Dual-Curable Unsaturated Polyester Inorganic/Organic Hybrid Films

Ahmet Nebioglu, Ganghua Teng, Mark D. Soucek

Department of Polymer Engineering, University of Akron, 250 S. Forge Street, Akron, Ohio 44325

ABSTRACT: An unsaturated polyester, based on maleic anhydride, 1,6-hexanediol, and trimethylol propane, was formulated with tetraethylorthosilicate (TEOS) oligomers and a coupling agent to prepare inorganic/organic hybrid films. TEOS oligomers were prepared through the hydrolysis and condensation of TEOS with water, and 3-(triethoxysilyl)propylisocyanate was used as the coupling agent between the organic and inorganic phases. The hybrid materials were cured by moisture via sol–gel chemistry and by the UV curing of unsaturated polyesters. To compare the properties of the moisture-cured inorganic/organic hybrid films, a conventional 2K polyurethane system was also prepared. The tensile, adhesion, abrasion, and fracture tough-

ness properties were investigated as functions of the coupling agent and relative amount of UV cure versus thermal cure. Although no difference could be observed in the tensile properties, the abrasion resistance, fracture toughness, and adhesion were enhanced by the incorporation of TEOS oligomers into polyurethane films. Also, the abrasion resistance, fracture toughness, and tensile properties were increased with both moisture and UV exposure. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 115–126, 2006

**Key words:** adhesion; films; polyesters; viscoelastic properties

INTRODUCTION

Unsaturated polyesters (UPEs) are extensively used in glass-reinforced composites as gel coats[1] and in wood finishing as fillers, sealers, and topcoats.[2] UPEs are prepared by the condensation reaction of diacids, one of which is typically maleic anhydride (MA) with glycols.[3] It is necessary to use inhibitors as radical scavengers to inhibit the polymerization of the carbon–carbon double bonds with respect to pot-life stability. Styrene is usually incorporated into the formulations to reduce the viscosity, increase the crosslink density, and decrease cost. The cured resin is a copolymer of polystyrene chains connecting the polyester via the maleic or fumeric alkene.

There are two methods used to cure UPEs: (1) thermal curing by initiation with an organic peroxide[4] and (2) photochemical curing with a photoinitiator.[5,6] Conventional curing is normally performed at the ambient temperature via a metal salt catalyst. The initiator, methyl ethyl ketone peroxide, and a mixture of dimethylaniline and cobalt naphthenate are used as an accelerator/catalyst system. The photochemical-curing process has the advantages of shorter cure times, improved physical properties and product perfor-

mance, and reduced solvent emissions. However, there are limitations to UV curing: (1) the failure to cure complex-shaped parts and pigmented films and (2) rapid shrinkage during curing that can create adhesion problems. UPEs are used as the organic binders for glass-reinforced composites and are also used as pigmented gel coats on the exterior side of the composites for protective and decorative purposes. To overcome shelf-life stability and high emission problems, UV-curing UPE composites and gel coats were recently introduced.[7]

Another class of resins that rely on polyesters are polyurethanes. Polyurethane resins are synthesized from the reaction of isocyanate-functionalized monomers or oligomers with hydroxyl-functionalized polyesters,[8] as shown in eq. (1):

$$R-N=C=O + P$$

$$\smallsmile OH \rightarrow R-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O\sim P \quad (1)$$
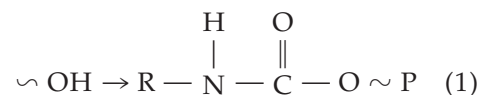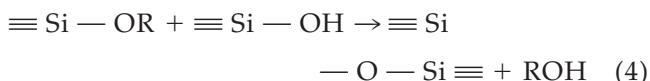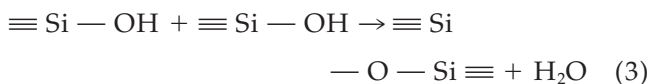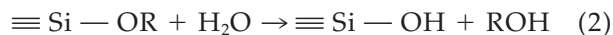
The high reactivity of the isocyanate group permits ambient-temperature preparation of the polyurethanes. Because of a balance of flexible segments and hydrogen bonding, polyurethane materials show superior abrasion resistance.[6] Polyurethane acrylates are usually prepared by the reaction of isocyanates with hydroxyethyl acrylate[9] and hydroxymethyl methacry-

late.[10,11] The versatile chemistry of polyurethane acrylates affords films with good flexibility, toughness, abrasion resistance, adhesion, and chemical resistance and excellent weathering resistance.[5,12]

Organofunctional silanes have an alkoxysilane group [—Si—(OR)$_3$] and an organic functional group (R′) and have been used as coupling agents for a variety of organic binders, including polyurethanes and UPEs.[6,13,14] Alkoxysilanes undergo sol–gel chemistry in water, as depicted in eqs. (2)–(4):

$$\equiv Si — OR + H_2O \rightarrow \equiv Si — OH + ROH \quad (2)$$

$$\equiv Si — OH + \equiv Si — OH \rightarrow \equiv Si$$
$$— O — Si \equiv + H_2O \quad (3)$$

$$\equiv Si — OR + \equiv Si — OH \rightarrow \equiv Si$$
$$— O — Si \equiv + ROH \quad (4)$$

Further hydrolysis and condensation reactions form crosslinks or, in the case of sol–gel precursors, a silicon oxide network. Soucek and coworkers[15–18] showed that alkoxysilanes play the critical role of the compatibilizer and the coupling agent for polyurethane/tetraethylorthosilicate (TEOS)-based inorganic/organic hybrid materials. They reported that alkoxysilane groups function as nucleation sites for silicon–oxo cluster growth, thus providing a template for the uniform dispersion of the silicon–oxo nanophase.

In addition to coupling agents, various researchers have used reactive monomers and acrylate or methacrylate functionality in the organic phase in UV-curing organic/inorganic hybrid materials. Gilberts et al.[19] prepared UV-curing hybrid films on polycarbonate with 1,6-hexanedioldiacrylate as the reactive diluent and 3-(trimethoxysilyl)propoxymethacrylate as the coupling agent. The incorporation of prehydrolyzed TEOS greatly improved the abrasion resistance. Gigant et al.[20] formed hybrid coatings based on vinyltriethoxysilane, tetrathoxysilane, and polyfunctional acrylates and characterized the films with Raman spectroscopy. Colloidal silica acrylates and methacrylates were also used by various researchers to form abrasion-resistant inorganic/organic hybrid films.[21–23]

In this study, a hydroxyl-functional UPE was synthesized and formulated with TEOS oligomers and 3-(triethoxysilyl)propylisocyanate (TEOSPI) as the coupling agent. The formulations were cured into films via a moisture-curing process or UV-initiated free-radical process, followed by a moisture cure. A conventional 2K polyurethane resin system was also prepared with a hydroxyl-functional polyester and a difunctional isocyanate. The resultant films were evaluated and compared with the 2K polyurethane system in terms of the tensile properties, abrasion resistance, fracture toughness, and viscoelastic properties.

EXPERIMENTAL

General information

1,6-Hexanediol (1,6-HD), trimethylol propane (TMP), and MA were purchased from Aldrich (Milwaukee, WI). The photoinitiator, 2,2-dimethoxy-1,2-diphenylethan-1-one (Irgacure 651), was obtained from Ciba Specialty Chemicals. Dicyclohexylmethane-4,4-diisocyanate (H$_{12}$MDI) was provided by Bayer Corp. (Desmodur W). TEOS, acetone, and the coupling agent, TEOSPI, were also obtained from Aldrich. Acetone was dried with molecular sieves. All the formulations were prepared under an argon atmosphere in a glovebox. The chemical structures of the monomers, crosslinker, coupling agent, and photoinitiator are shown in Scheme 1. Aluminum panels (type A, alloy 3105 h24) were obtained from Q-Panel Lab Products.

Synthesis of UPEs

A trihydroxyl-terminated UPE was synthesized with 1,6-HD, TMP, and MA with a two-stage method. For the first stage, the diol and anhydride (1 : 2) were reacted at 190°C for 2 h, and then a mixture of an equimolar diol and triol (1 : 1) was added to the reaction flask for a second stage. The mixture was then heated to 210°C until the oligoester had an acid value of ∼20 mg of KOH/g of resin. The oligoester was characterized by Fourier transform infrared (FTIR) spectroscopy and gel permeation chromatography (GPC). The number-average molecular weight was 800 with a polydispersity of 1.4.

Instrumentation

Tensile tests were performed on an Instron 5567 (Instron Corp., Grove City, PA). The viscoelastic properties were measured on a dynamical mechanical thermal analyzer (DMTA V, Rheometrics Scientific, Piscataway, NJ) with a frequency of 1 Hz and a heating rate of 4°C/min over a range of −50 to 250°C. FTIR spectra were obtained on a Mattson Genesis Series FTIR instrument (Madison, WI). A Waters system (Waters Corp., Milford, MA) was used for GPC with HR4, HT2, HR1, and HR0.5 Styragel columns and 500-Å Ultrastyragel columns connected in series. Tetrahydrofuran was applied as the mobile phase and delivered at a rate of 1.0 mL/min.

Formulations and film preparation

The formulations of the polyurethane films are listed in Table I. For the 2K system, H$_{12}$MDI was added to the formulation to crosslink the organic phase. In the 1K system, TEOSPI was used as a coupling agent
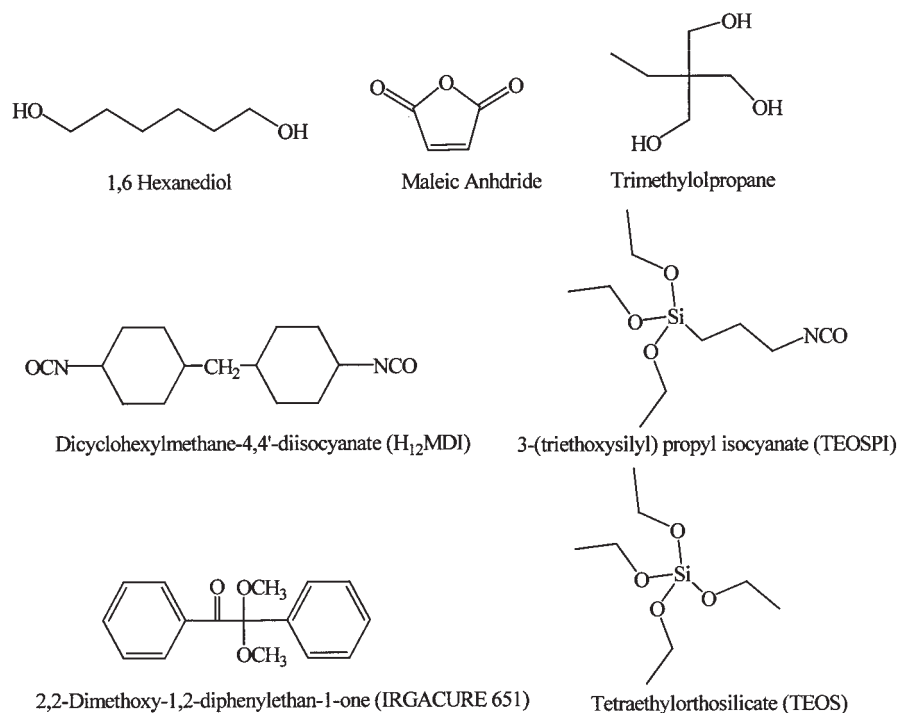
Scheme 1 Structures of the monomers, crosslinker, coupling agent, and photoinitiator.

between the organic and inorganic phases. All the formulations were prepared with an NCO/OH molar ratio of 1.1 to obtain the moisture-curable isocyanate group. The excess isocyanate formed urea crosslinks, minimized unreacted hydroxyl groups, and increased solvent resistance.[6] The reaction between the —N=C=O and OH groups was monitored by the disappearance of the —N=C=O peak at 2270 cm^{-1} via FTIR. The resin obtained after the reaction between UPE and TEOSPI was designated UPT (Table I).

To eliminate the evaporation of TEOS, the TEOS oligomers were prepared by the reaction of TEOS with water and hydrochloric acid.[18] Acetone (5 wt %) was used to adjust the viscosity of the resins. For UV curing, a unimolecular photoinitiator (Irgacure 651, Ciba Specialty Chemicals) was incorporated into the formulations at 4 wt %. Thin films of the formulations were cast onto

aluminum panels by a drawdown bar with a wet thickness of 101.6 μm and were kept at a constant relative humidity of 90% and the ambient temperature for 3 days. Then, the thermally crosslinked films were further cured at 90°C for 10 h at 100% relative humidity. In the UV-cured systems, the thin wet films were cured in a Fusion F300 UV processor (H-bulb, Fusion UV System, Inc.) for 0.2 min with an intensity of 151 mW/cm^2 and then were further moisture-cured at 90°C for 10 h at 100% relative humidity.

Evaluation of the properties

The pencil hardness (ASTM D 3363-74), crosshatch adhesion (ASTM D 3359-87), reverse impact resistance (ASTM 2794-84), and tensile properties (ASTM 2370-92) were measured according to ASTM standards.

TABLE I
Formulations of the Polyurethane Films

	2K						1K					
	UPHt0	UPHt2	UPHt5	UPTHt0	UPTHt2	UPTHt5	UPTt0	UPTt2	UPTt5	UV-UPTt0	UV-UPTt2	UV-UPTt5
UPE (mol)	1	1	1	1	1	1	—	—	—	—	—	—
H$_{12}$MDI (mol)	1.65	1.65	1.65	1.65	1.65	1.65	—	—	—	—	—	—
UPT (mol)	—	—	—	1.65	1.65	1.65	1	1	1	1	1	1
Acetone (wt %)	5	5	5	5	5	5	5	5	5	5	5	5
Irgacure 651 (wt %)	—	—	—	—	—	—	—	—	—	4	4	4
TEOS oligomers (wt %)	0	2	5	0	2	5	0	2	5	0	2	5
Viscosity (cPs)	—	—	—	—	—	—	2100	1950	1890	—	—	—

UP = UPE; H = H$_{12}$MDI; T = TEOSP1; t = 0, 2, and 5 wt % TEOS; UV = UV + Moisture cure. NCO/OH = 1.1 in all of the formulations.
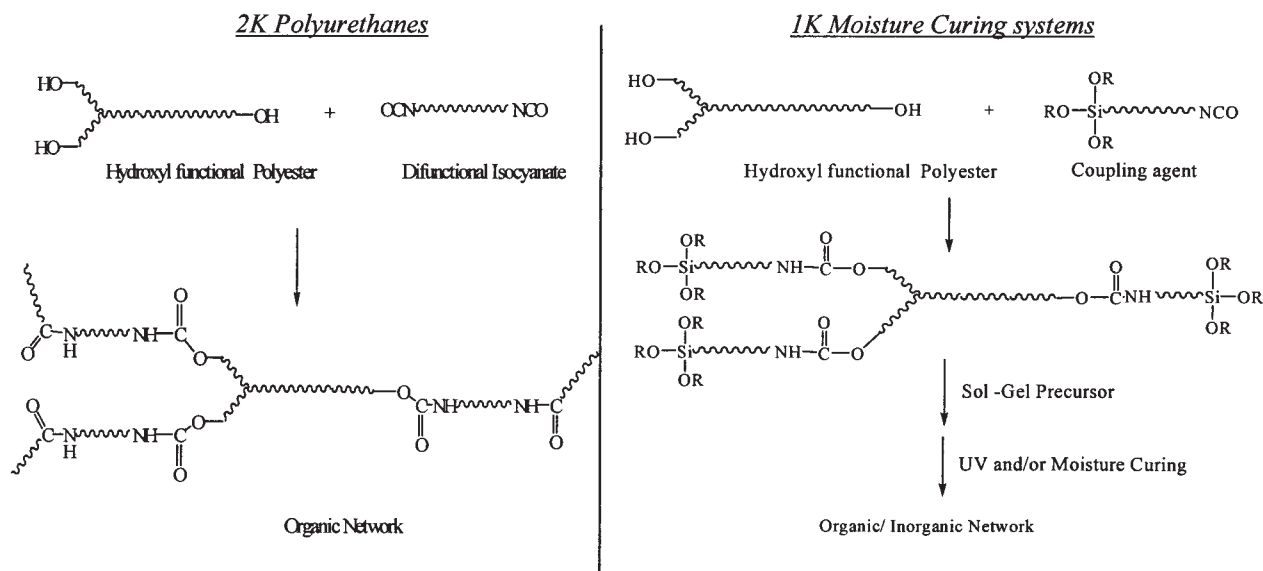
Scheme 2 Crosslinking chemistry of the thermal 2K and 1K moisture-curing materials.

Abrasion resistance tests were performed with a Taber abrader (ASTM D 4060-95). The weight losses of the cured films were recorded after 500 cycles with CS-10 standard abrasive wheels and a 750-g load. A vacuum system was used to remove the abraded particles during the test period. Erichsen cupping properties were tested with a TQC CP2000 test apparatus according to the ISO 1520 standard.

The viscoelastic properties of the polyurethane films were investigated with a dynamic mechanical thermal analyzer at a frequency of 1 Hz and a heating rate of

$4°C/min$ over a range of -100 to $200°C$. The gap distance was set at 5 mm for rectangular test specimens (10 mm long, 5 mm wide, and 0.06–0.10 mm thick).

The films used in the tensile tests were 10–13 mm wide and 0.06–0.10 mm thick and had a gage length of 40 mm. A crosshead speed of 10.0 mm/min was applied to determine the tensile strength, elongation at break, and tensile modulus. For each film, eight samples were tested. The data are reported as the mean of the data set, error, and standard deviation.
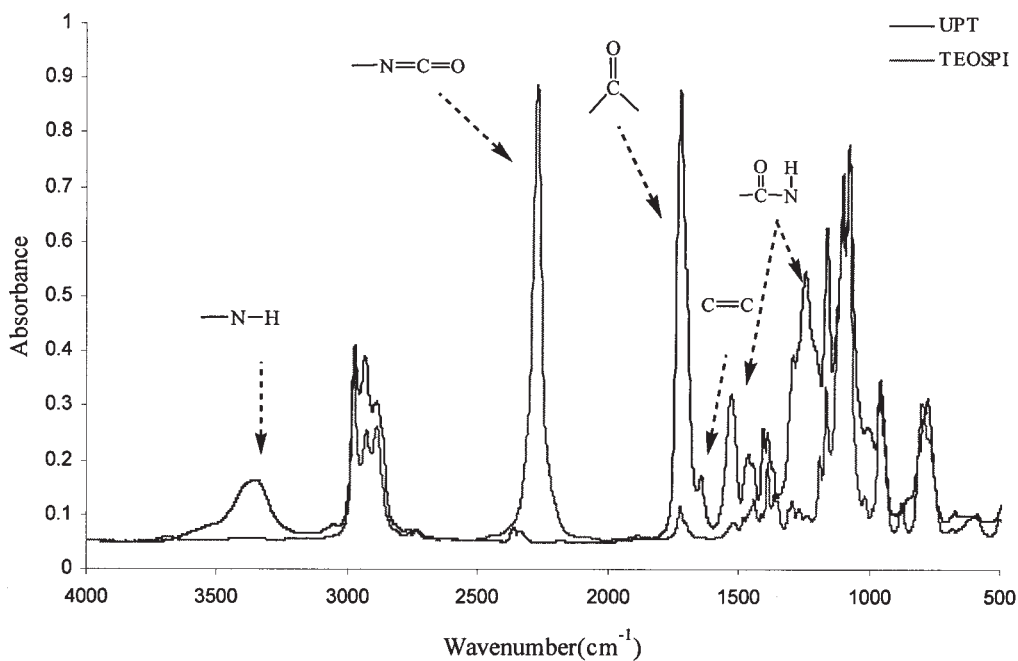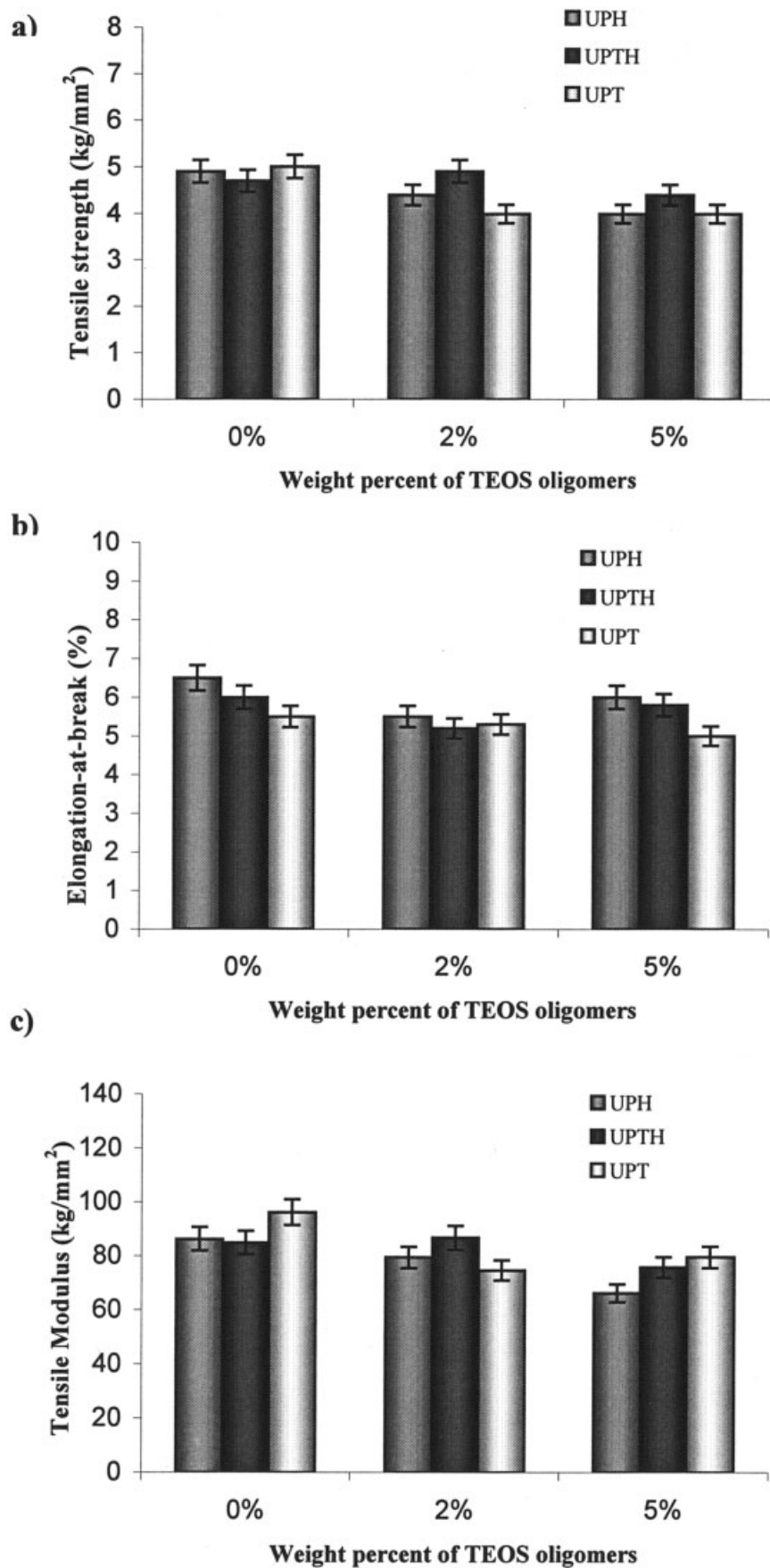

Figure 1 FTIR spectra of UPT and TEOSPI.

Figure 2 Tensile properties of the films as a function of the TEOS oligomers and the coupling agent: (a) tensile strength, (b) elongation at break, and (c) tensile modulus.
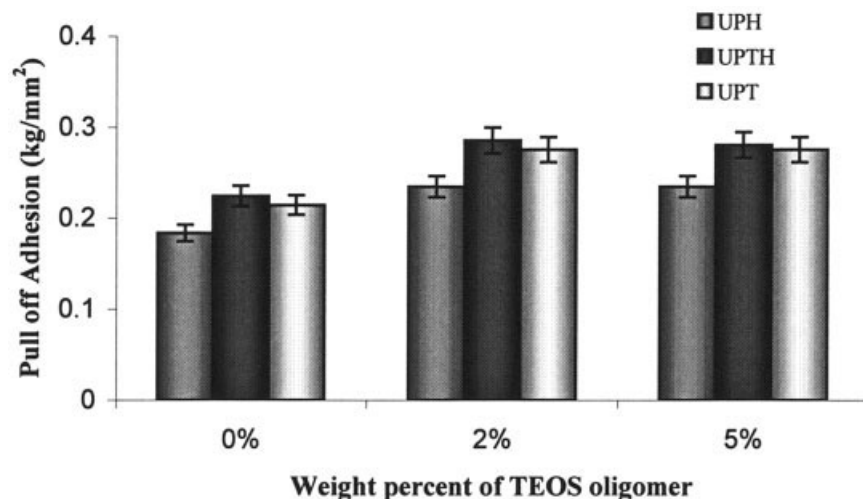
Figure 3 Effect of the UV cure on the tensile strength of the 1K moisture-cured polyurethane/polysiloxane films with 0, 2, and 5 wt % TEOS.

Plane-stress fracture toughness (K_c) measurements were conducted on rectangular specimens with single-edge-notch geometry. The dimensions of the films were 10.2 mm $\times$ 11.0 mm $\times$ 0.06–0.10 mm (width $\times$ length $\times$ thickness). Each film was cut with a razor blade to create the edge notch. The length of the notch was less than 10% of the width of the sample. A fracture toughness tester, which was mounted on a microscope stage and equipped with a 25 lbf load cell and a variable speed motor, was used to deform the specimen in a tensile mode. The crosshead speed was 0.583 mm/min. The load–displacement curve was digitally recorded by a computer. The crack tip region was observed at a magnification of 100$\times$ on the computer monitor, and the onset of crack propagation was noted and digitally marked on the load–displacement curve. The deformation zone near the crack tip could be observed continuously on the computer monitor during the loading. Six samples were tested for each film. The data are reported as the mean of the data set. K_c (i.e., the stress intensity factor at fracture) was determined with the following equation:[24]

$$K_c = \left[3.94\left(\frac{2w}{\pi a}\right) \tan\left(\frac{\pi a}{2w}\right) \right]^{1/2} \frac{F}{(w-a)b} \sqrt{a} \qquad (5)$$

where w is the width, a is the notch length, b is the thickness, and F is the force at which crack propaga-

tion begins. The energy release rate per unit of crack area at fracture (G_c) was calculated with the following equation:[24]

$$G_c = \frac{K_c^2}{E} \qquad (6)$$

where E is the tensile modulus. The G_c values were calculated with average values of K_c and E.

RESULTS AND DISCUSSION

The overall purpose of this study was to obtain a 1K moisture–UV dual-curable resin system based on UPEs. The primary advantage of this system is its ability to cure complex parts with UV light. With radiation curing, the drying time decreases enormously. Other advantages of UV-cured polyurethane/polysiloxane organic/inorganic hybrid materials are the increased adhesion, tensile strength, and abrasion resistance.[18,22,23,25] For comparison, 2K polyurethane systems were also prepared with H_{12}MDI as the crosslinker. In Scheme 2, different modes of crosslinking are illustrated. Although UPEs have relatively slow UV-curing rates compared with meth(acrylated) polyesters, UPEs are more cost-effective.[5] The effects of the coupling

TABLE II
Pencil Hardness, Impact Resistance, and Crosshatch Resistance

	UPHt0	UPHt2	UPHt5	UPTt0	UPTt2	UPTt5	UV-UPTt0	UV-UPTt2	UV-UPTt5
Pencil hardness	6H	6H	6H	6H	6H	6H	6H	6H	6H
Impact resistance (kg cm)	>100	>100	>100	>100	>100	>100	>100	>100	>100
Crosshatch adhesion	5B	5B	5B	5B	5B	5B	5B	5B	5B

Figure 4 Pull of adhesion of the coatings as a function of the TEOS oligomers and the coupling agent.

agent and TEOS oligomers on the adhesion, tensile strength, abrasion resistance, and hardness were investigated.

The reaction of UPE with the coupling agent, TEOSPI, was monitored with FTIR spectroscopy. In Figure 1, the FTIR spectra of TEOSPI and UPT resin are shown. The reaction of UPE and TEOSPI was monitored via the antisymmetric stretching vibration mode (2270 cm^{-1})[26] of the —N=C=O functionality of TEOSPI. A residual amount of isocyanate was due to excess isocyanate, which was converted into urea linkages during moisture curing. Urethane formation was also confirmed by the observance of amide bending modes at 1530 and 1260 cm^{-1}.[25]

The tensile strength, elongation at break, and tensile modulus of the films as a function of the coupling
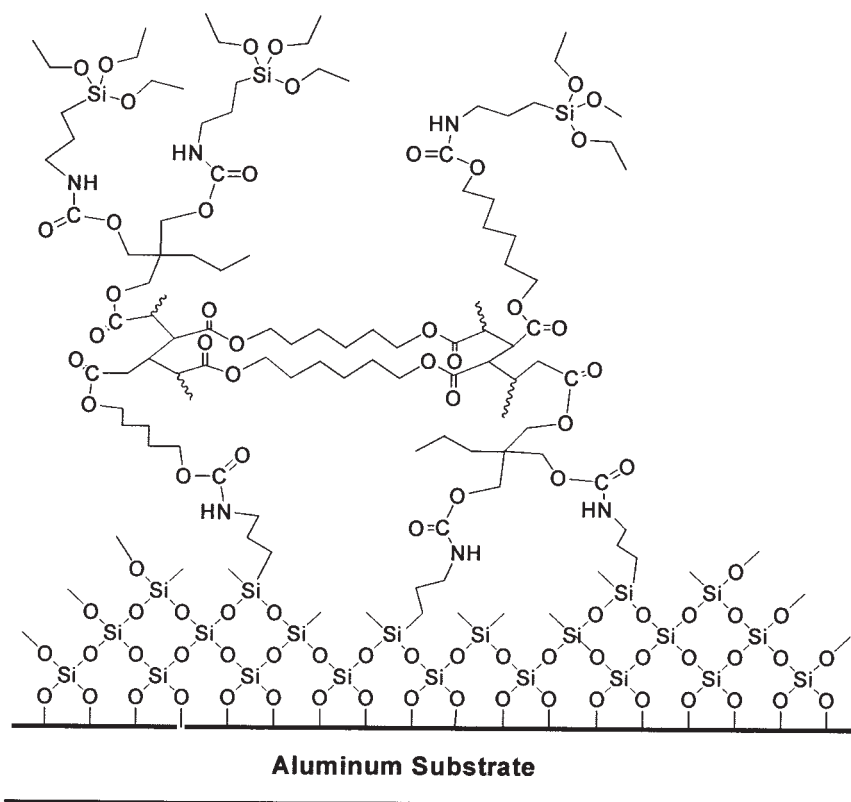
Scheme 3 Proposed self-assembly interaction of the UV-cured hybrid network and the substrate.
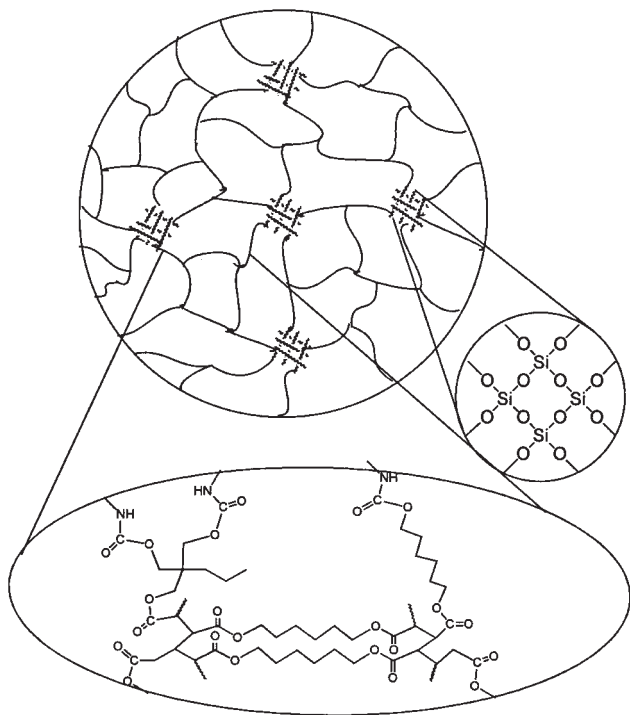
Scheme 4 UV-cured polyurethane/polysiloxane organic/inorganic network model.

agent and TEOS oligomers are shown in Figure 2. The tensile strengths were independent of the inclusion of either H_{12}MDI (UPH and UPTH) or TEOSPI (UPT and UPTH). The results from the tensile tests indicated that moisture curing was as effective as thermal curing.

The tensile strength slightly decreased as the TEOS concentration was increased. However, the elongation at break and the tensile modulus did not show any trend with an increase in the coupling agent (UPTH

and UPT) or TEOS concentration. This was consistent with the results previously obtained by Soucek and coworkers.[15–18] Therefore, it can be concluded that these properties depended principally on the organic phase.

In Figure 3, the effect of the UV cure on the tensile strength of the hybrid films is shown. UV curing increased the tensile strength slightly because of the formation of the additional number of crosslinks formed in the organic phase. However, the increase in the tensile strength was not as high as one would expect. The disappearance of the maleate double bonds was monitored via FTIR spectroscopy. The residual number of unreacted maleate bonds was observed at the end of the UV curing. The pencil hardness, impact resistance, and crosshatch adhesion behavior of the coatings are listed in Table II. The UV processing did not affect the pencil hardness, impact resistance, and crosshatch adhesion of the coatings.

The pull-off adhesion of the coatings as a function of the TEOS oligomers and the coupling agent is shown in Figure 4. The adhesion of the films increased with the addition of the coupling agent (UPH and UPTH). As the coupling agent further increased (UPTH and UPT), the adhesion was not increased further because of the reduction of the degree of the phase separation and hence the reduction of the amount of the TEOS oligomers on the substrate. The adhesion was also increased by the inclusion of the TEOS oligomers but leveled off with a further increase in the concentration of the TEOS oligomers. This behavior with increasing amount of the TEOS oligomer was observed by Soucek et al.[18] in a polyurea/polysiloxane ceramer system. The adhesion increase can be attributed to the increase in the number of Si—O—Al bonds formed on the sur-
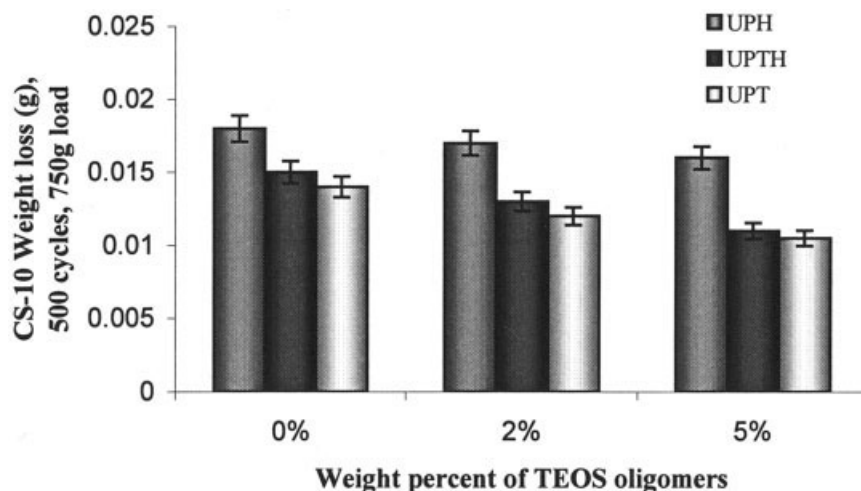
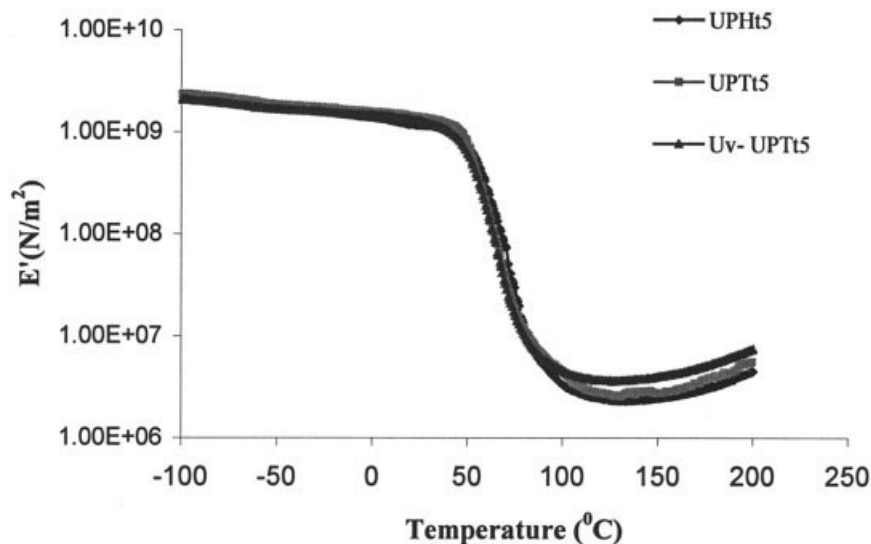**Figure 5** Abrasion resistance of the polyurethane films.

Figure 6 E' of diisocyanate-, moisture- and UV–moisture-cured films.

face of the aluminum panel, as shown in Scheme 3. Also, all the coating formulations showed the same pencil hardness (6H), impact resistance (>100), and crosshatch adhesion (5B) behavior. The proposed structure of the UV-cured polyurethane/polysiloxane hybrid network is shown in Scheme 4.

Polyurethanes show superior abrasion resistance behavior because of the hydrogen bonding. In the literature, it has been reported that inorganic/organic hybrids increase the abrasion resistance.[27] Figure 5 shows that increasing both TEOSPI and TEOS oligomers resulted in increased abrasion resistance because of the formation of the silicon–oxo cluster.

The viscoelastic properties of the films with 5% TEOS oligomer are shown in Figures 6 and 7. modulus

(E') showed a slightly decreasing trend until the temperature reached 50°C. Between 50 and 130°C, E' decreased dramatically for all the films. The crosslink density of the films was calculated with the following equation:[27]

$$E'(min) = 3\nu_c RT \; (T \gg T_g) \qquad (7)$$

where ν_e is the number of moles of elastically effective chains per cubic centimeter of the film, $E'(min)$ is the minimum storage modulus in the rubbery plateau, R is the gas constant and T is the absolute temperature. The glass-transition temperature (T_g) was obtained from the maximum of the α transition. $E'(min)$, ν_e, and T_g of the polyurethane films are given in Table III. It
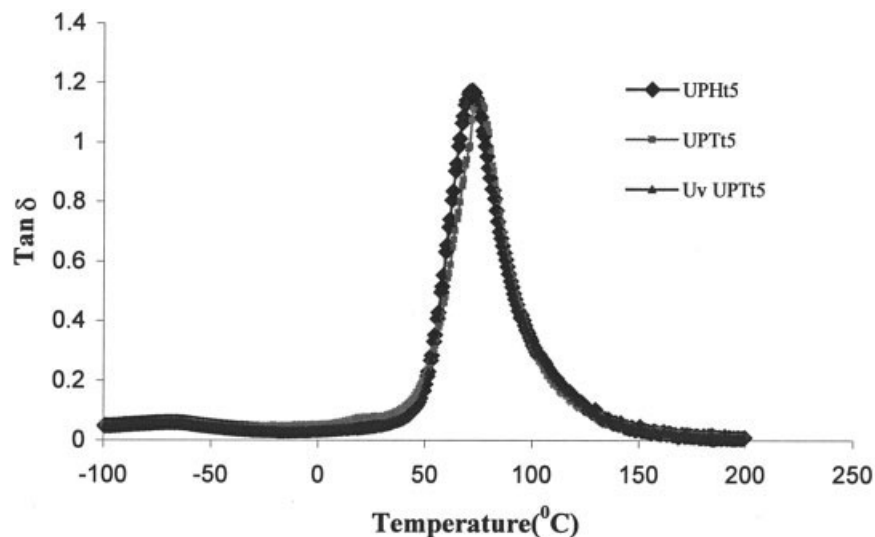

Figure 7 Tan δ of diisocyanate-, moisture-, and UV–moisture-cured films.

TABLE III
Viscoelastic Properties of the Hybrid Films with 5 wt %
TEOS

|	UPHt5	UPTt5	UV-UPTt5
E' (min) (N/m^2)	2.29×10^6	2.52×10^6	3.56×10^6
ν_e (mol/cm^3)	2.26×10^{-5}	2.50×10^{-5}	3.58×10^{-5}
T_g (°C)	72	76	72

was calculated that the moisture-cured film (UPTt5) had a slightly higher crosslink density than the conventional diisocyanate-cured polyurethane film (UPHt5). The incorporation of UV curing (UV-UPTt5) via internal double bonds besides moisture curing increased the crosslink density by 43%. A high initial maleate double-bond concentration before UV curing suggests a higher increase in the crosslink density. The obtained relatively low crosslink density for the UV–moisture dual-cured system can be attributed to a decrease in the effectiveness of the moisture-curing process due to the decrease in the free volume via UV curing.

K_c and G_c are measures of resistance to crack extension. K_c and G_c of the polyurethane films as a function of the TEOS oligomer content are shown in Figures 8 and 9, respectively. indicated that the moisture-cured films had slightly higher K_c values than the 2K polyurethane films because of the formation of silicon–oxo clusters. The K_c values implied also that moisture curing was as effective as the diisocyanate curing. For all TEOS concentrations, UPTH showed lower K_c values than UPH and UPT films. Therefore, diisocyanate and moisture curing have an antagonistic effect on K_c. It was also observed that UV curing before the moisture cure and/or increasing the level of TEOS oligomers in-

creased K_c and G_c. These results revealed that the inorganic network formation provided additional resistance to crack extension.

Erichsen cupping test results of the moisture-cured coatings are shown in Table IV. The cupping test is a measure of the flexibility and adhesion under sustained pressure. In this test, a ball bearing is mechanically forced under the uncoated side of the panel to create a cup on the coated surface. A reverse correlation between the hardness and cupping test was previously reported.[28] However, in this study, because of the increased adhesion with the TEOS oligomer, there was no relation between the hardness and cupping test. With the addition of the TEOS oligomer, the cupping distance increased because of the increase in adhesion. As TEOS further increased, the cupping distance leveled off. The incorporation of UV curing decreased the cupping distance because of the increased crosslinking density.

Inorganic/organic hybrid materials based on UPEs have not been previously reported in the literature. The UV curing of UPE requires 20–40% reactive diluent, usually styrene, to reduce the viscosity of the system. In this study, TEOS oligomers functioned as reactive diluents, replacing styrene. The addition of TEOS oligomers enhanced the overall properties of the films. This approach has the potential to cure complex parts with a dual-cure system, which could not be accomplished with UV curing alone. TEOSPI successfully functioned as a coupling agent, and moisture curing was also as effective as conventional diisocyanate curing. The UV–moisture dual-curing system increased the crosslink density and tensile strength and the fracture toughness as a result. The films developed in
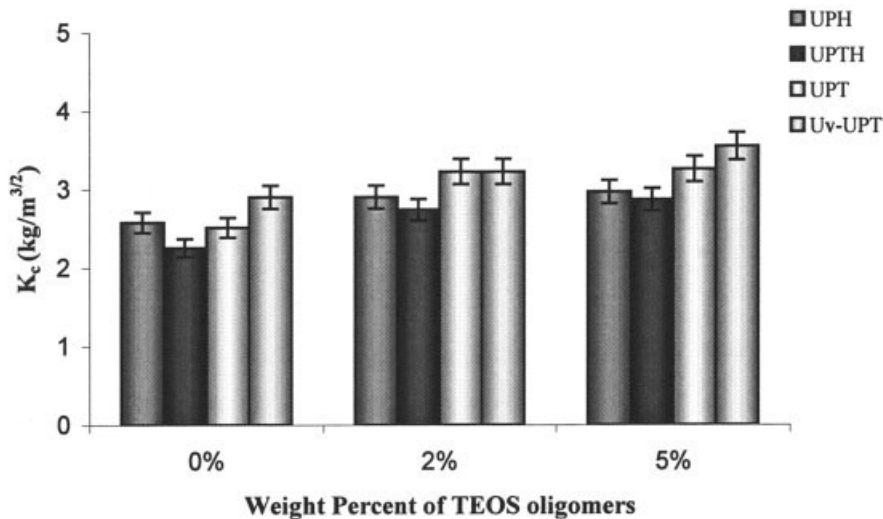
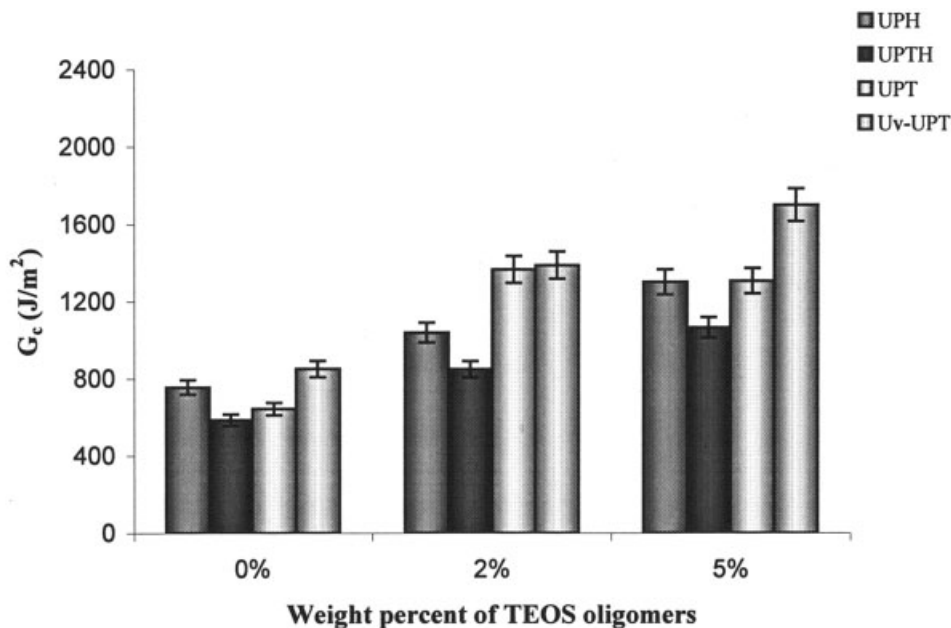**Figure 8** K_c of the films as a function of the TEOS oligomer content.

Figure 9 G_c of the films as a function of the TEOS oligomer content.

this study showed enhanced adhesion behavior, abrasion resistance, and reasonable flexibility that are suitable for a variety of substrates with a wide range of applications. The UV–moisture dual curing of the UPEs can be potentially used in glass-reinforced composites to overcome pigmentation problems in UV-curing gel coats. In further work, the effect of the TEOS oligomers and coupling agent on the reaction kinetics will be studied.

CONCLUSIONS

A new type of UV–moisture dual-curable inorganic/organic polysiloxane/polyurethane ceramer film was prepared based on an MA UPE. The adhesion on aluminum and abrasion resistance were enhanced by the interaction of the polysiloxane network with the substrate. TEOSPI functioned as a coupling agent between the organic and inorganic phases. This approach can be used as a replacement for $H_{12}MDI$ in polyurethane films without the alteration of the

tensile properties. With the incorporation of UV curing, the tensile strength and fracture toughness of the ceramer films increased because of a more complete crosslinked network.

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TABLE IV
Cupping Properties of the Moisture-Cured Films

	UPTt0	UPTt2	UPTt5	UV-UPTt5
Cupping length (mm)	7.18 ± 0.05	7.40 ± 0.06	7.38 ± 0.11	7.04 ± 0.05

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