings gloss values are also presented in table 10.

Table 10: Mechanical Properties of Aliphatic Tri-functional Oligomeric Urethane Methacrylate (ATOUA)

Mechanical Properties	ATOUA leafing A1	ATOUA non-leafing A1	ATOUA blank
Impact resistance	>35 direct	> 40 direct	> 45 direct
Cross cut	5B	5B	5B
Cupping (mm)	> 3	> 3	> 3
MEK Rub	> 100	> 100	> 100
Pendulum Hardness konig	104	114	128
Salt Spray 1000h	Passed	Passed	Passed
Mandrel	No crack	No crack	No crack
Gloss	20° 60° 60 89	20° 60° 49 85	20° 60° 63 85

As it was mentioned previously initial experiments were carried out using UTMA hybrid films. These films exhibited significant enhancements about stiffness, although gloss was cut down. Surface stiffness was influenced by interactions among organic-inorganic phases. Moreover, surface harshness the hybrid materials increased as a result of extent of silica content prior to phase segregation. The mechanical properties of UTMA are presented in Table 11. As it was concluded UTMA didn't have enough adhesion to the substrate and therefore the experiment were shifted toward synthesis of ATOUA.

Table 11: Mechanical and Physical Properties of UTMA

Sample	**Thickness (nm)**	**Gloss**		**Micro Hardness**
		60^o	**20^o**	
AI+UTMA+SP25	51.89	89	43	49.48
AI+UTMA+SP25+0.1VTES	54.21	88	43	54.98
AI+UTMA+SP25+0.3VTES	36.16	63	22	54.88
AI+UTMA+SP25+0.5VTES	49.05	77	37	61.6
Mica+UTMA+SP25	63.93	85	40	Na
Mica+UTMA+SP25+o.1VTES	22.07	91	47	Na
Mica+UTMA+SP25+o.3VTES	Na	Na	Na	Na
Mica+UTMA+SP25+o.5VTES	Na	Na	Na	Na
TiO_2+UTMA+SP25	43.13	102	72	Na
TiO_2+UTMA+SP25+0.1VTES	52.21	81	42	Na
TiO_2+UTMA+SP25+0.3VTES	Na	Na	Na	Na
TiO_2+UTMA+SP25+0.5VTES	Na	Na	Na	Na

Chapter 5

CONCLUSION AND FUTURE WORKS

5.1 Concluding Remarks

1) Aliphatic tri-functional oligomeric urethane methacrylate (ATOUA) resin was synthesized successfully in the current research.
2) ATOUA was formulated with leafing and non-leafing aluminium pigments to obtain metallic shine effect and produce crack free UV-curable coatings
3) Mica and titanium dioxide (TiO_2) were also used as a pigment in UV-curable coatings and it was concluded that aluminium was the best choice in these formulations.
4) The main reason for our interest in these coatings is the noticeable advantages provided by the UV-curing process over the traditional methods such as thermal curing. These advantages include lower energy consumption, low capital investment, low space consumption and reduction of volatile organic compounds emissions. More importantly the current process is industrially acceptable and environmental friendly.
5) The prepared coatings showed acceptable mechanical and physical properties such as solvent resistance to methyl ethyl ketone (MEK), impact resistance, flexibility, gloss and abrasion resistance and were comparable to industrial coatings.

6) Also, the hybrid organic-inorganic films successfully passed 1000 h of salt spray test.

5.2Future works

Since the obtained UV-cured coatings show reasonable properties including adhesion, hardness, corrosion resistance, etc., future study to use other polymers such as polyester is also suggested. Polyesters can be either thermoplastic or thermoset and can be used to make films, bottles, etc. Employing polyesters as an alternative result in low cost products since polyester raw materials are more commercially reachable.

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