

Novel Organic-Inorganic Hybrid Nano-Composite Coatings by UV-initiated Sol-Gel Process

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Abstract

UV-cure coatings have become systems of choice for plastic substrates, primarily due to their low-temperature cure, absence of potentially harmful solvents, and rapid curing. Free-radically curing acrylate resin systems are the most commonly used ones for commercial UV-cure systems for plastics. However, these systems have such inherent limitations as oxygen (air) inhibition of curing, poor substrate wetting, shrinkage, and odor that often limit their applications.

A novel chemistry, utilizing silane compounds, has been explored to study its suitability as an acrylate-free UV-curable system. We have demonstrated that such systems undergo cross-linking reactions through a UV initiated sol-gel process resulting in the formation of hybrid organic-inorganic nanocomposite films. A systematic design of experiment (DOE) methodology has been used to study the effects of various parameters on the properties of the nanocomposite films deposited on polycarbonate substrates.

Introduction

Among the number of available processes for producing organic-inorganic hybrid nano-composite coatings, the one based on a sol-gel process using silane-functional materials has been very promising. A traditional approach for sol-gel processing involves dissolving the silanes in water/alcohol/acid and allowing the silane-functional material to hydrolyze into silanols. The resulting sol can then be applied (by dipping or spraying, for example) onto a substrate and baked. Film formation results from the condensation reaction of the silanols.¹

A limitation of this approach is that the silane-functional materials must be soluble in water/alcohol. Percent solids are typically low. The viscosity is also low since the starting materials are typically low molecular weight (MW). This makes applying thick coatings challenging. Also, there are issues with pot-life; the coating properties can depend greatly on the age of the solution.

An alternate approach is to combine a photoacid generator (PAG) with the silane-functional material.²⁻¹⁰ Upon exposure to UV, the PAG generates an acid in-situ that catalyzes the hydrolysis and condensation reactions. The water necessary for hydrolysis is supplied by moisture in the atmosphere. This approach eliminates the hydrolysis step prior to application. Thus, the silane does not need to be soluble in water/alcohol. Also, these systems can be coated at much higher percent solids. Viscosity can also be more easily controlled. Since the curing reactions occur after UV-exposure, there are no issues with pot-life.

In the experiment described below, two model urethane-silane oligomers of differing molecular weights were synthesized from polycarbonate diols and an isocyanate-functional silane. Preliminary results indicated these materials, when UV-cured with a PAG, had excellent adhesion to untreated polycarbonate (PC) film. Also, the low temperature process used here is especially suitable for plastic substrates like PC.

An early patent⁶ describing the PAG-curing of silanes incorporates titanium isopropoxide (TIP) into some of the formulas. Preliminary experiments prior to the results described here showed that TIP, when used with silane-functional oligomers, greatly decreased the dry-to-touch time *prior to* UV-curing. TIP also seemed to improve the appearance of the coatings, especially in regard to clarity. Thus, it seemed possible that improvements in coating properties could be attained by adding TIP to the silane/PAG systems.

The present work investigates the effects on various physical properties of three variables: oligomer MW, presence of TIP, and humidity after UV-exposure. The experiment was set-up using a *Design of Experiment* (DOE) methodology using a 2³ matrix –each of the three variables is set to a low and high value for a total of eight tests. The DOE method is used to determine which of the three variables, as well as the interactions between them, have a significant effect on the results of a particular test.

Materials and Methods

Materials

Acetone and diacetone alcohol (DAA) were reagent-grade chemicals from Sigma-Aldrich. The titanium isopropoxide (TIP) was 97% active and was from Sigma-Aldrich. Dibutyltin dilaurate (DBTDL) was 95% active and was from Sigma-Aldrich. The isopropyl-9H-thioxanthene-9-one (ITX), 97% mixture of 2- and 4- isomers was from Sigma-Aldrich. The 3-isocyanatopropyltrimethoxysilane (IPTMS) was a sample from Momentive Performance Materials. The isocyanate (NCO) equivalent weight of the IPTMS was 205 grams/eq. The polycarbonate diols, Desmophen C 1100 (PC-diol-500) hydroxyl equivalent weight was 486 grams/eq, and Desmophen C 1200 (PC-diol-1000), hydroxyl equivalent weight was 944 grams/eq, were commercial samples from Bayer Materials Science. The PAG used was Irgacure 250 (Iodonium, (4-methylphenyl) [4-(2-methylpropyl) phenyl]-, hexafluorophosphate, 75% active in propylene carbonate) from Ciba Specialty Chemicals. All materials were used as received.

Concerning the substrates used, the polycarbonate (PC) used was 7 mil T2F OQ from GE. The

polycarbonate was used untreated. Using the methods described below, the uncoated PC has a haze of 0.0 and a Taber abrasion of 30.23. The PC is supplied with a protective film on both sides to prevent scratching. One side was peeled off prior to coating. The other side was removed later during haze testing. The fluoropolymer release (FPR) film was R-1655B from Precision Coatings, Inc (Walled Lake, Michigan). This is a white PET film that has been coated with a fluoropolymer to give it non-stick properties.

Coating Application and Curing

The coatings were applied to the substrates by manual draw-downs with a # 22 Mayer rod. The coatings were subjected to a pre-UV heating cycle (5 minutes at 120° C), followed by exposure to UV, and finally a post-UV heating cycle (15 minutes at 120° C). A Fusion UV system with a D-bulb was used for UV-curing. All UV-curing was done at 25 feet/min. Using a Compact Radiometer from UVPS, the energy density measured was 994.76 mJ/cm^2 . Two ovens were used: for the pre-UV heating cycle, a Scientific Products Constant Temperature oven DK-43 was used; A Tenney Environmental Test Chamber model BTRC with a VersaTenn III controller was used for the post-UV heating cycle (where the humidity needed to be controlled).

Testing and Evaluation

A Bruker Tensor 27 FTIR was used to analyze the urethane-silane oligomers that were synthesized. NaCl plates were used. NCO determination by titration was performed according to ASTM D 2572-97.

The physical and mechanical properties of the coatings made from the urethane-silane oligomers were determined by several different methods. Adhesion was tested by a cross-hatch tape pull (ASTM D 3359-02). Scotch 610 tape was used for all tests. Solvent resistance was determined by MEK double rubs. A Sheen 707KP Pendulum Hardness Rocker was used for all König tests. For all samples tested, at least three readings were taken and averaged. Results are reported in seconds. Coating thickness on polycarbonate was measured with a Heidenhain thickness gauge. Thermal Gravimetric Analysis (TGA) was performed with a TGA Q 500 from TA instruments. The rate of temperature increase was 20° C/min and the max temperature was 560° C. The onset of degradation (the temperature at which 95% of the original material remains) was recorded, as was the weight of the residue remaining at the end of the test. Glass Transitions temperatures of the cured films were determined by a Q 2000 Differential Scanning Calorimeter (DSC) from TA instruments. Hermetically sealed T-zero pans were used. The temperature program was as follows: Room temperature to 175° C at a rate of 20° C/min; 175° C down to -80° C at a rate of -5° C/min ; -80° C to 175° C at a rate of 20° C/min. Haze was measured with a Hunter Lab Colorquest II Colorimeter –"T-tran" Haze mode was used. Three readings were taken on each sample and the average was reported. Taber abrasion was measured with a Taber abraser model #5130. Each sample tested was subjected to 100 cycles using 500 grams weights. One sample of each variation was tested. The difference in haze before and after abrasion was reported. The contact angle of four solvents (toluene, benzyl alcohol, formamide, and water) on the coated films was determined by a FTA200 Dynamic Contact Angle analyzer from First Ten Angstroms. Surface energy was determined by using a Zisman plot¹¹. The coated samples were analyzed by Attenuated Total Reflectance IR (ATR-IR); a Bruker Hyperion ATR system was used.

DOE Methodology

Statgraphics Software (Statgraphics Plus 5.1 from Statistical Graphics Corp.) was used to design the experiment and to determine which variables had significant effects on each of the physical properties.

Experimental

Synthesis

Two urethane silane oligomers were synthesized from a diol, IPTMS, DBTDL, and acetone – the lower MW oligomer **U1** was made with the PC-diol-500 and the higher MW **U2** used PC-diol-1000. The NCO:OH ratio for **U1** and **U2** was 1.01:1.0. Acetone was used to adjust the percent solids to 76%. DBTDL was 0.02% of the total formula. The synthesis was performed in a 500 mL three-neck flask under nitrogen and with continuous stirring. Temperature was controlled with a heating mantle. After charging the reactor with all of the components, the solution was heated to 67–70° C and held for 3.5 hours. The solution was cooled to room temperature and transferred to a plastic container.

Application and Curing of Coatings

The **U1** and **U2** urethane-silane oligomers were used in a series of coatings. The experiment was set-up according to a DOE methodology. This is a 2³ (L-8) experiment – three variables at two levels: **A**) MW of urethane-silane oligomer (the low and high MW oligomers described above); **B**) amount of TIP added (0 or 5% by weight based on solids); **C**) humidity of post-UV heating cycle (low and high humidity). Since two of the variables are related to the coating formulation, there are four formulas total (designated **F1–F4**). The DOE matrix is summarized in table 1. The eight coated samples that result from this matrix are designated **S1–S8**.

The coating formulations **F1–F4** used are listed in table 2 and were made in the following manner: the PAG and ITX were dissolved in diacetone alcohol; then the urethane-silane oligomer (**U1** or **U2**) was added, followed by the acetone and TIP (if applicable); finally, this was hand-stirred for about 3 minutes.

For each of the eight experiments in the series, the coatings were applied to both PC and FPR. All coatings were applied to the substrate with a #22 rod and heated for 5 minutes at 120° C to remove the solvents (this is the pre-UV heating cycle). Then, the coatings were passed through the UV-cure unit five times. Finally, the coatings were heated for 15 minutes at 120° C (this is the post-UV heating cycle); the humidity of the oven was set according to variable **C**. The low humidity setting was about 5% RH (55 grams of water per 1 meter³ of air) and the high humidity setting was about 44% RH (480 grams of water per 1 meter³ of air).

The coated samples were then evaluated for appearance, adhesion, König pendulum hardness, thickness, solvent resistance, haze, Taber abrasion, pencil hardness, surface energy, DSC, TGA, and ATR-IR. The samples for DSC and TGA were prepared by scrapping the coating off of the samples coated on the FPR.

	Oligomer MW	TIP	humidity	
Sample	A	B	C	Formula
S1	low MW (U1)	0%	low	F1
S2	high MW (U2)	0%	low	F2
S3	low MW (U1)	5%	low	F3
S4	high MW (U2)	5%	low	F4
S5	low MW (U1)	0%	high	F1
S6	high MW (U2)	0%	high	F2
S7	low MW (U1)	5%	high	F3
S8	high MW (U2)	5%	high	F4

Table 1: 2^3 DOE matrix: three variables at two levels. Since two of the variables are formulation parameters, there are four formulas (designated **F1–F4**, see table 2). The resulting eight coated samples are designated **S1–S8**.

Component	F1	F2	F3	F4
Urethane-Silane (U1 or U2)	63.4%	62.6%	59.9%	59.1%
titanium isopropoxide	0.0%	0.0%	2.4%	2.4%
diacetone alcohol	34.7%	34.7%	34.7%	34.7%
acetone	0.1%	0.9%	1.1%	1.9%
PAG	1.5%	1.5%	1.5%	1.5%
ITX	0.3%	0.3%	0.3%	0.3%
Total	100.0%	100.0%	100.0%	100.0%
Urethane-Silane used	U1	U2	U1	U2

Table 2: The formulations of the four coatings used in this experiment.

Results and Discussion

Synthesis

NCO content was tested by both titration (ASTM D-2572) and FTIR. The titration showed that < 0.01% NCO remained. The absence of a peak at 2270 cm^{-1} in both FTIR spectra (shown in figure 1) confirms all of the NCO had reacted.¹²

Coating Application and Curing

The pot-life of the formulas with TIP seems very short – the usable time is one hour, at most. This can be explained based on the very high hydrolysis /condensation rate of TIP in presence of ambient moisture. The formulas without TIP seemed very stable (certainly over a period of a few days).

The coated samples containing TIP were dry-to-touch after the pre-UV baking cycle, while the samples without TIP were still obviously wet. The samples without TIP became dry-to-touch after the first pass of UV-curing. The samples with TIP coated on both PC and FPR had a very uniform

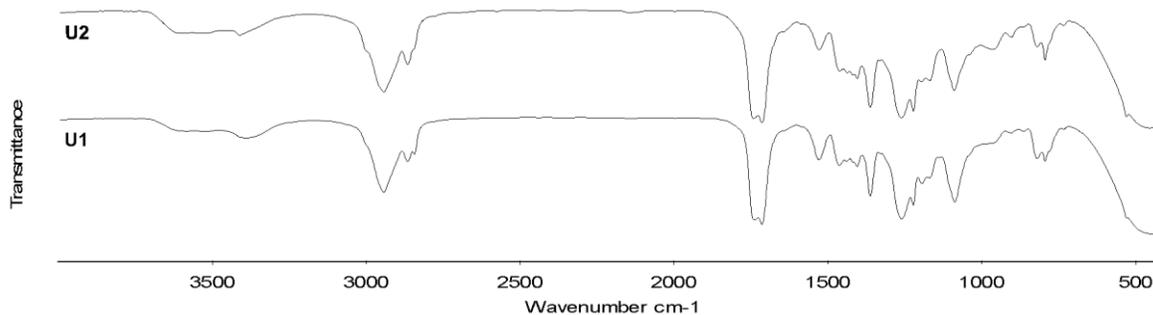


Figure 1: IR spectra of **U1** and **U2** oligomers. The absence of a peak at 2270 cm^{-1} confirms the absence of NCO groups.

appearance (coatings were free of orange peel and did not de-wet). The coatings on PC without TIP had slight orange peel, while those on FPR completely de-wetted – the de-wetting occurred during the pre-UV heating cycle. The de-wetting was more severe for the coatings made with the lower MW oligomer (**U1**). All of the coatings turned slightly yellow during the UV-curing process. All of the coatings had a soft, elastomeric (rubbery) feel. The thickness of all coatings was in the range $7 - 10\ \mu$.

Adhesion to PC was excellent – all samples were rated as 5B with the cross-hatch adhesion test. Surprisingly, the adhesion to the FPR was very good – the coating could not be removed with tape. It could, however, be scrapped off with a metal spatula. Solvent resistance, determined by MEK rubs, was very low for all samples. The best sample resisted 10 double rubs with MEK.

As the coated samples aged, some of them became increasingly hazy. The haze could be partially removed by wiping the film. The haze readings taken were on areas where the haze was not wiped away.

The results for the König pendulum, pencil hardness, haze, Taber abrasion, surface energy, TGA, and DSC are summarized in table 3. A representative TGA thermogram (of sample **S1**) is seen in figure 2. DSC thermograms of samples **S1** and **S2** are seen in figure 3.

The humidity of the oven during the post-UV heating cycle had no significant effect on any result. This is somewhat surprising. Water is required to hydrolyze the Si-O-CH_3 groups. The acid liberated during UV-exposure catalyzes this reaction. If there were still unhydrolyzed methoxy silane groups after UV-cure, then exposure to a humid environment would likely help complete hydrolysis. However, because the humidity level did not seem to cause any real change, then either hydrolysis was complete during UV-exposure or the amount of moisture present at the low humidity conditions was sufficient to allow complete cure..

Decreasing the MW of the oligomer increases both the cross-linking and the number of urethane groups. This is likely the reason that the König pendulum damping time and T_g increased as the MW of

Samples	König	Pencil	Haze	Taber	Surface Energy	TGA 95%(°C)	TGA Residue	DSC T _g (°C)
S1	134.4	6B	6.10	6.56	27.7	321.9	13.02	-46.41
S2	70.0	4B	7.07	37.73	23.4	329.5	7.05	-51.39
S3	136.1	2B	0.27	45.8	29.6	206	14.29	-46.93
S4	106.9	2B	0.22	59.95	28.3	214.1	10.92	-53.95
S5	137.5	6B	4.28	3.56	28.9	320.4	12.02	-44.45
S6	87.1	4B	5.04	54.64	22.3	329.2	7.06	-52.46
S7	141.4	2B	0.26	50.72	29.3	219.7	15.74	-48.51
S8	99.0	2B	0.40	67.39	27.7	227.2	10.37	-53.09

Table 3: *Physical characteristics of coatings.*

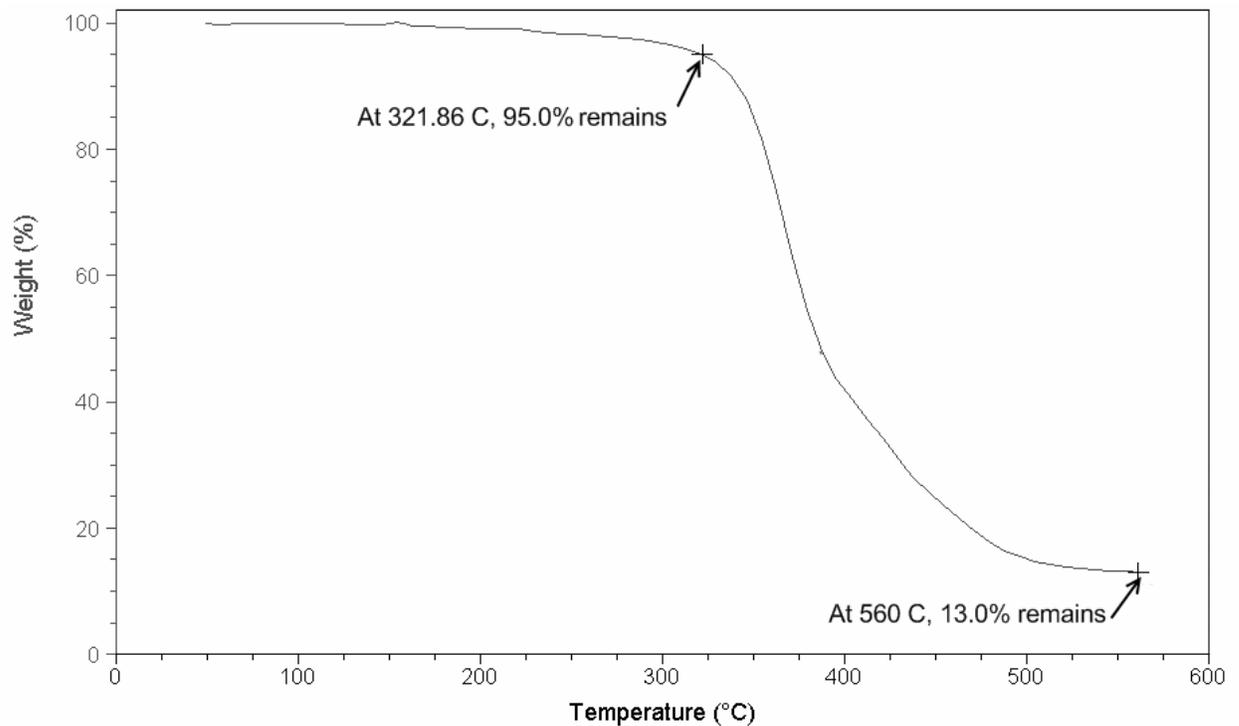


Figure 2: *A representative TGA thermogram (sample S1) showing the onset of degradation (i.e. the point where 95% remains), and the percent residue remaining at 560° C.*

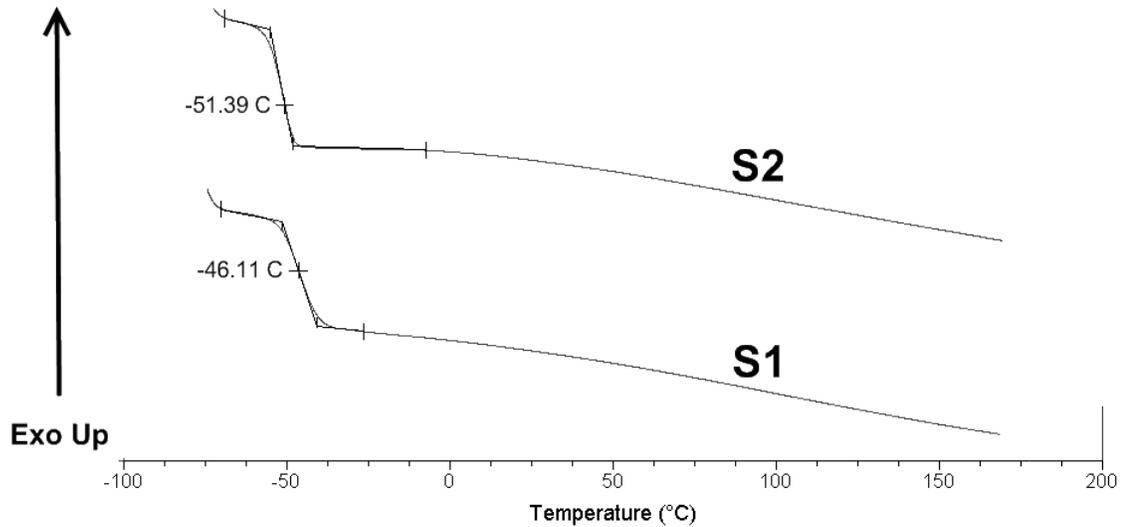


Figure 3: A DSC thermograms for **S1** and **S2**. The T_g is taken to be the midpoint of the endothermic baseline shift.

the oligomer decreased. This also explains the improvement in abrasion resistance. The increased number of urethane groups may explain the slight increase seen in surface energy. Increasing the MW of the oligomer seemed to improve wetting. This is likely because of the higher viscosity.

The presence of TIP had a major effect on many of the coating properties. It completely prevented de-wetting on both the PC and FPR. Given that the coatings with TIP become dry-to-touch during the pre-UV heating cycle, it appears that the viscosity is rising fast enough (due to cross-linking) to prevent de-wetting. The effect of TIP on the haze of the coatings was drastic. With TIP, the coatings are extremely clear; without TIP, they are obviously hazy. This haze seemed to worsen over time. Given that the haze could be partially wiped off, it appears the TIP prevented something from blooming to the surface. Exactly what is causing the haze is unknown. The effect of TIP is interesting. It greatly improved the appearance as well as improving the pencil hardness. However, it had only a minor effect on the König Pendulum and it actually decreased the abrasion resistance. It also only had a minor effect on the T_g of the coating. The TIP appears to be acting as a catalyst for the degradation reaction. There is over 100° C difference in the degradation temperatures. The exact role TIP plays in the curing reaction is not known, but it appears it is acting as a cross-linker by forming Si-O-Ti bonds (as will be discussed below).

The most encouraging result from these experiments is that *all* formulations had outstanding adhesion to polycarbonate. (It is unfortunate that the surface energy of the coatings is much too low to be useful as a primer.) Also encouraging was the increase in Taber abrasion resistance seen in **S1** and **S5** over uncoated PC.

A summary of the major influences on each of the physical properties is included in table 4.

Structure of Cured Coating

Both IR and DSC provide insight into the structure of the cured coating.

In comparing the IR spectra of the oligomers with those of the coated film samples, it shows that an Si-O-Si network is forming as expected. The important wavenumbers to consider are: the peak at 1087 cm^{-1} (Si-O-C asymmetric stretching)^{2,13}; the wide band from $1000 - 1140\text{ cm}^{-1}$ (Si-O-Si stretching)¹⁴; a peak at 850 cm^{-1} (Si-OH)¹³; a peak at $600 - 620\text{ cm}^{-1}$ (Ti-O-Ti)¹⁵; and a band at 910 cm^{-1} (Si-O-Ti)¹⁶.

The IR spectra (from 600 to 1800 cm^{-1}) for **S1**, **S3**, and **U1** (shown in figure 4) show the differences between starting material (**U1**) and the coatings without and with TIP (**S1** and **S3**, respectively). These spectra confirm that UV exposure caused the Si-O-CH₃ groups on the oligomer to form a Si-O-Si cross-linked network. The diminishing of the peak at 1087 cm^{-1} indicates the Si-O-CH₃ groups have been hydrolyzed into Si-OH. The absence of a peak at 850 cm^{-1} indicates that the Si-OH that were formed during hydrolysis have condensed into an Si-O-Si network. The wide band from $1000 - 1140\text{ cm}^{-1}$ in the coated film confirms that an Si-O-Si network has formed. The reaction scheme shown in figure 5 illustrates how the silica network forms after UV-exposure.

The coated samples containing Ti have a band around 910 cm^{-1} which seems to indicate the formation of Si-O-Ti bonds (this is easily seen in figure 4). Also, there is not an obvious peak or band around 600 cm^{-1} that would conclusively indicate Ti-O-Ti bond formation. The formation of Si-O-Ti bonds means that the TIP is acting as a cross-linker for the silanes. This would certainly explain the decrease in dry-to-touch time as well as the short pot-life.

The DSC thermograms for all eight variations (those of **S1** and **S2** are shown in figure 3) show a single endothermic base-line shift indicative of a glass transition. No other features are present. The single T_g suggests that no phase separation occurred during curing.

Conclusion

Two urethane-silane oligomers were synthesized from polycarbonate diols and IPTMS. These oligomers were combined with PAG to form UV-curable coatings. Upon exposure to UV, the PAG forms an acid that catalyzes both the hydrolysis of the silanes (using moisture in the atmosphere) and the subsequent condensation. This results in a cross-linked silica structure.

These oligomers were used in a series of experiments that investigated the effects of oligomer MW, the presence of TIP, and exposure of the coating to humidity after UV-curing on various physical properties. The experiments were organized as 2^3 DOE matrix.

The coatings produced by the urethane-silane oligomers had a soft, elastomeric feel with excellent adhesion to polycarbonate and a low T_g . It was found that the effect of humidity on the post UV-cure cycle had virtually no effect on any of the coatings' properties tested. The MW of the oligomer and the presence of TIP had major effects on the properties of the coating.

Response	Desired Direction	Important Variables
König Pendulum	up	Decreased MW → Increased König
Pencil Hardness	up	Increased TIP → Increased Pencil Hardness
Haze	down	Increased TIP → Decreased Haze
Taber: Haze After Abrasion	down	Decreased MW → Decreased Haze Change Decreased TIP → Decreased Haze Change
Surface Energy	up	Decreased MW → Increased Surface Energy Increased TIP → Increased Surface Energy
Degradation Temperature	up	Decreased TIP → Increased Degradation Temperature
Residue Remaining at 560°C	up	Decreased MW → Increased Residue Increased TIP → Increased Residue
T_g	n/a	Decreased MW → Increased T_g

Table 4: *The major influences on the coating physical properties are shown.*

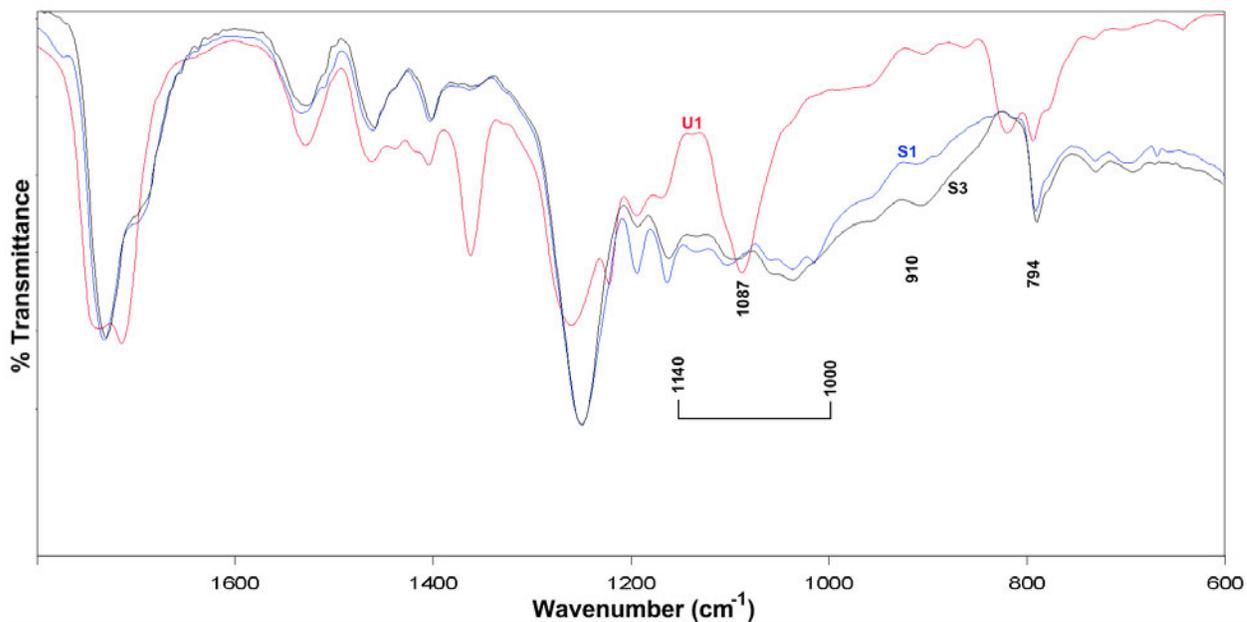


Figure 4: *FTIR spectra of U1 (unreacted low MW oligomer), S1 (coating made from U1), and S3 (coating made from U1 and TIP).*

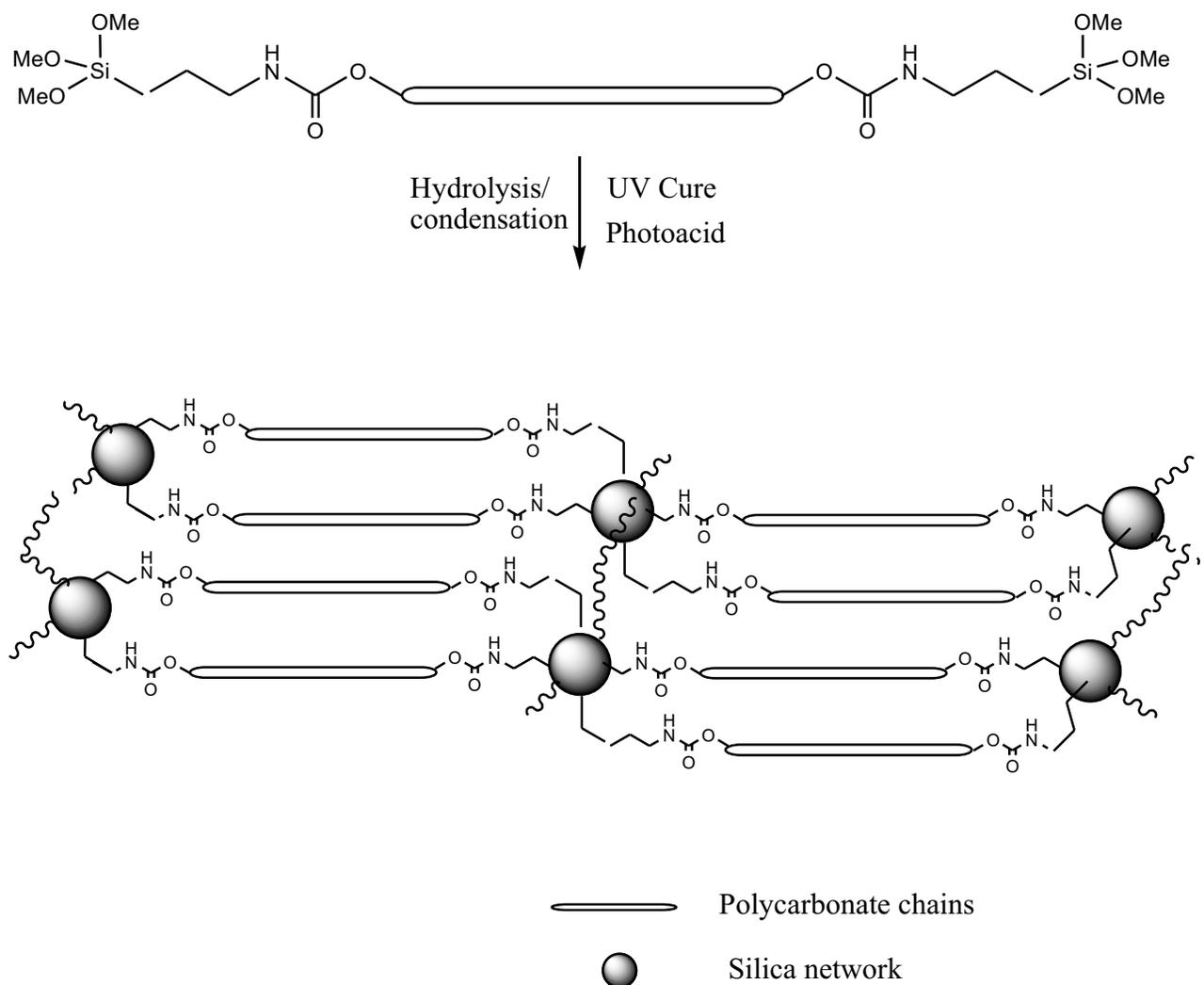


Figure 5: Reaction scheme showing the formation of a silica network after UV-exposure.

Decreasing the MW of the oligomer increased the König Pendulum Hardness as well as the Taber abrasion. In fact, the only coatings that improved the Taber abrasion over uncoated polycarbonate were when the low MW oligomer was used without TIP.

The TIP appears to be acting as a cross-linker as well as catalyzing the thermal degradation reaction. The TIP appears to be weakening the coating; this is seen in the decreased abrasion resistance. However, the presence of TIP dramatically improved the appearance of the coating (by preventing de-wetting and improving clarity).

ATR-IR was used to confirm that the Si-O-CH₃ groups had hydrolyzed and condensed into an Si-O-Si network. It was also shown that Si-O-Ti bonds formed in the coatings that contained TIP.

As shown, a series of organic-inorganic nano-composites were formed by the in-situ hydrolysis and condensation of silane-functional urethane oligomers. The physical properties were varied by changing the molecular weight of the urethane-oligomer, as well as by incorporating TIP.

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