UV-Curable Vinyl Functionalized Siloxane Colloids

By M. D. Soucek and J. He

A functionalized siloxane colloid was prepared for use as hyper-crosslinker for UV-curable systems. The UV-crosslinkable silica-colloids were prepared from vinyltrimethoxysilane (VTMS) via a sol-gel method. The silica colloid structure and size was characterized using spectroscopy and microcopy. The colloid was formulated into an acrylated polyester (AP), and a radical photoinitiator was added. The viscoelastic, thermomechanical and surface properties of the VTMS/AP films were evaluated In addition, coating properties such as adhesion, scratch resistance, pencil hardness and impact resistance were also investigated. The tensile and scratch data show that VTMS oligomer dramatically increased hardness and scratch resistance. The VTMS oligomer also increased storage modulus, glass transition temperature and crosslink density. It was postulated that the VTMS oligomer functioned effectively as a hyper-branched crosslinker, a surface modifier and reactive diluent.
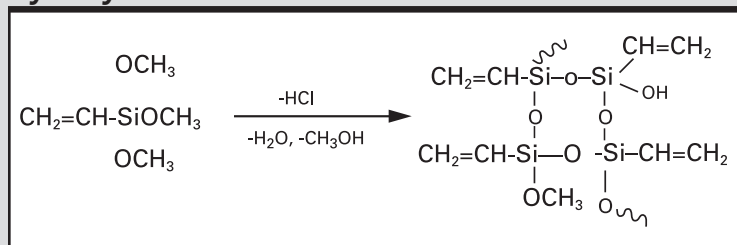
Introduction

In recent years, organic-inorganic hybrid materials have received considerable attention as new functional materials.[1-8] Nanoparticles based upon a silicon-titanium system can be prepared by sol-gel method, which includes hydrolysis and condensation of alkoxysilanes in a liquid. Generally, the hybrid material is formed through the hydrolysis and condensation of organically modified silicates. These materials are of great interest since they both impart organic and inorganic characteristics. The organic component usually accounts for flexibility of the composites whereas the inorganic component is responsible for hardness and mechanical impact resistance.[9] Organic-inorganic hybrid coating provides some properties to the substrate including wear, corrosion, erosion, optical, magnetic, electric-electronic, biological and thermal attack properties. These coatings properties are very important in surface engineering applications. It has also an aim of decorative attractiveness for the surface.[10]

Tetraethoxysilane (TEOS) precursor is one of the most commonly used precursors for UV-light curable system.[11-15] It was found that the additional TEOS could enhance adhesion, corrosion, modulus, tensile strength, and hardness when the continuous organic phase was epoxy, polyester, polyurethane, and or epoxynorbornane linseed oil.[16-21] However, the need for rapid cure materials with improved properties stimulated researchers to develop novel functional siloxane monomers or oligomers suitable for curable organic and inorganic hybrid materials. Vinyltrimethoxysilane (VTMS) can be used to prepare vinyl functional silica-colloids by sol-gel method as previously reported.[22] T. Gunji *et. al.*

SCHEME 1

Hydrolysis reactions of VTMS

SCHEME 2

Unsaturated polyester structure

{(1, 4-CHDM: HO-R1-OH), (NPG: HO-R2-OH), (1, 6-HD: HO-R3-OH) and (ADA: HOOC-R4-COOH)}

prepared Polyvinylpolysilsesquioxane organic-inorganic hybrid gel films containing polyethylene and siloxane backbone linkages through the radical polymerization of VTMS followed by the acid-catalyzed hydrolytic polycondensation of trimethoxysilyl groups.[6] Polyvinyl-polysilsesquioxane gel films were transparent and homogeneous. Hu *et.al.* measured hardness and elastic modulus profiles of thin organic/inorganic hybrid coatings on glass surfaces with a continuous stiffness measurement technique. Hybrids were synthesized by the hydrolytic condensation of VTMS, with 5-30 wt% TEOS, in the presence of formic acid.[23]

The factors that determine the coating properties are the constitution of material composition of material composition parameters such as coating process and thickness, etc. By varying these factors, the properties of resistance to corrosion, flame, bond strength, and wear strength of polymeric-based coatings can be changed, and the service life can be increased. A UV-curable acrylated polyester, shows good properties such as high hardness, toughness, solvent resistant and an excellent ratio value of properties to cost.[24] Therefore, it has been widely used as a binder for UV-curable films.

In this study, multi-functionalized VTMS oligomers were prepared *ex-situ* by the sol-gel method and UV-cured with an acrylated polyester. The effects of the concentration of VTMS oligomer on the coating properties such as adhesion, scratch resistance, pencil hardness and impact resistance were investigated. In addition, the mechanical, viscoelastic, thermomechanical and surface properties of the hybrid films were also evaluated using tensile strength, fracture toughness, dynamic mechanical thermal analysis (DMTA), and pull-off adhesion.
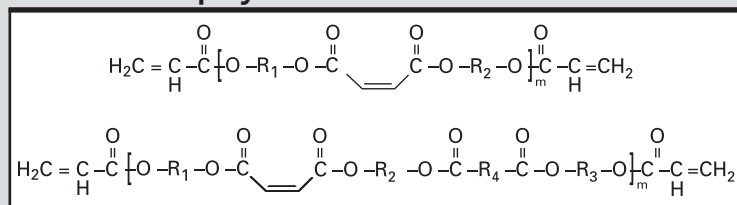
Results and Discussion

The overall objective of this study was to investigate the effects of incorporating a VTMS oligomer in UV-curable organic/inorganic hybrid coatings. It was anticipated that a high UV-curing activity and hyper-branched crosslinking and penetration of VTMS/AP would lead to improved film performance compared to a slower curing and lower crosslink density system. Five levels of VTMS (0, 5, 10, 15, and 20 wt %) were used in this study to evaluate the effects of the VTMS oligomer on the final film properties. The VTMS structure contains siloxane- and vinylfunctional-group, therefore VTMS colloids provide the control of cluster size and UV-crosslinkable functional group, which can couple the inorganic to the organic phase. In addition, it was thought that the size of colloid could be better controlled than TEOS derived colloids by virtue of the silane functionality.

The hydrolysis reaction of VTMS is illustrated in Scheme 1. The resultant products were characterized by 1H NMR and FT-IR. The average molecular weight by GPC was M_n = 1907, and the polydispersity was PDI = 1.49. A typical polycondensation technique[25] was used to prepare an acrylated polyester resin. The formulation of the acrylated polyester is listed in Table 1. The synthesis process, reported previously, consisted of two steps. The average molecular weight was found to be M_n = 2420, with a PDI = 2.4 via GPC. The acid number and hydroxyl number were measured according to ASTM Standards D 1639 and D 4274-94,

respectively. There was a mixture of possible chemical structures for the acrylated polyester. The following are the possible chemical structures of acrylated polyester as shown in Scheme 2.

The UV-curable hybrid coatings were formulated using an acrylated polyester resin (PA), VTMS oligomer and photoinitiator (Ciba Darocur 4265). The formulations are shown in Table 2.

The photoinitiator used consists of 50% 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide and 50% 2-hydroxy-2-methyl-1-phenyl-propan-1-one. Their structures are shown below.
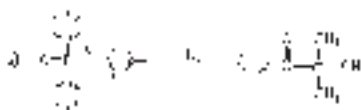
a) 2, 4, 6-trimethylbenzoyl-diphenyl-phosphine oxide b) 2- hydroxy-2-methyl-1-phenyl-propan-1-one

For the acrylated unsaturated polyester, only the lower masses below 3500 Da were observed due to the high polydispersity of the sample (PD = 2.2 by GPC).[26] Peaks in the lower molecular weight range (below m/z 900) showed incorporation of either one or two terminal acrylic acid groups. Peaks observed in the higher molecular weight range of the acrylated polyester also

TABLE 1

Formulation of acrylated polyester

Diol (mol)	Diacid (mol)	Acrylic Acid (mol)
1, 4-CHDM: 1.5	MA: 2.3	AA: 4
NPG: 2	ADA: 1.2	
1,6-HD: 2		

showed terminal acrylic acid groups. Thus providing evidence that acrylic polyester contains the MA- and the AA-terminated structures.

Dynamic Mechanical Property

Dynamic mechanical thermal analysis (DMTA) of thin films provides the information of crosslink density, glass transition temperature (T_g) and extent of cure. The crosslink density (v_e) is the number of moles of elastically effective network chains per cubic centimeter of material. The viscoelastic properties of the hybrid films as a function of VTMS oligomer content are

TABLE 2

The formulation of acrylated polyester with different content of VTMS oligomer

	Wt%					
AP/VTMS films	0#	1#	2#	3#	4#	5#
Acrylated polyester	96	91	86	81	76	66
VTMS Oligomer	0	5	10	15	20	30
Photoinitiator	4	4	4	4	4	4

TABLE 3

Viscielastic properties of the hybrid films as a function of VTMS oligomer

Hybrid films	0#	1#	2#	3#	4#
VTMS oligomer (wt.%)	0	10	15	20	30
Film thickness (µm)	102.6	105.5	112.2	106.3	106.6
Glass Transition Temp. T_g (°C)	9.1	8.1	31.2	37.2	70.2
Crosslink density (mol/m³) (x10³)	2.58	3.38	3.46	3.47	4.25
E′ (Pa) (x10⁷) (beyond T_g 80°C)	2.33	3.04	3.24	3.23	4.46

shown in Figures 1-2. There is a rubbery plateau at >70°C for all of the samples indicating a crosslinked network. Higher concentrations of VTMS oligomers tended to shift the transition to a higher temperature. In addition, the increasing VTMS oligomer content broadened the transition region, and ultimately, increased the storage modulus. At 20°C the storage modulus (E') of the organic film was 1.710 7 Pa, while the E' of the hybrid film with 20 wt.% VTMS oligomer loading was 1.9510 8 Pa, more than 10 times higher than that of the organic film.

FIGURE 1

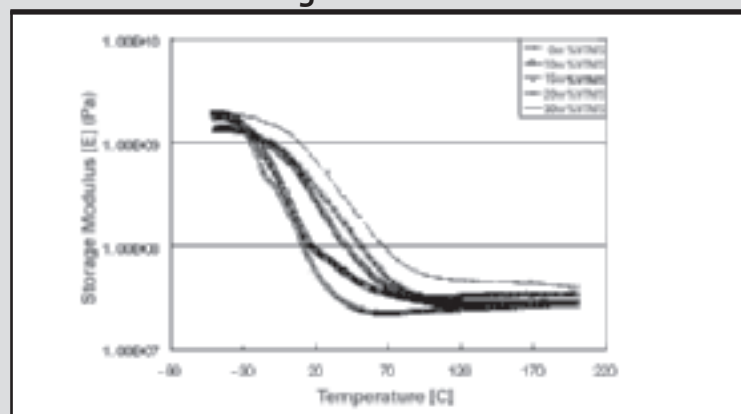## Storage modulus (E') of the hybrid films as a function of VTMS oligomer content

Table 3 shows the crosslink density and glass transition temperature (T_g) of the hybrid films as a function of VTMS oligomer content. The T_g was determined from the maximum tan δ, and increased from 9.1°C to 70.2°C as the VTMS oligomer content increased from 0 to 30 wt.%. An increase in crosslink density was observed when VTMS oligomer was introduced. As compared to the organic film, the crosslink density with 10 wt.% VTMS oligomer loading increased 31%. The highest crosslink density (4.25 mol/cm³) was found at 30 wt.% of VTMS oligomer loading, which was 64.7% higher than that of the organic film.

Crosslink density has a direct impact on the tan δ. Figure 2 shows that the height of the tan δ peak decreased, the apex of the peak (corresponding to T_g) shifted to a higher temperature and the peak was broadened as the loading content of VTMS oligomer increased. This is because the increasing of crosslink density reduces long range segment motion required for viscous flow behavior. Therefore, the cure extent of the hybrid films increased. The area under the tan δ curve can also be used

to measure the extent of cure.[27-28] It was calculated from Figure 2 that the area under the tan δ curve decreased as the loading content of VTMS oligomer increased, which further indicated the increasing of the degree of cure.

The increased storage modulus, crosslink density, T_g and degree of cure were all attributed to the intramolecular reactions of the VTMS oligomer and the intermolecular reaction between the VTMS colloid and acylated polyester.

FIGURE 2

Tan delta (δ) of the hybrid films as a function of VTMS oligomer content


The acrylated VTMS oligomer functioned as a hypercrosslinker, which coupled the inorganic segment to organic phase. As a result, a crosslink network between the inorganic and organic phases enhanced the overall performance of ceramer films and altered the mechanical properties.

Tensile Properties and Fracture Toughness

Figures 3-4 shows the tensile strength and elongation at break as a function of VTMS colloidal content. The tensile strength (shown in Figure 3) shows an initial increase in tensile strength from 0 to 5 wt.% VTMS colloids, then a large increase from 15.4 MPa to maximum of 20.5 MPa at 10 wt.% VTMS colloidal content. This is attributed to the intimate interaction between the reinforcing inorganic colloids in the organic matrix. The tensile strength decreased to 14.3 MPa when VTMS colloidal content increased to 20 wt.%. This could be due to the aggregation of VTMS colloids, which caused stress induced cracks, then resulted in a reduction in tensile strength. It is very interesting to note that the lowest elongation at
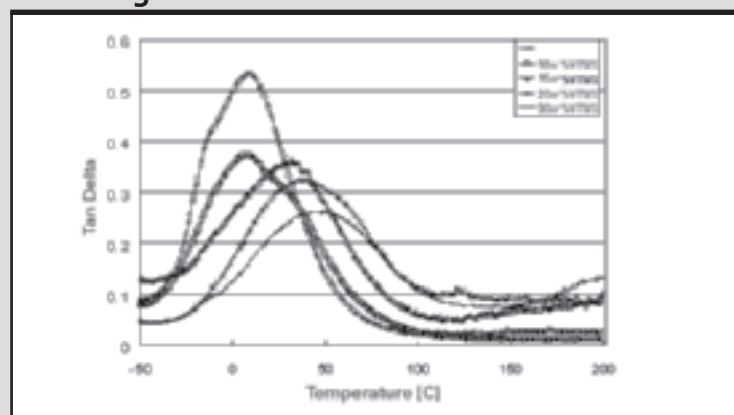
break was obtained for the hybrid, which contained 15 wt.% VTMS colloidal content (shown in Figure 4). This is nanometer-effect of inorganic particles and their dispersions at low concentration of VTMS colloids. Therefore, at low VTMS colloidal loading with uniform particle dispersions, on both tensile strength and elongation of the hybrid film were improved.

The fracture toughness (K_c) and energy release rate (G_c) of the hybrid films are shown in Figures 5-6, respectively. Fracture toughness and energy release rate are the measurements of resistance to crack extension. The fracture toughness of the hybrid films shows a little decrease when VTMS colloidal content increased from 5 wt.% to 20 wt.%. Energy release rate (G_c) of the hybrid films shows the same trend except for 15 wt.% VTMS colloidal content. There is a large increase of energy release rate for the hybrid films at 15 wt.% VTMS colloidal content. The data of fracture toughness and energy release rate indicated that the VTMS colloids enhanced the resistance to crack extension of the hybrid films and then gave optimum content of VTMS colloids for the existing hybrid films.

Coating Properties

One of the likely industrial applications of hybrid coatings is topcoats. The enhancement of surface abrasion resistance, hardness, adhesion and impact resistance are important for its application.

Table 4 shows the general mechanical properties of the hybrid film as a function of VTMS colloidal concentration. The pencil hardness increased when the VTMS colloidal content was increased. However, the abrasion weight loss decreased. Due to the high hardness of VTMS colloids, the strong interaction and interpenetrated
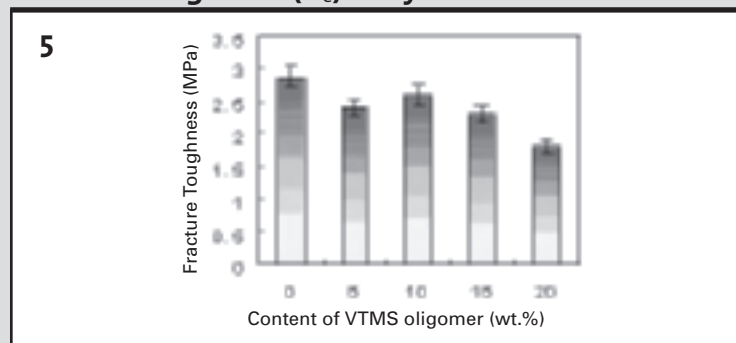
FIGURE 3,4,5 AND 6

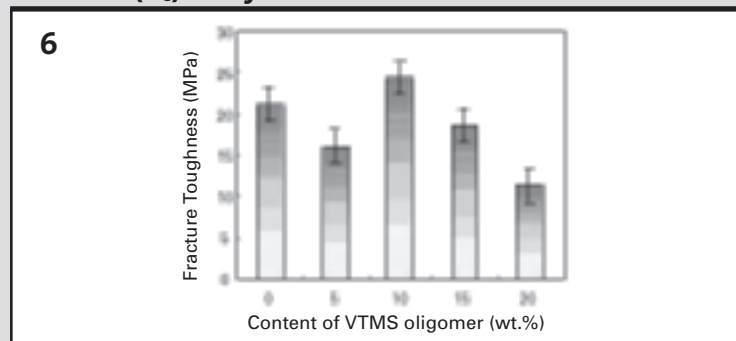**Tensile strength of the hybrid films**
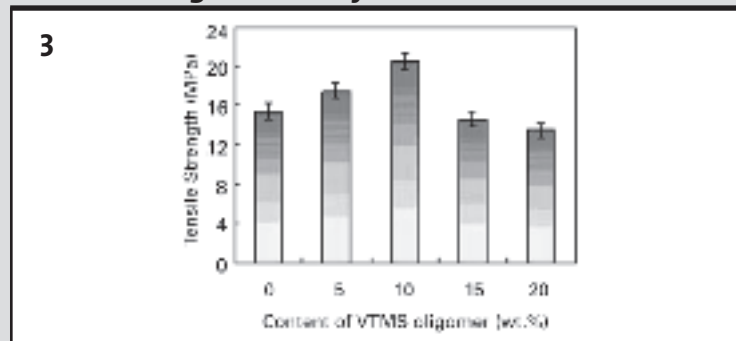
Elongation at-break of the hybrid films
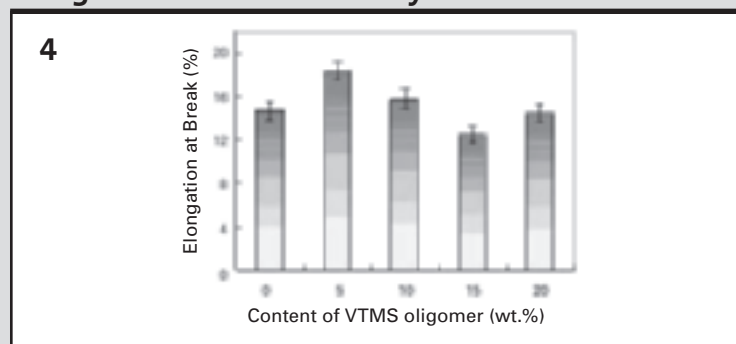
Fracture toughness (K_c) of hybrid films

Energy release rate per unit creak area at the fracture (G_c) of hybrid film

nature between chains of the organic phase and inorganic particles induce the high pencil hardness of the hybrid film. The alkene functionalized VTMS oligomer of the organic phase increased crosslink density, and the inorganic silica particles also possess an inherent hardness and abrasion resistance. Further, the improvement of scratch and abrasion resistance of such hybrid coatings was impressive with higher content of VTMS oligomer. However, the impact resistance of the films limited high content of the inorganic phase.

As the content of VTMS oligomer increased, the pull off adhesion increased and reached a maximum at 15 wt.% VTMS loading. The enhancement of adhesion has been attributed to both the chemical bonding between the Si-OH groups and the Al-OH on the aluminum substrate to form a Si-O-Al linkage and hydrogen bonding to the substrate.[19] With the presence of VTMS oligomer, the film surface quality was also improved. The effect of modification depended on appropriate content of VTMS oligomer.

The falling impact indenters are normally the most severe due to the "shock" nature of the test. The bending and stretching of the aluminum panel base on which a coating was applied provided valuable information on the plastic and adhesion characteristics of the coating. As the content of VTMS oligomer increased, the impact resistance only decreased marginally. That may be attributed to the increase in crosslink density of the organic phase, which reduced the flexibility of the hybrid system. Since the inorganic phase is the discontinuous phase, it does affect the bulk properties of the coating until—20 wt.%.

The photopolymerization activity of TEOS/acrylated polyester system was compared by Photo-DSC at similar formulation to VTMS/acrylated polyester system.[9] For VTMS hybrid formulations the time to reach the exotherm peak was 0.04 min, three times faster than the time for TEOS hybrid formulations (0.15 min). The integrated exotherm of VTMS/acrylated polyester was more than two times greater than that of corresponding TEOS/acrylated polyester film. The slope to reach the exotherm peak for VTMS system is very steep, while for TEOS/acrylated polyester system was gradual. This means that the polymerization of VTMS/acrylated polyester system is much faster than that of TEOS/acrylated polyester system, which may be attributed to the structure difference of TEOS oligomer and VTMS colloid. There are more vinylic groups in the VTMS structure; thus adding VTMS not only reduced the viscosity of the formulation and increased the mobility of the organic polymer chain during propagation but also provided additional double bonds, which participated as a hybrid crosslinker during the free radical photopolymerization.

Conclusions

UV-curable organic-inorganic hybrid films based on acrylated polyester were prepared using vinyl functionalized silica colloid. Results show that adding the VTMS oligomer could greatly improve thermal stability, as well as storage modulus, crosslink density, T_g and extent of cure. In addition, the VTMS increased tensile strength (10 wt.%), abrasion resistance (15 wt.%) and pencil hardness. The average silica size of VTMS silica-colloids is around 90 nm, and silica-colloids were dispersed mostly at the nanoscale and with very little aggregation. It was

TABLE 4

Coating properties of hybrid films with varies concentration of VTMS

	AP/VTMS 0	AP/VTMS 1	AP/VTMS 2	AP/VTMS 3	AP/VTMS 4
Pencil hardness	1 H±.3	2 H±.3	3 H±.5	4 H±.5	5.5H±.5
Taber abrasion weight loss (mg)	5.6	4.3	3.2	3	3
Pull off adhesion (MPa)	0.92	1.05	1.1	1.28	1.2
Direct impact resistance (kg/cm²)	67.5	63	62	60	56
inverse impact resistance (kg/cm²)	62	57	55	51	50

proposed that the VTMS oligomer can have the functions of a reactive diluent, crosslinker, surface modifier and reactive inorganic filler. ◗

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