## UV-CURABLE HYBRID POLYURETHANES

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### UV-CURABLE HYBRID POLYURETHANES

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### ABSTRACT

The organic/inorganic hybrid coatings have been intensively studied in recent years and it have been reported that the incorporation of inorganic components enhanced both the corrosion resistance and adhesion of organic coatings. The UV radiation has been widely used to cure coating resins for many years. The UV-curing process exhibits several distinguished advantages including rapid curing rate, low volatile organic compound (VOC) emission, high efficiency (energy, labor, and space), availability of curing heat sensitive substrates and so on.

Given the advantages and distinguished features of hybrid coatings and UV-curing technique, a new type of UV-curable polyurethane/polysiloxane hybrid coating system was successfully developed in this study. The hybrid coating system was composed of three major components: organic phase, inorganic phase, and reactive diluents. The organic phase was based on acrylated urethane prepolymers which were prepared from isophorone diisocyanates (IPDI), 2-hydroxyethyl methacrylates (HEMA), and polyether polyols. The inorganic phase was based on tetraethyl orthosilicate (TEOS) oligomers which were prepared via sol-gel chemistry. UV-active reactive diluents were synthesized using IPDI, HEMA, and (3-aminopropyl) triethoxysilanes (APTES) to adjust the viscosity of coating formulations and afford compatibility between organic and inorganic phases as well. Fourier transform infrared spectroscopy (FTIR), <sup>1</sup>H NMR spectroscopy and electrospray ionization-mas

spectroscopy (ESI-MS) were used for the structural characterization of synthesized urethane prepolymers, reactive diluents, and TEOS oligomers. The UV-initiated photo-curing kinetics, viscoelastic properties, tensile properties, and general coating properties of the hybrid coatings were investigated. The results indicated that the photopolymerization process, viscoelastic properties, tensile and general properties were affected by the reactive diluents and TEOS oligomers.

### DEDICATION

To my beloved parents, Kechang Xu and Zhenjie Sun, for their exceptional love and endless support ever since I was born.

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#### CHAPTER I

#### INTRODUCTION AND LITERATURE REVIEW

### 1.1 Organic Coatings

Organic coatings can be defined as thin films applied on substrates. A typical organic coating is a composite consisting of four components: (1) organic binders; (2) volatile substances; (3) pigments; (4) additives. The organic binders are materials that bind other elements in the coating together to form continuous films adhered on substrates. Most of the mechanical and viscoelastic properties of the coating are attributed to organic binders. Volatile substances are liquids used to assist coating application as well as film formation process and will evaporate after the coating is applied. Pigments are insoluble solid particles dispersed in the continuous phase, affording colors, corrosion protection, and barrier properties to coatings. Yet not all organic coatings contain pigments and those without pigments are usually referred as clear coats. Additives are very small amount of materials used to modify certain properties of the coating. Additives commonly used in organic coating products are wetting agents, leveling agents, antifoaming agents, matting agents, adhesion promoters and so on.<sup>1</sup>

In terms of classification, organic coatings can be categorized from different angles. Based on the polymer binders, there are polyester, polyurethane, epoxy, alkyd, polyurea, acrylic, phenolic, silicone, and vinyl acetate coatings. Also, organic coatings can be classified according to the state of matter: either liquid or powder. Liquid coatings are further categorized by the continuous phase: either solventborne or waterborne.<sup>2</sup> For a solventborne organic coating, polymer binders and other substances are dissolved in organic solvents which will evaporate after application. As the regulation of VOC (volatile organic compound) emission becomes stricter, more efforts have been made to reduce the use of organic solvents in coating products, which resulted in the invention of high solid coatings. Fewer organic solvents are used in high solid coatings with compared to traditional solventborne coatings and the amount of non-volatile components in a high solid coating is usually higher than 60wt%. The increasing motivation to reduce harmful organic solvents in coating products led to the born of waterborne coatings in which water is used as a solvent to disperse organic binders, pigments, and other substances in the coating. Currently there are two types of waterborne based organic coatings: Latex and Water-reducible. In comparison to solventborne coatings, waterborne coatings are less toxic, less flammable and more environmental friendly.<sup>1</sup>

Organic coatings can be designed to be either thermosetting or thermoplastic. For thermosetting coatings, crosslinking networks are formed via chemical reactions of polymer resins, a process often referred as "cure". Various curing methods have been developed, including thermal curing, radiation curing (UV or electron beam), and moisture curing. Thermoplastic coatings, on the other hand, form condensed films through coalescence after being applied on substrates.<sup>2</sup>

Organic coatings are currently ubiquitous in our modern world. They are applied on furniture, floors, walls, automobiles, food cans and so on. In general, organic coatings have two major functions: protection and decoration, which are not mutually exclusive in application.<sup>1</sup> For instance, automobile coatings not only afford various colors to cars but also protect car bodies from corrosion and rusting. Due to the current advanced polymer synthesis and processing techniques, coating scientists and engineers now are able to develop coating products with excellent performance for various end-usages.

### 1.2 Polyurethane Coatings

Polyurethanes (PU) are polymers consisting of repeated urethane linkages (-NH-CO-O-). PU was first discovered by Dr. Otto Bayer and his colleagues in Leverkusen, Germany in 1937.<sup>3</sup> It was found that this new type of polymers exhibited several advantages over most commonly used plastics at that time. But initial applications of polyurethanes were only limited to fibers and flexible foams.<sup>4</sup> At the beginning of 1950s, flexible PU foams were produced from toluene diisocyanates (TDI) and polyester polyols in the United States, which can be considered as a milestone in PU industry and built the foundation for the development of polyurethane materials.

In 1956 DuPont developed polyether polyols that showed some technique as well as commercial advantages in comparison to polyester polyols, such as low manufacture cost, easy to handle and better hydrolytic stability, which made polyether polyols more popular in PU industry.<sup>4</sup> During 1960s the polyurethane industry grew rapidly and due to the invention of chlorofluoroalkane blowing agents and methylene diphenyl diisocyanate (MDI) along with the inexpensive polyether polyols, polyurethane rigid foams were able to be applied as high performance insulation materials. In early 1970s thermoplastic polyurethanes (TPU) were successfully developed and the TPU exhibited several useful properties, including excellent mechanical strength, elasticity, water, oil, and abrasion resistance, easy to process. The polyurethane industry has been rapidly growing since the early 1980s and currently PU based products are widely applied in various areas all over the world.

Polyurethanes are usually obtained by reacting multifunctional isocyanates with polyols. The urethane linkage is generated by the reaction of an isocyanate group with a hydroxyl group, as shown in Figure 1- 1.<sup>1</sup>

Figure 1- 1 Formation of urethane linkage via reaction between isocyanate with hydroxyl group.

Since the isocyanate plays a significant role in urethane chemistry, it is necessary to briefly introduce isocyanate chemistry related to the preparation of polyurethanes. Isocyanates refer to materials containing the -N=C=O functional groups. Based on the number of -N=C=O group, isocyanates can be categorized into monoisocyanates, diisocyanates, and polyisocyanates. The primary reactions that lead to the formation of urethane linkages are reactions of isocyanate groups with hydroxyl groups. However, some side reactions may also occur during the formation of urethane

linkages. The yield urethanes groups could react with free isocyanates to form allophanates, as shown in Figure 1-2.<sup>1</sup>



Figure 1-2 Formation of allophanates via reactions of urethanes with isocyanates

Isocyanates also react with water to form unstable intermediate acids that will decompose into carbon dioxides and amines. The yield amines then can rapidly react with isocyanates to form ureas. The overall process is illustrated in Figure 1-3.<sup>1</sup>



Figure 1-3 Reactions of isocyanates with water and the formation of ureas

In addition to react with other chemicals, isocyanates might also react with themselves to form dimers (uretdiones) and trimers (isocyanurates), as shown in Figure 1-4.The dimers are thermally unstable and will decompose to regenerate isocyanate monomers upon heating, while the trimers are quite stable and can be used to produce rigid polyurethane foams.<sup>1,5</sup>



Figure 1-4 Chemical structures of Uretdione and Isocyanurate

Various isocyanates are used to produce polyurethane products according to different end-usages. In general, aromatic isocyanates are more reactive with hydroxyl groups than aliphatic isocyanates.<sup>5</sup> Aromatic isocyanates primarily used in PU industry are 2, 4-tolylene diisocyanate (TDI) and diphenyl-methane-diisocyanate (MDI). In comparison to MDI, TDI is more volatile and hence it is usually converted to prepolymers with relatively high molecular weight to reduce toxic hazard. One of the distinguished features of TDI is that it contains two isocyanate groups that have significant difference in terms of reactivity, which makes it possible to produce mono-functionalized prepolymers. Hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) and bis(4-isocyanatocyclohexyl)methane (H<sub>12</sub>MDI) are examples of most widely used aliphatic isocyanates. HDI monomers are highly toxic and thus can only be handled in chemical plants with caution and care. IPDI has two different types of isocyanate groups (aliphatic and cycloaliphatic isocyanate groups). The unequal reactivity of the primary and secondary isocyanate groups of IPDI can be used to make prepolymers with low molecular distribution.<sup>1</sup> The chemical structures of these isocyanates are shown in Figure 1-5.



2, 4-tolylene diisocyanate



Isophorone diisocyanate



hexamethylene diisocyanate



Diphenyl-methane-diisocyanate



bis(4-isocyanatocyclohexyl)methane

Figure 1- 5 Chemical structures of commonly used isocyanates

In addition to isocyanates, polyols are also important starting materials used to produce polyurethanes. By definition, polyols are chemical compounds containing multiple hydroxyl groups per molecule. Although chemicals containing urethane linkages are often referred as polyurethanes, only small portions of the entire composition are actually urethane groups. As a result, the properties of a polyurethane product largely depend on the polyols. Two classes of polyols are widely used to make polyurethane products: polyester and polyether polyols. Polyester polyols are prepared via poly-condensation reactions between diols or polyols and diacids. Various combinations of diols and diacids will result in polyester polyols with different properties. Polyether polyols are made by reacting low molecular weight diols with epoxides in the presence of strong base catalysts. The diols used are usually polyethylene glycols and polypropylene glycols, while the epoxides could be ethylene oxides or propylene oxides.<sup>5</sup>

With compared to other types of polymeric materials, polyurethanes exhibit relatively high design flexibility, which is based on the concept of "hard" (high Tg) and "soft" (low Tg) segments. Whereas the hard segments afford high rigidity and hardness to the PU products, the soft segments give the PU good extension and flexibility. Because a large variety of polyols are readily available on the market and the combination of polyols and isocyanates are almost infinite, the final properties of polyurethanes can be designed in a very wide range to meet different application requirements. Besides, intermolecular hydrogen bonds could form between urethane groups, as shown in Figure 1-6. The hydrogen bonds could break upon external stress and regenerate when the stress is removed, which helps absorb energy and avoid irreversible bond breaking. The presence of hydrogen bonds increases the intermolecular force, affording polyurethanes good abrasion resistance and toughness.<sup>1</sup>



Figure 1- 6 Formation of H-bonds between polyurethane molecular chains

Because of all these unique properties and features, polyurethanes are currently applied in different areas including plastic, rubber, fiber, foam, adhesive, and coating. PU coatings have excellent mechanical properties, abrasion resistance, chemical resistance, good adhesion and low temperature performance, which make them be widely used in automotive, wood, and plastic industries.<sup>6</sup>

### 1.3 Organic/Inorganic Hybrid Coatings

The organic/inorganic hybrid material, also known as "ceramer", is a relatively novel type of materials that have been intensively studied since 1980s.<sup>7</sup> The term "ceramer" was derived from the words of "ceramic" and "polymer", representing inorganic and organic characteristics, respectively. The major driving force in this field is that hybrid materials have the potential advantage to display combination of both organic and inorganic features in one single material,<sup>2</sup> such as ductility and ease of processing of organic polymers and thermal stability, corrosion resistance, and abrasion resistance of inorganic components. Yet the overall properties of a hybrid material are not simply the sum of physical and chemical properties from individual organic and inorganic components. The interactions between organic/inorganic phases have significant influence on the final properties of hybrid materials. Typically, the organic/inorganic interactions existing in hybrid materials are covalent bonds, hydrogen bonds, ionic bonds, Van der Waals, coordinative bonds. Based on the strength of interactions, hybrid materials can be divided into two classes: Class I (weak interactions provided by hydrogen bonds, ionic bonds, Van der Waals and so on) and Class II (strong interactions provided by covalent bonds).<sup>8</sup>

The main technique commonly used to prepare hybrid materials is the sol-gel chemistry in which small molecules (usually referred as precursors) undergo hydrolysis and condensation reactions to form polymeric structures. Metal alkoxides are usually used as sol-gel precursors and some examples of metal alkoxides sol-gel precursors are shown in Figure 1-7.<sup>2</sup> The sol-gel process is illustrated using tetraethyl

orthosilicates (TEOS) as the model compound, as shown in Figure 1-8. With an acid or a base as catalyst, sol-gel precursors will hydrolyze to generate silanols and alcohols. The silanols then can react either with themselves or with precursor molecules to form siloxane groups via condensation reactions. A Si-O-Si network could form through further hydrolysis and condensation reactions.<sup>9</sup> The sol-gel process as well as the structure of final products is affected by several factors, including alkoxy group (R), pH of the system, temperature, solvent, and the ratio of water to sol-gel precursors. Among all these factors, the pH and the ratio of water to sol-gel precursors are the most important ones. When acids are used as catalysts (low pH) and the ratio of water to sol-gel precursors is low, the rate of hydrolysis is faster than that of condensation, resulting in products with linear or branched structures. On the contrary, at basic (high pH) and high ratio of water to sol-gel precursor conditions where the rate of condensation is relatively fast compared to the rate of hydrolysis, highly condensed clusters are produced.<sup>9-11</sup>





Tetraethyl orthosilicate



Titanium Diisopropoxide





Titanium (IV) Isopropoxide

Figure 1-7 Examples of commonly used sol-gel precursors



Figure 1-8 Sol-gel process of tetraethyl orthosilicates (TEOS)

Due to the rapid development of sol-gel chemistry and polymer synthesis techniques in the past several decades, a variety of starting materials are available for the preparation of organic/inorganic hybrid materials. Different combinations of organic and inorganic components along with various organic/inorganic phase interactions lead to hybrid materials with various properties and performance, which render them as potential candidates for a wide range of applications, one of which is for coating usages.

Coatings derived from poly(methylsiloxane) and related colloidal silica have been developed and commercialized decades ago to protect plastics from wear and abrasion, such as coatings on the surface of headlights of automotives made from polycarbonate (PC). Due to the high crosslink density of inorganic components, the hybrid coatings have improved scratch and abrasion resistance in comparison to pure organic coatings, which makes hybrid coatings suitable for protecting plastic substrates.<sup>12</sup> Ophthalmic lens made from polymeric materials have been widely used since 1990s. Coatings are commonly used on top of the plastic lens to protect them from wear and abrasion. One of the first hybrid coatings developed for plastic lens was derived from (3-glycidoxypropyl) methyldiethoxysilane (GPTMS), tetramethyl orthosilicate (TMOS), and titanium tetraethylate via sol-gel process. The coated lens had high refractive index and better abrasion resistance than non-coated lens.<sup>13</sup> In another case, a UV-curable hybrid coating was developed for polycarbonate (PC) substrates and the coated PC also exhibited improved abrasion resistance.<sup>14</sup> A hybrid coating for substrate made from poly(methyl methacrylate)(PMMA) has also been developed. The hybrid coating system is composed of nano-sized inorganic particles crosslinked by organic polymer chains. It displayed good index matching to the substrate as well

as high abrasion resistance. One of the commercial applications of this coating is to protect PMMA-based polymeric magnifying lenses. Since hybrid coatings were able to afford high scratch and abrasion resistance to plastic substrates according to previous studies, it is possible that coated polycarbonates may have the potential to replace glass products in automobile industry. A company named Exatec was a pioneer in this area, whose primary goal is to develop polycarbonate products coated by sol-gel derived hybrid coatings as replacements for glasses in automotive application.<sup>12</sup>

A lot of research works have also been done in the area of organic/inorganic hybrid coatings for corrosion protection of metal substrates. In one of the previous studies, Holmes-Farley and Yanyo used TEOS and aminosilanes to prepare anisotropic coatings to prevent corrosion on aluminum substrates. The results indicated that the TEOS layer formed on the substrate afforded the coating good adhesion and corrosion resistance.<sup>15</sup> A new type of polyurea/polysiloxane hybrid coatings for corrosion protection of metal substrates was prepared and intensively studied by Soucek and coworkers. In their research, hexamethylene diisocyanate isocyanurates (HDI) were first functionalized with 3-aminopropyltriethoxysilane (APTES). Then the resultant alkoxysilane functionalized HDI was used as coupling agent which provided the connection between the organic phase composed of polyureas and the inorganic phase based on TEOS oligomers. The hybrid coatings were moisture cured via reactions of alkoxysilanes and isocyanates with water. Adhesion and anti-corrosion properties of this hybrid coating were evaluated and the results showed that the inorganic TEOS

oligomers functioned as adhesion promoter and corrosion inhibitor in this hybrid coating system. The proposed mechanism of the interaction between hybrid coatings and metal substrate is that TEOS oligomers absorb water from atmosphere and then undergo hydrolysis and condensation reactions to form Si-O-Si networks on metal substrates as shown in Figure 1-9. The condensed Si-O-Si networks behaved like barriers reducing the permeation of moisture and oxygen, which protected the substrate from corrosion. The enhanced adhesion may be due to the formation of Si-O-Al bonds between coating films and substrates.<sup>9,16</sup> Inspired by a series previous works of hybrid coatings<sup>17-20</sup>, a similar polyurethane/ polysiloxane hybrid coating system was formulated by Soucek and coworkers using HDI isocyanates, alkoxysilane-functionalized HDI isocyanurates, hydroxyl terminated polyesters, and TEOS oligomers.<sup>21</sup> The hydroxyl terminated polyesters were also prepared in Soucek's lab based on two types of diols (2-Butyl-2-ethyl-1,3-propanediol (BEPD) 1,4- cyclohexanedimethanol (CHDM)) and two types of diacids and (1,3-Cyclohexanedicarboxylic acid (1,3-CHDA) and 1,4-Cyclohexanedicarboxylic acid (1,4-CHDA)).<sup>22, 23</sup> The synthesized cycloaliphatic polyesters exhibited enhanced hydrolytic stability as well as corrosion resistance and good hardness/flexibility balance in comparison to aromatic or linear aliphatic polyesters.<sup>24-26</sup> In this hybrid system, polyurethanes contributed to general coating properties, while the TEOS oligomers were added to improve the adhesion and anti-corrosion properties of the coating. It was concluded that the hybrid coating demonstrated better adhesion and

corrosion resistance than polyurethane coatings and may have the potential to replace conventional aircraft coatings containing carcinogenic chromate.<sup>27</sup>



Aluminum Substrate

Figure 1- 9 Proposed mechanism of the interaction between hybrid coatings and metal substrate<sup>9</sup>

#### 1.4 Free-radical initiated ultraviolet (UV) Curing

The radiation curing technique has been of great interests in both academic research field and coating industries for many years. The ultraviolet (UV) light is widely used as radiation source to initiate polymerization reactions of coating resins, leading to the formation of crosslinking networks. A typical UV-curing coating formulation is composed of four major components: (1) reactive resins; (2) reactive diluents; (3) photoinitiators; (4) additives. The reactive resins are usually oligomers containing UV-active functional groups, which will form the continuous phase after curing and contribute to most of the mechanical and viscoelastic properties of coating films. The reactive diluents are relatively small molecules functionalized with UV-active groups which could participate in the crosslink reactions and adjust the viscosity of coating formulations for application as well as film formation process. Upon the exposure of UV lights, the photoinitiators disassociate to generate reactive species that could initiate polymerization reactions of the coating resins. Additives are commonly used to modify certain property of the coatings and reduce costs as well.<sup>1, 28</sup> With compared to conventional thermal curing process, UV-curing exhibits several distinguished features and advantages that can be concluded as follows: (1) almost zero volatile compound (VOC) process (environmental friendly); (2) rapid curing rate (within tens of seconds) and easy to control; (3) high efficiency; (4) relatively low energy consumption; (5) less labor are needed and small space requirements; (6) availability for heat sensitive substrates such as wood, plastic, and paper. Coatings cured via UV radiations have the potential advantages to display excellent scratch, abrasion, stain, and chemical resistance as well as high toughness. Despite of all these advantages, the application of UV curing technique in coating industry is still quite limited due to some drawbacks which are concluded as follows. Firstly, since the intensity of UV radiation decreases with the square of the distance, it is difficult to uniformly cure coatings applied on substrates with complex shapes. Secondly, it is hard to design UV-curable coatings for exterior applications because photoinitiators in the cured film will also promote the photodegradation process of the coating. Thirdly, the rapid UV-curing rate leads to high extent of film shrinkage and as a result a lot of internal stresses will develop in the cured film, which is detrimental to final coating performance. Finally, the costs of materials for UV-curing systems are relatively high in comparison to other conventional coatings. In general, UV-curable coatings are mainly applied on heat sensitive substrates, like wood furniture, parquet, or plastic

products. Yet applications of UV-curing technique are not limited to heat sensitive substrates and have been extended to metal as well as glass substrates.<sup>29</sup>

Based on the mechanism of polymerization, UV-curable coatings can be divided into two classes: free-radical initiated UV-curable coatings and cationic initiated UV-curable coatings.<sup>28</sup> For a free-radical induced UV-curing system, photoinitiators are transformed into excited states by absorbing photons in UV radiation and the excited photoinitiators will then decompose to generate reactive free radicals to initiate the polymerization of coating resins to form crosslinked films. This process is briefly illustrated in Figure 1-10.<sup>1,28,29</sup>



 $PI^* \longrightarrow R \cdot (reactive radicals)$ 

 $R \cdot + nM$  (reactive resins)  $\longrightarrow$  crosslinked structures

Figure 1-10 Free-radical initiated UV-curing process

Two types of photoinitiators are used for free-radical induced UV-curable coatings: unimolecular and bimolecular photoinitiators. The former generates reactive radicals via homolytic fragmention process, while the latter forms reactive radicals by hydrogen abstraction process.<sup>28,30-32</sup> The first widely used unimolecular photoinitiators were benzoin ethers which fragment to generate benzoyl and benzyl ether radicals as illustrated in Figure 1-11. But the package stability of coating products using benzoin ethers as photoinitiators is poor because of the ease of abstraction of benzylic hydrogen. The package stability could be enhanced by using 2, 2-dimethoxy-2-phenylacetophenone as photoinitiators due to the completely substituted benzylic carbons.<sup>1, 28</sup>



Figure 1-11 Photolysis of benzoin ethers

Another type of commonly used unimolecular photoinitiators is the acylphosphine oxides. They can be used to cure both clear coatings and coatings containing pigments.<sup>33-35</sup> Besides, acylphosphine oxides exhibit nonyellowing tendency as well as good package stability when used as photoinitiators compared to benzoin ethers.<sup>28</sup> The photolysis of diphenyl-2, 4, 5-trimethylbenzoylphosphine oxide is given in Figure 1-12.



Figure 1-12 Photolysis of acylphosphine oxides

Bimolecular photoinitiators consist of aromatic ketones such as benzophenones or thioxanes and hydrogen donors. Under the exposure of UV radiations, aromatic ketones abstract hydrogen from hydrogen donors to form reactive radicals capable of initiating the polymerization of coating resins, as shown in Figure 1-13.<sup>1,28</sup> Tertiary amines are widely used as hydrogen donors and bimolecular photoinitiators with amine hydrogen donors usually reduced inhibition effect of oxygen.<sup>28, 36-38</sup>



Figure 1-13 Photolysis of bimolecular photoinitiators

In the early stage, the free-radical induced UV-curable coatings were based on mixtures of unsaturated polyesters (UPEs) with styrenes.<sup>28</sup> The UPEs alone could be cured upon UV radiation via C=C bonds in the molecules, but the viscosity of pure UPEs system was very high and needed to be reduced for application. Therefore, styrenes were added into the system, behaving like reactive diluents which not only reduced viscosity of the system but also reacted with UPEs to form the final coating films.<sup>39,40</sup> The UV-curable UPEs / styrene coatings were largely applied in wood industry due to low costs as well as relatively rapid cure rate at ambient temperature.<sup>1,28,41</sup> However, the high volatility of styrene has limited the wide application of these coatings.<sup>1</sup>

Currently, most free-radical UV-curable coatings are based on acrylated reactants including monofunctional acrylates, multifunctional acrylates, acrylated oligomers with different molecular weights. Here the term "acrylates" could represent both acrylates and methacrylates. The former cures significantly faster than the latter and shows less oxygen inhibition effect as well. Monofunctional acrylates are low viscosity compounds mainly used as reactive diluents to reduce viscosity of the coatings, which is conducive for coating application as well as film formation process. Multifunctional acrylates are also relatively low viscosity molecules used to accelerate curing rate and increase crosslink density due to their polyfunctionality. Acrylated oligomers contribute to most of the coating properties, like adhesion, hardness, abrasion resistance, and so on.<sup>1.28</sup>

Some of the most commonly used monofunctional acrylates are shown in Figure1-14. The 2(2-Ethoxyethoxy) ethyl acrylates have very low viscosity at ambient temperature. The isobornyl acrylates are also effective diluents which can not only decrease the viscosity of the coating but also increase Tg of the cured films. Both 2-hydroxyethyl acrylates and 2-hydroxyethyl methacrylates have hydroxyl groups that can be used to react with isocyanate-terminated oligomers to form urethane acrylates. But the 2-hydroxyethyl acrylates have to be handled under controlled conditions due to their high toxicity, which restricts their applications.<sup>28,42</sup>



Figure 1-14 Commonly used monofunctional acrylates for UV-curable coatings

The 1, 6-hexanediol diacrylates, tripropyleneglycol diacrylates and trimethylolpropane triacrylates are examples of widely used multifunctional acrylates for free-radical induced UV-curable coatings. Their chemical structures are shown in Figure 1-15. Their high functionality provides faster curing rate as well as higher crosslinking density, but they can also cause skin irritation issues and hence have to be handled very carefully.<sup>1,28,42</sup>



tripropyleneglycol diacrylate

Figure 1-15 Commonly used multifunctional acrylates for UV-curable coatings

Two types of acrylated oligomers, urethane acrylates and acrylated epoxides, are mainly used for the preparation of UV-curable coatings. The urethane acrylates, also referred as acrylated urethane prepolymers, are made by reacting polyols or hydroxyl terminated oligomers with isocyanates and hydroxyethyl acrylates<sup>43,44</sup> and an example of urethane acrylates is given in Figure 1-16. The acrylated urethane prepolymers tend to afford coating films a good balance of mechanical properties due to the combination of soft and hard segments in the system.<sup>1</sup>



Figure 1-16 Example of acrylated urethane prepolymer

Acrylated epoxides are prepared by the reaction of epoxy resins with acrylic acids and the typical structure of acrylated epoxides is shown in Figure1-17. UV-cured coating films based on acrylated epoxides usually exhibit good adhesion, thermal stability, chemical resistance, which are characteristics of conventional epoxy resin based coatings.<sup>1</sup>



Figure 1-17 Example of acrylated epoxides

One of the tough problems for free-radical induced UV-curing process is probably the oxygen inhibition effect. The excited photoinitiators could be quenched by oxygen in the air and return to ground state, which reduces the efficiency of initiation, hence retarding the curing process. Furthermore, oxygen also could react with generated radicals or propagating radicals to form peroxides, resulting in the termination of polymerization, as illustrated in Figure 1-18.<sup>1,28,29</sup> The overall results of oxygen inhibition are molecular weight reduction and incomplete cure, thereby poor coating performance.



Figure 1-18 Illustration of oxygen inhibition for free-radical induced UV-curing

Several approaches have been used to address the oxygen inhibition problem. Increasing the intensity of UV radiations and the concentration of photoinitiators can minimize but not prevent this problem. Because of the high UV radiation intensity as well as high photoinitiator contents, a relatively high concentration of reactive radicals are rapidly generated and parts of the radicals can consume oxygen at the film surface, allowing other radicals to participate the polymerization.<sup>45</sup> But the use of high UV radiation intensity and high photoinitiator concentration will also lead to an increase of manufacture costs. The curing process could be carried out in inert atmosphere where no oxygen is present. In coating industry, carbon dioxides, instead of nitrogen, are usually used to protect the coating film from oxygen inhibition due to the economical concerns.<sup>46,47</sup> The addition of chain transfer agents is also an effective way to minimize oxygen inhibition issue. Tertiary amines containing  $\alpha$ -CH groups are commonly used as chain transfer agents. The formed peroxy radicals can abstract H atoms from amine molecules containing  $\alpha$ -CH groups, resulting in the formation of

hydroperoxides and new amine radicals that can initiate the polymerization. And oxygen can also be consumed rapidly by reacting with amine radicals and the resultant peroxy radicals will repeat the process described above.<sup>1,48</sup> Furthermore, the oxygen inhibition could also be minimized by incorporating waxes into coating formulations. The added waxes tend rise to the surface of the film to form a barrier, shielding the film from oxygen.<sup>49,50</sup>
# CHAPTER II

# UV-CURABLE POLYURETHANE BASED HYBRID COATINGS

### 2.1 Introduction

Inspired by the advantages of organic/inorganic hybrid coatings and UV-curing techniques, a new type of UV-curable hybrid polyurethane based coating system was developed in this study. The hybrid coating system was composed of three major components: organic phase, inorganic phase, and reactive diluents. The organic phase was based on acrylated urethane prepolymers which were prepared using isophorone diisocyanates (IPDI), 2-hydroxyethyl methacrylates (HEMA), and polyether polyols. The inorganic phase was based on tetraethyl orthosilicate (TEOS) oligomers which were prepared via sol-gel chemistry. UV-active reactive diluents were synthesized using IPDI, HEMA, and (3-aminopropyl) triethoxysilanes (APTES) to adjust the viscosity of coating formulations and afford compatibility between organic and inorganic phases as well. Fourier transform infrared spectroscopy (FTIR), <sup>1</sup>H NMR spectroscopy and electrospray ionization-mass spectroscopy (ESI-MS) were used for the chemical structural characterization of synthesized urethane prepolymers, TEOS oligomers, and reactive diluents. The UV-initiated photopolymerization kinectis, viscoelastic properties, tensile properties, and general coating properties of the hybrid coatings were investigated.

### 2.2 Materials

Tetraethyl orthosilicate (TEOS, 98%), hydrochloric acid (37%), ethanol (99.98%), isophorone diisocyanate (IPDI, 98%), 2-hydroxyethyl methacrylate (HEMA, 97%), (3-aminopropyl) triethoxysilane (APTES, 99%), dibutyltin dilaurate (DBTDL, 95%), hydroquinone (99%), Chloroform (99.8%) were purchased from Sigma-Aldrich. The polyether polyols (DESMOPHEN 1915 U) were provided by Bayer Material Science and the specification of the product are: hydroxyl value =33-37 mg/g; acid number =0.06; viscosity (25 °C) = 790-890 mPa • s; Water content = 0.05wt%. The photoinitiator, Darocur® 4265, was obtained from Ciba. All chemicals were used as received. Aluminum panels were purchased from Q-panel Lab Products.

### 2.3 Instrumentation and Characterization

The Thermo Scientific Nicolet 380 FTIR spectrometer was used to measure the FTIR spectroscopy of synthesized acrylated urethane prepolymers and reactive diluents. All <sup>1</sup>H NMR spectra of synthesized TEOS oligomers, urethane prepolymers, and reactive diluents were recorded by a Varian Mercury 300 MHz NMR spectrometer. Chloroform-d (CDCl<sub>3</sub>) was used as solvents to prepare all samples for the <sup>1</sup>H NMR analysis. Mass analysis was performed using Electrospray ionization-mass spectrometry (ESI-MS).

The photopolymerization kinectis of hybrid coatings were studied using a TA instrument Q2000 differential scanning calorimeter (DSC) equipped with a N2001-A1 Novacure radiometer as UV light source.

The viscoelastic properties of all cured hybrid coating films were investigated using a TA instrument Q800 dynamical mechanical thermal analyzer (DMTA). All testing specimens were rectangular shape with the following dimensions: length 10-15 mm, width 9-11 mm and thickness 0.07-0.08 mm. The gap distance was set up at 5mm and the testing frequency is 1 Hz with a heating rate of 3 °C/min over a range of -100°C to 200 °C.

The tensile properties of all cured hybrid films were studied according to ASTM standards (ASTM D 2370-82) using an Instron Universal Tester model 1000. All testing specimens were rectangular shape with the following dimensions: length 50mm, width 13-15 mm and thickness 0.07-0.08 mm. The initial gap length was set up at 25 mm. All tests were performed at ambient temperature and a crosshead speed of 10 mm/min was applied. The tensile stress, modulus, and elongation at break were measured.

General coating properties of all cured hybrid films were investigated according to ASTM standards, including: cross-hatch adhesion (ASTM D 3359-87), pencil hardness (ASTM D 3363-74), direct impact resistance (ASTM D 2784-94), and pull-off adhesion (ASTM D 4541-85).

2.4 Synthesis

#### 2.4.1 Synthesis of Reactive Diluents

Isophorone diisocyanates (IPDI, 0.1mol, 22.68g,) and dibutyltin dilaurate (DBTDL, catalyst, 0.5wt %) were dissolved in chloroform and added into a 3-necked round bottom flask (500 ml) equipped with a magnetic stirrer. The mixture was under

nitrogen purge for 30 minutes. Then 2-hydroxyethyl methacrylates (HEMA, 0.1mol, 13.42g) were added into the mixture through an addition funnel in cold water bath (around 10 °C). The reaction was carried out under cold water bath (around 10°C) condition for 1 hour and then the cold water bath was removed and the reaction was carried out at ambient temperature for another 1.5 hours. Hydroquinone (inhibitor, 0.1wt%) was added into the flask and the mixture was heated to 50 °C (oil bath) and reacted for another 2 hours at 50 °C. The (3-aminopropyl) triethoxysilane (APTES, 0.1mol, 22.82g) was dissolved in chloroform to yield a 20% APTES solution. The solution was then added into the mixture through an addition funnel at ambient temperature. After addition, the reactants were stirred at ambient temperature until the -NCO peak (2247 cm<sup>-1</sup>) on the FTIR spectrum disappeared. The chloroform in the mixture was removed using a rotary evaporator. The overall synthesis process is shown in Figure 2-1. The resultant product was characterized by FTIR, <sup>1</sup>H NMR and ESI-MS.



Figure 2-1 Synthetic route of reactive diluents

#### 2.4.2 Synthesis of Acrylated Urethane Prepolymers

IPDI (0.1mol, 22.68g) and DBTDL (catalyst, 0.5wt%) were dissolved in chloroform and added into a 3-necked round bottom flask (500 ml) equipped with a magnetic stirrer. HEMA (0.1mol, 13.42g) was added into the mixture through an addition funnel under cold water bath condition (around 10 °C). After addition, the reaction was carried out in cold water bath for 1 hour and then reacted at ambient temperature for another 1.5 hours. Hydroquinone (inhibitor, 0.1wt%) was added into the flask and the mixture was heated to 50°C (oil bath) and reacted for 2 hours at 50°C. Finally, polyether polyols (1915U, 0.1mol, 169.7g) dissolved in chloroform were added into the flask and the reaction was kept running at 50 °C until the –NCO peak (2247 cm<sup>-1</sup>) on the FTIR spectrum disappeared. The chloroform in the mixture was removed using a rotary evaporator. The overall synthesis process is shown in Figure 2-2. The resultant product was characterized by FTIR and <sup>1</sup>H NMR spectroscopy.



Figure 2-2 Synthesis process of acrylated urethane prepolymers

### 2.4.3 Synthesis of TEOS Oligomers

Tetraethyl orthosilicate (TEOS, 50g, 0.24mol) and ethanol (44.23g, 0.96mol) were added into a four necked flask equipped with stirrer, condenser, and nitrogen inlet. Distilled water (4.32g, 0.24mol) was added to the mixture. Hydrochloric acid (0.99ml, 37wt%) dissolved in 10 ml of ethanol was added into the mixture through an addition funnel. The reactants were magnetically stirred for 48 hours at ambient temperature. The ethanol in the mixture was removed using a rotary evaporator to yield TEOS oligomers (52.23g). The resultant product was characterized by <sup>1</sup>H NMR and ESI-MS.

# 2.5 Coating Formulations and Film Preparation

The UV-curable hybrid coatings were formulated with acrylated urethane prepolymers (1), reactive diluents (2), TEOS oligomers, and photoinitiators (Darocur® 4265). Table 2-1 shows the hybrid coating formulations as a function of reactive diluents. Three formulations were prepared as the ratio of reactive diluents (2) to urethane prepolymers (1) increased from 15/85 to 35/65. Table 2-2 shows formulations of hybrid coatings as a function of TEOS oligomers. Four formulations were prepared as the concentration of TEOS oligomers increased from 0wt% to 10wt%.

Hybrid	Urethane	Reactive	TEOS	Ratio	Photo-initiator
coatings	prepolymers	diluents(2)	oligomers	of 2/1	(wt%)
	(1) (wt%)	(wt%)	(wt%)		
F15	79.47	14.03	2.50	15/85	4.00
F25	70.12	23.38	2.50	25/75	4.00
F35	60.77	32.73	2.50	35/65	4.00

Table 2-1 Formulations of hybrid coatings as a function of reactive diluents

Table 2-2 Formulations of hybrid coatings as a function of TEOS oligomers

Hybrid	Urethane	Reactive	TEOS	Ratio	Photo-initiator
coatings	prepolymers	diluents(2)	oligomers	of 2/1	(wt%)
	(1) (wt%)	(wt%)	(wt%)		
Т0	72.00	24.00	0	25/75	4.00
T2.5	70.12	23.38	2.50	25/75	4.00
T5	68.25	22.75	5.00	25/75	4.00
T10	64.50	21.50	10.00	25/75	4.00

For preparation of UV-curable hybrid coatings, acrylated urethane prepolymers, reactive diluents, TEOS oligomers, and photoinitiators were mixed in glass vials at ambient temperature. The photoinitiator (Darocur® 4265) is a blend consisting of 50wt% acyl phosphine oxides and 50wt% of alpha hydroxy ketones, as shown in Figure 2-3. Both the aluminum panels and glass plates were degreased with acetone

and dried before casting any coating films. For general coating properties test, coating films were cast on aluminum panels with the thickness of 4 mil by a drawdown bar. For viscoelastic property and tensile property tests, coating films were cast on glass plates with the thickness of 6 mil. The wet films were initially cured using a Fusion UV-system processor (F300) with an H-bulb. Then the UV-cured coating films were further moisture-cured under ambient environment for 100 hours.



2, 4, 6-trimethylbenzoyldiphenyl-phosphine oxide



2-hydroxy-2-methyl-1-phenyl-propan-1-one

Figure 2-3 Compositions of photoinitiator Darocur® 4265

#### 2.6 Results and Discussion

The objective of this study was to develop a new type of UV-curable polyurethane based organic/inorganic hybrid coating system. Conventional polyurethane organic coatings have good mechanical properties and chemical resistance, good adhesion, and excellent abrasion resistance as well as low temperature performance. In this project, isophorone diisocyanates (IPDI) were selected as starting materials to prepare UV-active reactive diluents and acrylated urethane prepolymers. The IPDI has cycloaliphatic structure which could give polyurethane products based on IPDI intermediate mechanical as well as viscoelastic properties between polyurethanes based on linear and aromatic diisocyanates. And the "yellowing effect" can be avoided for polyurethanes based on IPDI due to the lack of aromatic rings, resulting in better exterior durability. It has been reported in previous studies that the incorporation of inorganic components could enhance both adhesion and anti-corrosion properties of organic coatings.<sup>6,9</sup> The UV-curing technique has been widely applied in coating industry for many years and it demonstrates several distinguished features and advantages, such as rapid curing rate, high efficiency, low volatile compound (VOC) process and so on. The hybrid coatings prepared in this study may have the potential to combine all the advantages of polyurethanes, hybrid materials, and UV-curing techniques in one system.

In this study, the UV-curable hybrid coatings were formulated using acrylated polyether based urethane prepolymers, reactive diluents functionalized with both a UV-reactive methacrylate and alkoxylsilance groups, and TEOS oligomers. FTIR, <sup>1</sup>H NMR, and mass spectroscopy were used for the structural characterization of synthesized chemicals. Two series of formulations were designed to investigate the effects of reactive diluents and inorganic components on coating properties, respectively. The photo-curing behaviors of all hybrid coating formulations were studied via photo-DSC. DMTA was used to evaluate the viscoelastic properties of hybrid films. Tensile and general coating properties of hybrid coating films were also tested according to ASTM standards.

#### 2.6.1 Structural Characterization of Reactive Diluents

The UV-active reactive diluents were prepared based on IPDI, HEMA, and APTES (mole ratio: 1:1:1) and the synthesis was basically a two-stage process. For the first stage, HEMA and IPDI reacted with each other to yield mono-acrylated isocyanates.

For the second stage, APTES was added to react with the residual –NCO group to form the final reactive diluents. A small amount of DBTDL (0.5wt%) was used as catalyst to accelerate reactions between hydroxyl groups in HEMA and isocyanate groups in IPDI.

The FTIR spectrum of resultant reactive diluents was shown in Figure 2-4. The disappearance of characteristic peak of free –NCO around 2250 cm<sup>-1</sup> confirmed the completion of the reaction. The peaks at 3350 cm<sup>-1</sup> and 1730 cm<sup>-1</sup> regions correspond to N–H and C=O respectively, indicating the formation of urethane linkages. The peaks at 1630 cm<sup>-1</sup> and 956 cm<sup>-1</sup> regions are attributed to C=C and C=C–H, respectively. The 780 cm<sup>-1</sup> region represents the characteristic peak of Si-O-CH<sub>2</sub>CH<sub>3</sub>.<sup>51</sup> The results of FTIR analysis indicated that the synthesized reactive diluents contained both UV-active acrylate groups and moisture curing alkoxylsilance groups.



Figure 2- 4 FTIR spectrum of UV-active reactive diluents

The resultant reactive diluents were also characterized by <sup>1</sup>H NMR and the spectrum was shown in Figure 2-5. <sup>1</sup>H NMR chemical shifts were  $\delta = 5.60$  and 6.15 (-C(CH<sub>3</sub>)=CH<sub>2</sub> from HEMA), 1.96 (-C(CH<sub>3</sub>)=CH<sub>2</sub> from HEMA), 4.30-4.62 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O- from HEMA), 3.80-3.85 (-Si(-O-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> from APTES), 3.72 (-CH- in the cyclic ring of IPDI), 3.15-3.19 (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si- from APTES), 2.97 and 2.62 (-CH<sub>2</sub> attached to primary –NCO from IPDI), 1.08, 1.42, and 1.62-1.75 (-CH<sub>2</sub>- in cyclic ring of IPDI), 1.60 (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si-) 1.20-1.26 (-Si(-O-CH<sub>2</sub>-CH<sub>3</sub>)<sub>3</sub> from APTES), 0.89 and 0.93 (-CH<sub>3</sub> attached to cyclic ring of IPDI), 0.63-0.66 (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si- from APTES) ppm.<sup>52</sup>



Figure 2- 5<sup>1</sup>H NMR spectrum of resultant reactive diluents

Several side reactions may occur during the synthesis of reactive diluents. For example, the formed urethane groups might react with free –NCO groups, leading to the formation of allophanates. If moisture exists in the reaction flask, the –NCO

groups can also react with water to generate unstable intermediate acids which will dissociate into carbon dioxides and amines. The amines could react with -NCO groups rapidly to form ureas.<sup>1</sup> The water may also cause hydrolysis and condensation reactions of alkoxylsilance groups in APTES. In addition, a certain amount of HEMA would still react with both primary and secondary -NCO groups in IPDI to yield diacrylated diisocyanates (DAD) although the two -NCO groups have unequal reactivity.<sup>53</sup> To avoid all possible side reactions as well as to keep the concentration of DAD as low as possible, several measures were taken to control the synthesis process. Firstly, nitrogen was purged through the flask for 30 minutes before the reactions started to remove moisture in the flask. Secondly, HEMA instead of APTES was added for the first stage because reactions between -NH2 and -NCO are too rapid to control. Thirdly, DBTDL was chosen as catalyst in the synthesis since it was reported in previous research that DBTDL promoted high degree of selectivity of IPDI even at elevated temperature and catalyzed urethane formation reactions without catalyzing other side reactions.<sup>1</sup> Finally, the initial reaction in the first stage was carried out in cold water bath (around 10 °C) to further increase the difference of reactivity between primary and secondary -NCO groups in IPDI. The maximum reaction temperature in the first stage was set at 50 °C so that the urethane formation reactions proceeded at relatively fast rate while the reactive selectivity of IPDI was still at relatively high level.

ESI-MS analysis was performed to identify chemical composition of the synthesized product and the spectrum was shown in Figure 2-6. The sample was

ionized by sodium cations to generate sodiated molecular ions without any fragmentation. Thus, the molecular weight shown on the spectrum is equal to the molecular weight of certain chemical compound plus the molecular weight of sodium cation. The molecular weight of synthesized reactive diluents is 573 Da and sodium cation adds 23 Da, hence the molecular weight of expected reactive diluents ions should be 596 Da, which corresponds to the strongest peak (596.2) on the spectrum. The weak peak at 505.1 is attributed to ionized diacrylated diisocyanates (DAD) (482 Da + 23 Da). The 687.3 distribution corresponds to ionized dialkoxylsilance functionalized IPDI (664 Da + 23 Da). The peak assignment of ESI-MS spectrum is listed in Table 2-3. By comparing the intensity of each peak, it can be concluded that the synthesis process was well controlled and the major products were the intended reactive diluents.



Figure 2- 6 ESI-MS spectrum of Reactive Diluents



Table 2- 3 Peak assignment of ESI-MS spectrum of Reactive Diluents

# 2.6.2 Structural Characterization of Acrylated Urethane Prepolymers

The synthesis process of acrylated urethane prepolymers (AUP) was also a two-stage process. For the first stage, IPDI and HEMA reacted to yield monoacrylated diisocyanates. Then polyether polyols (1915 U) provided by Bayer Material Science were added into reaction flask to yield acrylated urethane prepolymers for the second stage. Similar methods used to control the synthesis of reactive diluents were also used in the synthesis of AUP. DBTDL was used to accelerate the reactions and promote reactive selectivity of IPDI. Since more side reactions might occur at high temperature and the reactive selectivity of IPDI decreased with increasing temperature, the maximum reaction temperature was also kept at 50 °C. The resultant prepolymers

were characterized by FTIR and <sup>1</sup>H NMR. The result of FTIR analysis was shown in Figure 2-7.



Figure 2-7 FTIR spectrum of acrylated urethane prepolymers

The disappearance of characteristic peak of free –NCO around 2250 cm<sup>-1</sup> confirmed the completion of the reaction. The peaks at 3340 cm<sup>-1</sup> and 1730 cm<sup>-1</sup> regions are attributed to N–H and C=O respectively, indicating the formation of urethane linkages. The peaks at regions of 1109, 1297, 1343, and 1373 cm<sup>-1</sup> may be ascribed to -C-O. The peaks at 1630 cm<sup>-1</sup> and 940 cm<sup>-1</sup> regions corresponds to C=C and C=C–H, respectively.<sup>51,54</sup>

The <sup>1</sup>H NMR spectrum of polyether based acrylated urethane prepolymers was shown in Figure 2-8. <sup>1</sup>H NMR chemical shifts were  $\delta = 5.59$  and 6.13 (-C(CH<sub>3</sub>)=C<u>H<sub>2</sub></u> from HEMA), 4.21 and 4.32 (-O-C<u>H<sub>2</sub>-CH<sub>2</sub>-O-</u> from HEMA), 3.54 (-C<u>H</u>- in the cyclic ring of IPDI), 2.93 (-C<u>H<sub>2</sub></u> attached to primary –NCO), 1.95 (-C(C<u>H<sub>3</sub>)=CH<sub>2</sub></u> from

HEMA), 1.06, 1.33, 1.42, and 1.68 (-C $\underline{H}_2$ - in cyclic ring of IPDI) 0.88 and 0.93(-C $\underline{H}_3$  attached to cyclic ring of IPDI) ppm.<sup>52</sup>



Figure 2-8<sup>1</sup>H NMR spectrum of acrylated urethane prepolymers

The polyether polyols (1915 U) were commercial products and the exact chemical structure of the products was not provided. The unassigned chemical shifts in <sup>1</sup>H NMR spectrum thus might be attributed to the protons in polyether polyols. Yet the FTIR analysis has confirmed the formation of urethane linkages and existence of ether functional groups. And the <sup>1</sup>H NMR results proved the existence of methacrylate C=C double bonds which could be used for UV initiated photopolymerization.

# 2.6.3 Structural Characterization of TEOS oligomers

The TEOS oligomers were first characterized by <sup>1</sup>H NMR and the spectra of TEOS oligomers and TEOS monomers were shown in Figure 2-9. The quartet centered at 3.85 ppm is the resonance of methylene protons associated with TEOS. The quartet

centered at 3.70 ppm is the resonance of methylene protons of ethanol. Two changes occurred after the sol-gel process of TEOS monomers. One is the resonance of methylene protons in ethanol is observed on Figure 2-10 (b), which is the result of hydrolysis and condensation reactions between TEOS monomers, water, and silanols. In addition, the intensity of resonance of methylene protons associated with silicon decreased after the sol-gel process. The reason for this is that methylene protons in alkoxysilane transferred to ethanol as hydrolysis proceeds.<sup>55</sup>



Figure 2-9<sup>1</sup>H NMR spectra of (a) TEOS and (b) TEOS oligomers



Figure 2- 10 <sup>1</sup>H NMR spectra of (a) TEOS and (b) TEOS oligomers at the regions between 3.60-4.00 ppm

The synthesized TEOS oligomers were further characterized by ESI-MS and the results are shown in Figure 2-11. The molecular weight shown on the spectrum is equal to the molecular weight of certain chemical compound plus the molecular weight of sodium cation. The results were compared with previous studies and the peak assignments of the mass spectra are summarized in Table 2-4. In general, the sol-gel process of TEOS monomers resulted in linear, branched, and cyclic polysilicates. The peaks observed at 633, 767, and 605 correspond to linear or branched oligomers containing linear or branched structures. The peaks observed at 693, 827, 961, 1095, 1411 are attributed to oligomers containing monocyclic structures, for example. Oligomers with bicyclic structures were also observed in the

spectra, corresponding to peaks in the values of 753, 1021, and 1155, for instance. The relatively high peak values may be attributed to oligomers with tricyclic structures, such as peaks at 1081 and 1215.<sup>56,57</sup>





Figure 2- 11 ESI-MS spectrum of TEOS oligomers: (a) full spectrum; (b) zoomed region from 500 to 1000; (c) zoomed region from 1000 to 1500.

Peaks	Molecular	Structural Formula	Structural Features
	Weight		
633,767	97+134n	$Si_n(OC_2H_5)_{2n+2}$	
605	69+134n	$Si_n(OC_2H_5)_{2n+1}(OH)$	$C_2H_5O - (31 O) OH_5C_2$ $OH_5C_2$
693,827,961,1095 799,933,1067	23+134n -5+134n	$\begin{array}{l} Si_n(OC_2H_5)_{2n}\\ Si_n(OC_2H_5)_{2n-1}(OH)\end{array}$	$C_2H_5O$ $OH_5C_2$ $C_2H_5O$ $OH_5C_2$ $C_2H_5O$ $OH_5C_2$ $C_2H_5O$ $OH_5C_2$ $C_2H_5O$ $OH_5C_2$
753,1021,1155 993,1127	-51+134n -79+134n	(SiO) <sub>n</sub> O(OC <sub>2</sub> H <sub>5</sub> ) <sub>2n-2</sub> (SiO) <sub>n</sub> O(OC <sub>2</sub> H <sub>5</sub> ) <sub>2n-3</sub> (OH)	$\begin{array}{c} C_2H_50 \\ O \\ C_2H_50 \\ C_2H_$
1081,1215	-125+134n	$(SiO)_nO_2(OC_2H_5)_{2n-4}$	$C_{2}H_{5}O \xrightarrow{C_{2}H_{5}O}_{I} \xrightarrow{O} \xrightarrow{O} H_{5}C_{2}$
1187	-153+134n	(SiO) <sub>n</sub> O <sub>2</sub> (OC <sub>2</sub> H <sub>5</sub> ) <sub>2n-5</sub> (OH)	$\begin{array}{cccc} C_{2}H_{5}O & & & & OH_{5}C_{2} \\ C_{2}H_{5}O & & & & Si & OH_{5}C_{2} \\ C_{2}H_{5}O & & & & OH_{5}C_{2} \\ C_{2}H_{5}O & & & & OH_{5}C_{2} \\ C_{2}H_{5}O & & & & & Si & OH_{5}C_{2} \\ C_{2}H_{5}O & & & & & Si & OH_{5}C_{2} \\ C_{2}H_{5}O & & & & & Si & OH_{5}C_{2} \\ C_{2}H_{5}O & & & & & Si & OH_{5}C_{2} \\ \end{array}$

Table 2- 4 Peak assignments for mass spectra of TESO oligomers

# 2.6.4 Photo-curing Kinetics of Hybrid Coatings

The UV-initiated photo-curing kinetics of the hybrid coatings were investigated using photo differential scanning calorimetry (photo-DSC). The photopolymerization process was based on free radical polymerization mechanism in which upon the UV exposure, photoinitiators in the system dissociate to generate free radicals which could induce the polymerization of coating resins to form crosslinked films. The curing process is exothermic and can be monitored through measuring the heat flow generated from the sample during UV exposure. UV-active functional groups in the hybrid coating systems developed in this study are methacrylate C=C bonds in HEMA and it was assumed that the reaction of C=C bonds contributed to all the heat generation during the polymerization process. The photopolymerization process for a given system is affected by many factors, including type and concentration of photoinitiators, time of exposure, intensity and wavelength distributions of the UV light source.<sup>58</sup> Since the purpose of this study was to investigate the influence of reactive diluents and TEOS oligomers on the photo-curing process of hybrid coatings, same amount of photoinitiators (4wt%, Darocur® 4265) was used for all formulations and the intensity of UV light was set at constant value ( $220 \pm 20 \text{ mW} \cdot \text{cm}^{-2}$ ) for each test.

Figure 2-12 shows the photo-DSC exotherms of hybrid coating formulations (F15, F25, and F35) containing different concentration of reactive diluents. The times for peak maximum of all formulations were listed in Figure 2-13. In general, typical auto-acceleration followed by auto-deceleration behaviors were observed for all hybrid systems. The photopolymerization rates of all formulations reached maximum within 2s and the all the curing processes were completed after 40s of UV exposure, reflecting rapid curing character of UV-curable system. The results also indicated that the polymerization rates increased with increasing amount of reactive diluents. This may be attributed to the enhanced auto-acceleration effect occurred in hybrid systems with higher reactive diluents contents. As the photopolymerization proceeded

crosslinked structures formed in the system, reducing the mobility and diffusion of propagating radicals. Since the termination reaction occurred by effective collision between two propagating radicals, the reduction of propagating radical mobility resulted in a decrease of the probability of effective collision, which led to the reduction of termination reaction rate. As termination reaction rates decreased, the concentration of propagating radicals correspondingly increased, which accelerated the polymerization of coating resins. Higher reactive diluents concentration contributed to higher concentration of crosslinked structures, which resulted in lower termination reaction rate and correspondingly higher propagating radical concentration. As a result, formulation with higher reactive diluents contents exhibited faster polymerization rate.<sup>59</sup>



Figure 2- 12 Photo-DSC curves of hybrid coatings as a function of reactive diluents



Figure 2-13 Peak Maximum Times for formulations as a function of reactive diluents Photo-DSC exothermic curves of hybrid formulations as a function of TEOS oligomers were shown in Figure 2-14. Peak maximum times for all formulations were summarized in Figure 2-15. Similarly, all hybrid systems exhibited auto-acceleration followed by auto-deceleration behaviors. The polymerization rates of all formulations rapidly increased to maximum within 2s of UV exposure and all curing processes were finished within 40s. The photopolymerization rates gradually increased when the amount of TEOS oligomers increased from 0wt% to 5wt%. But the reaction rates decreased when the concentration of TEOS oligomers further increased to10wt%. The increase of reaction rates with addition of TEOS oligomers up to 5wt% could be ascribed to two factors. On the one hand, some TEOS oligomers in the system may aggregate to form larger particles that could reflect or scatter UV lights, extending the path length of UV lights and thereby enhancing the efficiency of initiation reactions.<sup>60</sup> On the other hand, TEOS particles in the system may behave like "effective flow agents" promoting the mobility and diffusion of propagation radicals during the

UV-curing process, which led to the increase of photopolymerization rates of hybrid coating systems.<sup>61</sup> However, when the concentration of TEOS oligomers increased up to 10wt%, more large size TEOS aggregates formed in the system, which hindered the absorption of UV lights during the initiation stage, resulting in the decrease of photopolymerization rate.<sup>60</sup>



Figure 2-14 Photo-DSC curves of hybrid coatings as a function of TEOS oligomers



Figure 2-15 Peak Maximum Times for formulations as a function of TEOS oligomers

2.6.5 Viscoelastic Properties of Hybrid Films

The viscoelastic properties of hybrid coating films were investigated via DMTA. Figure 2-16 shows the storage modulus (E') and tanδ transition of hybrid coatings as a function of reactive diluents.



Figure 2- 16 Storage modulus (a) and tanδ (b) of hybrid films (F15, F25, and F35) as a function of reactive diluents.

The results showed that for all hybrid films studied, the storage modulus (E<sup>\*</sup>) slightly decreased from -100 °C up to -50 °C and then started to decrease dramatically with increasing temperature to reach roughly a constant value, leading to formation of rubbery plateau. At the rubbery plateau, hybrid coatings with higher content of reactive diluents demonstrated higher storage modulus (E<sup>\*</sup>) value. The tan $\delta$  curves exhibited bimodal shapes and two  $\alpha$  transitions, a sharp transition at low temperature ( $\alpha_{s}$ ) and a broad transition at relatively high temperature ( $\alpha_{H}$ ), could be notably observed for each hybrid film. The transition temperatures were summarized in Table 2-5. The results indicated that the  $\alpha_{s}$  transitions for all hybrid films appeared to be independent of the reactive diluents contents, while  $\alpha_{H}$  transitions broadened toward higher temperatures as the concentration of reactive diluents increased. Yet the onset of  $\alpha_{H}$  transitions for all hybrid films with different amount of reactive diluents almost started at the same temperature.

The bimodal feature of tan $\delta$  curves observed in this study is mainly due to the inhomogeneity of UV-curing system.<sup>62</sup> During the photopolymerization process, multiple crosslinking reactions may occur simultaneously in the hybrid system within a very short period of time, including reactions between reactive diluents (RD), reactions between acrylated urethane prepolymers (AUP), reactions between RD and AUP, and reactions between diacrylated diisocyanates (DAD), as shown in Figure 2-17, which resulted in the formation of highly heterogeneous structures. According to previous studies,<sup>63-65</sup> the heterogeneous networks formed in the hybrid system consisted of soft polyurethane (polyether polyols endcapped by IPDI molecules)

chains linked together by hard microgel-like clusters based on polyacrylate chains and DAD units. The soft polyurethane segments have much higher mobility compared to the hard segments and thereby relaxed at relatively low temperatures ( $T_{\alpha S}$ ). The rapid UV-curing process resulted in the formation of rigid microgel-like clusters of different sizes, which were responsible for the broad transition peaks at high temperatures  $(T_{\alpha H})$ . As the amount of reactive diluents increased, more rigid clusters formed leading to a further reduction of the mobility of polymer chains trapped inside these clusters, and the system became more heterogeneous as well. Therefore, hybrid films containing higher concentration of reactive diluents exhibited higher E' value as well as higher  $T_{\alpha H}$  due to the existence of more hard segments. And the width of transition peak became broader due to the increased structural inhomogeneity. The onset of  $\alpha_{\rm H}$ transitions is independent of reactive diluents contents probably because the relaxations of molecules around the vicinity of hard clusters were not heavily affected by the internal structure of these clusters. While the soft segments consisting of long and flexible polyether chains were unaffected by the hard segments, thus temperatures of the  $\alpha_{\rm S}$  relaxations were almost the same for all hybrid films containing different concentration of reactive diluents.<sup>62</sup>





Formulations	Ratio of reactive diluents to AUP	$T_{\alpha S}(^{\circ}C)$	$T_{\alpha H}(^{o}C)$
F15	15/85	-36±1	$61 \pm 1.5$
F25	25/75	-36±2	$98\pm1$
F35	35/65	-37±2	$120\pm1$

Table 2- 5 Viscoelastic properties of hybrid films as a function of reactive diluents with 2.5wt% of TEOS oligomers

The storage modulus (E') and tanð curves of hybrid films as a function of TEOS oligomers are shown in Figure 2-18. The E' displayed a slightly decreasing trend from -100 °C to -50 °C and then decreased significantly between -50 °C to 130 °C for all hybrid films. The bimodal shapes of transitions could also be observed on the tanð curves in Figure 2-18 (b). The  $T_{\alpha S}$  and  $T_{\alpha H}$  for all hybrid films are summarized in Table 2-6. As discussed before, the inhomogeneity resulting from the rapid UV-curing process is mainly responsible for the bimodal tanð transitions where soft polyether chains corresponded to transitions at low temperatures and hard micro-gel like clusters contributed to transitions at relatively high temperatures, respectively. The  $\alpha_S$  transitions occurred around -37 °C for all hybrid films because the flexible polyether chains are rather unaffected by TEOS oligomers. The  $\alpha_H$  transitions slightly shifted to higher temperature as the concentration of TEOS oligomers increased. The reason for this is that more rigid polysiloxane formed in the hybrid films containing higher TEOS oligomer content.<sup>9</sup>



Figure 2- 18 Storage modulus (a) and  $tan\delta$  (b) of hybrid films (T0, T2.5, T5, and T10) as a function of TEOS oligomers.

Formulations	TEOS oligomers content (wt%)	$T_{\alpha S}(^{o}C)$	$T_{\alpha H}(^{o}C)$
Т0	0	-37±1	90±1
T2.5	2.5	-36±2	98±1
T5	5	-37±1	98±1.5
T10	10	$-37 \pm 0.5$	$105 \pm 0.6$

Table 2- 6 Viscoelastic properties of hybrid films as a function of TEOS oligomers with the ratio of reactive diluents to acrylated urethane prepolymers: 25/75.

#### 2.6.6 Tensile and General Coating Properties

The elongation-at-break, modulus, and tensile strength of hybrid films as a function of reactive diluents are show in Figure 2-19. The results show that for all hybrid films studied, the elongation-at-break dramatically decreased while the modulus as well as tensile strength significantly increased with increasing amount of reactive diluents. The reason for this is that as the concentration of reactive diluents increased, the concentration of soft segments (polyether chains) correspondingly decreased, which reduced the flexibility of the hybrid film, thereby the elongation-at-break which is proportional to the flexibility of the film decreased. On the contrary, higher concentration of reactive diluents led to the formation of more hard segments in the system as well as higher crosslinking density, enhancing the rigidity of the hybrid film, hence the modulus and tensile strength increased.



Figure 2- 19 Tensile properties of hybrid films as a function of reactive diluents with 2.5 wt% of TEOS oligomers. (a) elongation-at-break; (b) modulus; (c) tensile strength

The elongation-at-break, modulus, and tensile strength of hybrid films as a function of TEOS oligomers are show in Figure 2-20. The results indicate that the elongation-at-break, modulus, and tensile strength of all hybrid films appeared to be unaffected by the concentration of TEOS oligomers within deviation, hence these properties only depend on the organic phase in the hybrid system.<sup>9</sup>





Figure 2- 20 Tensile properties of hybrid films as a function of TEOS oligomers with the ratio of reactive diluents to urethane prepolymers: 25/75. (a) elongation-at-break; (b) modulus; (c) tensile strength

The general coating properties of hybrid films as a function of reactive diluents are listed in Table 2-7. The pencil hardness of hybrid films appeared to be independent of the reactive diluents contents. And all hybrid films tested in general exhibited relatively high impact resistance (maximum measured value: 100kg/cm) and with increasing amount of reactive diluents the impact resistance slightly decreased. The excellent impact resistance performance of all hybrid films is mainly due to the synergistic effect between polyether chains and hydrogen bonds formed in the system. The polyether chains are highly flexible soft segments (low Tg) which have high mobility and are able to extend between hard segments (high Tg) upon external impact forces. The hydrogen bonds will break upon impact and could regenerate when the stress is removed, which helps absorb energy and thereby reduce the

possibility of irreversible breaking of the film. The combination of these two factors led to the high impact resistance property of the hybrid films.<sup>1</sup> The crosshatch adhesion increased from 1B to 3B as the concentration of reactive diluents increased from 14.03wt% up to 32.73wt%. The pull-off adhesion increased significantly from 0.80 to 1.63 N/mm<sup>2</sup> when the concentration of reactive diluents increased from 14.03 to 23.38wt% and slightly decreased to 1.36 N/mm<sup>2</sup> as the amount of TEOS oligomers further increased. The reason for the enhanced adhesion indicated by crosshatch adhesion and pull-off adhesion tests is that with compared to hybrid films F25 and F35, the amount of reactive diluents in F15 is too low to provide enough compatibility between organic and inorganic phases, thereby resulting in poor adhesion behavior. But as the concentration of reactive diluents increased from 23.38 to 32.73wt%, the compatibility between organic/inorganic phases was further improved and the degree of phase separation correspondingly decreased. As a result, the amount of TEOS oligomers distributed on the substrate surface may be reduced, leading to the slightly decreased adhesion.9

Hybrid Coatings	F15	F25	F35
Ratio of reactive diluents to	15/05	25/75	25/65
urethane prepolymer	15/85	25/75	35/65
Pencil hardness	5B	5B	5B
Impact resistance	> 100	$07.2 \pm 1.6$	010+22
(direct, kg/cm)	>100	97.3±1.0	91.0±2.2
Crosshatch adhesion	1B	3B	3B
Pull-off adhesion (N/mm <sup>2</sup> )	$0.80 \pm 0.1$	$1.63 \pm 0.11$	1.36±0.09

Table 2- 7 General coating properties of hybrid films as a function of reactive diluents with 2.5wt% TEOS oligomers.

Table 2-8 shows the general properties of hybrid films as a function of TEOS oligomers. All hybrid films demonstrated same pencil hardness as well as similar high impact resistance. Thus, it can be concluded that both the pencil hardness and impact resistance are rather unaffected by the amount of TEOS oligomers and predominantly determined by organic phase (polyurethane) in the system. Besides, it seems that TEOS oligomers did not have much influence on the adhesion property of hybrid films according to the results of crosshatch adhesion tests. But the results of pull-off adhesion tests show that the adhesion of hybrid films slightly increased as the concentration of TEOS oligomers increased up to 5wt% and then decreased significantly as the amount of TEOS oligomers reached 10wt%. The reason for the difference in results indicated by the two measurements is probably because the
pull-off adhesion is a more sensitive way to measure adhesion of coating films than the crosshatch adhesion. The improved adhesion may be attributed to the increasing amount of Si-O-Al bonds on the substrate as more TEOS oligomers were added into the system.<sup>6,9</sup> But when the concentration of TEOS oligomers further increased to 10wt%, the reactive diluents in the system were not able to provide enough coupling connections between organic and inorganic phases and hence the adhesion of hybrid coating reduced.<sup>9</sup>

Table 2- 8 General coating properties of hybrid films as a function of TEOS oligomers with the ratio of reactive diluents to urethane prepolymers: 25/75

Hybrid coatings	Т0	T2.5	Τ5	T10
Content of TEOS	0	2.5	5	10
oligomers (wt%)	Ĩ		-	
Pencil hardness	5B	5B	5B	5B
Impact resistance	93.3±1.9	97.3±1.6	95.3±1.4	94.0± 2.2
(direct, kg/cm)				
Crosshatch adhesion	3B	3B	3B	3B
Pull-off adhesion	$1.29 \pm 0.07$	$1.63 \pm 0.11$	$1.55 \pm 0.11$	$1.13 \pm 0.13$
$(N/mm^2)$				

## CHAPTER III

## CONCLUSION

In this study, a new type of UV-curable organic/inorganic hybrid coating system was successfully developed. The organic phase was based on acrylated urethane prepolymers prepared by reactions of polyether polyols and 2-hydroxyethyl methacrylates (HEMA) with cycloaliphatic isophorone diisocyanates (IPDI). The inorganic phase was based on tetraethyl orthosilicates (TEOS) oligomers synthesized via sol-gel process. Reactive diluents were prepared using IPDI, HEMA, and (3-aminopropyl) triethoxysilanes (APTES) and behaved as coupling agents capable of providing the connection between organic/inorganic phases. The synthesized acrylated urethane prepolymers, reactive diluents, and TEOS oligomers were characterized using various analysis techniques including FT-IR, <sup>1</sup>H NMR, and ESI-MS spectroscopy.

The free-radical initiated UV-curing kinetics of hybrid coatings were investigated using photo-DSC. The results indicated that in general hybrid coating systems based on different formulations all demonstrate relatively rapid photopolymerization rates. At constant TEOS contents (2.5wt%), formulations containing higher concentration of reactive diluents exhibited faster polymerization rates due to the decrease of termination reaction rate and correspondingly increase of the propagating radicals concentration. At constant ratio of reactive diluents to acrylated urethane prepolymers (25/75), the addition of TEOS oligomers up to 5wt% apparently accelerated the photopolymerization process, which may be attributed to the facts that the TEOS particles in the system behaved like "effective flow agents" improving the mobility of reactive radicals during the UV-curing process and also extended the path length of UV lights by partial reflection or scattering. But the photopolymerization rate of the hybrid coating system decreased when the amount of TEOS oligomers further increased to 10wt%, and this might result from the aggregation of TEOS particles, which reduced the efficiency of initiation process.

The hybrid coating systems exhibited two  $\alpha$  transitions on the tan $\delta$  curves as indicated by DMTA results, which is mainly due to the inhomogeneity of UV-curing system. The transitions ( $\alpha_s$ ) occurred at low temperatures (around -38 °C) appeared to be independent of the concentration of reactive diluents or TEOS oligomers and thus were only determined by the soft polyether chains for all hybrid systems. However, the transitions ( $\alpha_H$ ) corresponding to the relaxation of hard segments shifted towards higher temperatures as the amount of reactive diluents increased. This is because higher reactive diluents concentration contributed to the formation of harder segments in the system and correspondingly lower chain mobility, which in turn resulted in the increase of transition temperatures. In addition, the increase of TEOS oligomers contents led to a slightly increase of the T<sub>att</sub> and this may due to the formation of more rigid polysiloxane structures in the system.

Both the tensile strength and modulus of the hybrid films dramatically increased while the elongation-at-break decreased significantly when the amount of reactive diluents increased. The reason for this is that high concentration of reactive diluents contributed to the increase of both hard segments contents and crosslinking density. The tensile properties of hybrid films appeared to be rather unaffected by the concentration of TEOS oligomers within the deviation. For general coating properties, the hardness of hybrid films was independent of the reactive diluents or TEOS oligomer contents. The impact resistance slightly reduced with increasing reactive diluents content, but did not change with the TEOS oligomer content within the deviation. The adhesion of the hybrid coatings was affected by both the reactive diluents and TEOS oligomer concentrations. For hybrid coatings with the addition of 2.5wt% of TEOS oligomers, the optimum adhesion behavior was observed when the concentration of reactive diluents was 23.28wt%. For hybrid coatings with constant ratio of reactive diluents to urethane prepolymers (25/75), the adhesion was improved slightly with the increase of TEOS oligomers contents up to 5wt%.

In future work, the morphology of the hybrid films will be studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The morphology studies could provide information about the internal structure of the crosslinked hybrid system, which may shed some light on the interactions between the organic and inorganic phases as well as the interactions between the coating film and the substrate. Besides, the morphology studies may also help verify the existence of soft and hard segments in the system and thereby provide better explanations for the bimodal shapes of tan  $\delta$  curves as indicated by DMTA analysis.

The solid state <sup>29</sup>Si-NMR analysis will be performed for all cured hybrid films to monitor the network formation of the inorganic components during the UV-curing process.

The free radical induced UV-curing reaction kinetics of the hybrid coating systems will be further investigated using the time resolved FT-IR spectrometer under controlled humidity. The UV-initiated reactions of acrylate C=C bonds as well as the moisture-curing process of the alkoxysilane groups can be monitored in time-resolved FT-IR and the final conversion of the double bonds as well as the conversion of alkoxysilane groups could also be calculated according to the results of time-resolved FT-IR analysis.

During the DMTA test, the trapped reactive radicals may be able to move and react with each other at elevated temperatures, which will affect the crosslinked structures and film properties as well. Thus, a repeat test will be performed for each hybrid films after the first run of DMTA test in the further work and then the effects of DMTA test on the hybrid films can be studied by comparing the first and second DMTA thermograms.

Furthermore, UV-cured films based on pure urethane prepolymers, pure di-HEMA functionalized isocyanates, and pure di-alkoxysilane functionalized isocyanates will be prepared. The photo-curing kinetics and viscoelastic properties of all these films will be measured and the results will be compared with the results of hybrid films to investigate the effect of each individual component on the hybrid coating system.

In addition, the UV-cured hybrid films will be analyzed by DSC and the results may provide information about the thoroughness of cure. Since the increasing temperature may cause reactions between the trapped reactive radicals in the cured films, which may change the thermal properties of the film. Therefore, repeat thermal DSC tests will be carried out for all the UV-cured hybrid films.

Finally, the gel contents for all the UV-cured hybrid films will be measured via extraction to further study the crosslink properties. The solution will be collected after the extraction and samples based the yield solution will be prepared for NMR and mass analysis.

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