Nanostructured Polyurethane Ceramer Coatings for Aircraft

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A new low VOC (volatile organic compounds) polyurethane/oligosiloxane coating was formulated using 1,6-hexamethylene diisocyanate (HDI) isocyanurate, alkoxysilane-functionalized HDI isocyanurate, tetraethyl orthosilicate (TEOS) oligomers, and three cycloaliphatic polyesters. One series of polyesters was synthesized using 1,4-cyclohexanedimethanol (CHDM) with 1,4-cyclohexanedicarboxylic acid (1,4-CHDA) and 1,3-cyclohexanedicarboxylic acid (1,3-CHDA). A second series of polyesters was synthesized using 2-butyl-2-ethyl-1,3-propanediol (BEPD) with 1,4-CHDA or 1,4-CHDA, and 1,3-CHDA, respectively. The polyurethane provided the general mechanical properties and the polysiloxane functioned as an adhesion promoter and corrosion inhibitor. The continuous organic polyurethane phase was coupled with the inorganic polysiloxane phase via the alkoxysilane-functionalized HDI isocyanurate. The general coatings, tensile, and viscoelastic properties were evaluated for the ceramer coatings as functions of the polyester and concentration of TEOS oligomers. Damage tolerance was evaluated via fracture toughness and development of the film deformation zone prior to crack propagation. The coatings' properties were dominated by the organic phase. The film morphology was investigated using the combination of SEM (scanning electron microscope) and X-ray analysis. Phase separation was observed for ceramer coatings resulting in SiO_2 particles. The size of the preceramic silicon-oxo-particles was controlled by the T_g of the organic phase and the concentration of TEOS oligomers.

INTRODUCTION

The coating system currently used on the aluminum substrates for aircraft includes many steps.[1] First, a chromate pretreatment is applied as a conversion layer to prevent corrosion. Then, a washing primer of passivating chromium is used as pretreatment to aid in the adhesion of the primer to the surface. Following that, a two-component epoxy-amine system is applied as a primer. The topcoat is typically a two-component polyurethane consisting of an HDI oligomer and a polyester polyol. These systems offer many advantages, including good adhesion and corrosion protection, excellent fluid resistance, and good intercoat adhesion. Unfortunately, chromates are a known carcinogen, and, as a consequence, future disposal of chromates into the environment will be severely curtailed.

Many approaches have been carried out in this area to limit the usage of chromate.[2,3] A relatively recent approach for aircraft coatings is the "Unicoat" system developed by Hegedus and co-workers.[3] The concept of a Unicoat system is to replace the above system of coatings with a single self-priming coating system, which would eliminate the usage of chromate in the pretreatment step. The self-priming coating is a 2K polyurethane system based on hexamethylene diisocyanate isocyanurate. Passivating pigments such as molybdate and zinc phosphate are used as chromate replacements to protect the aluminum substrate from corrosion. A reduction in volatile organic compounds and application cost over the traditional multistep aircraft coating systems were reported. However, adhesive failure has undermined this coating system.

Silicon sol-gel techniques have been widely used to prevent the corrosion of metals and to improve the coatings' adhesion.[4-7] One of the commonly used sol-gel precursors is tetraethyl orthosilicate (TEOS), $Si(OEt)_4$, which has been applied in coating for preparing zinc-rich primers.[8] After application, TEOS absorbs water from the atmosphere and undergoes hydrolysis and condensation reactions. Holmes-Farley and Yanyo[2] used TEOS in conjunction with an aminosilane adhesion promoter to pre-

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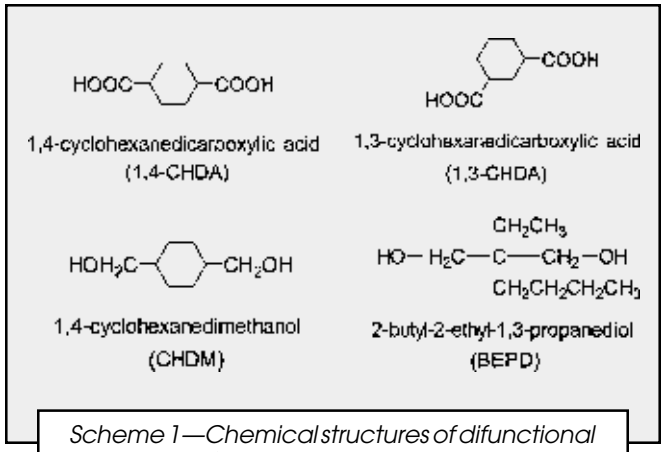
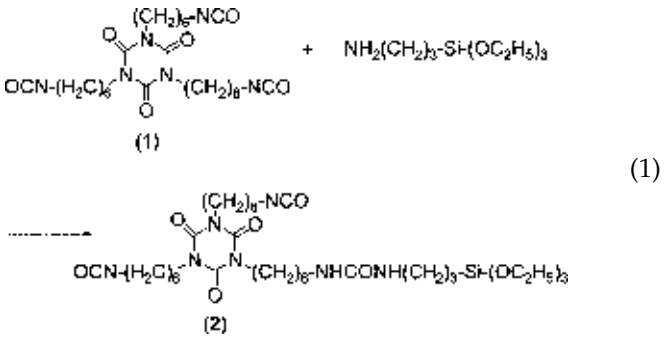


Scheme 1—Chemical structures of difunctional acids and difunctional alcohols.

vent corrosion on the aluminum substrate. In their study, anisotropic coatings were developed using various alkoxysilanes to form multilayered films. The results indicated that a combination of a TEOS layer on the substrate attached along with a layer of aminosilane gave optimal adhesion and corrosion protection. The TEOS functions as a corrosion inhibitor, and the aminosilane as an adhesion promoter.

Our approach is to develop a polyurethane/poly-siloxane ceramer self-priming coating, or "Unicoat" system. In this system, the polyurethane provides the general mechanical properties and the polysiloxane functions as an adhesion promoter and corrosion inhibitor. There has been a series of papers emanating from our laboratory which chronicle the advancement of this research project from the demonstration of the concept using polyurea coatings to the presently reported polyurethane coatings.[9,10] The seminal work was the synthesis and characterization of the alkoxysilane-functionalized isocyanurate, as shown in equation (1).[11] A hybrid coating system, polyurea/alkoxysilane, was then prepared using the alkoxysilane-functionalized isocyanurate and HDI isocyanurate.[12-14] On the basis of the hybrid coating system, the organic/inorganic polyurea/polysiloxane coatings were formulated with the addition of TEOS oligomers to form a ceramer. In the ceramer coating system, the effect of acid catalyst on the ceramer coatings properties was also evaluated. These previous studies showed that the alkoxysilanes have a dramatic effect on the adhesion enhancement. The polysiloxane formed by the sol-gel precursor, tetraethyl orthosilicate (TEOS) oligomers, has a strong effect on the corrosion inhibition.



(1)

The ceramer concept was applied to aircraft coatings. Cycloaliphatic polyesters were added into the polyurea/polysiloxane ceramer coating system to formulate polyurethane/polysiloxane ceramer coating systems. To improve the UV resistance, a series of cycloaliphatic polyesters were synthesized in two previous studies.[15,16] The cycloaliphatic polyesters[17,18] have been reported to provide better flexibility and yellowing resistance than aromatic diacids usually used in polyester formulations. Compared with mixtures of linear aliphatic and aromatic diacids, cycloaliphatic polyesters offered improved hardness/flexibility balance, hydrolytic stability, and corrosion resistance.[19-21] The chemical structure of the cycloaliphatic polyesters is shown in *Scheme* 1. The mixtures of diacids were shown to reduce the polyester application viscosity, and therefore a higher solids formulation was achievable.[15-17]

In this paper, three polyurethanes derived from cycloaliphatic polyesters were used to formulate polyurethane/polysiloxane ceramer coatings. Similar to the previously described polyurea ceramer coatings,[9,10] TEOS oligomers and the phase coupling agent were used to create the ceramer coating. The effect of polyester on the polyurethane ceramer coating properties was investigated. In addition to general mechanical coating properties, tensile, viscoelastic, and fracture properties were also evaluated. Phase separation of the ceramer films was investigated using SEM and X-ray.

EXPERIMENTAL

Synthesis of Cycloaliphatic Polyesters

A typical polycondensation technique was used to prepare the polyester resin. The reaction is shown in equation (2) for the CHDM with 1,4-CHDA and 1,3-CHDA. The reactor (1000 mL) was equipped with a mechanical stirrer, partial condenser, condenser, and a collector used for separating water and xylene. The reaction was run under nitrogen purge and the maximum temperature at the post stage was 210°C. This temperature was maintained until an acid number range of 3-6 mg KOH per gram of resin was reached to control the degree of reaction. The acid number and

Table 1—Formulations and Properties of Polyesters

Polyesters	CHDM(4/3)	BEPD(4/3)	BEPD(4)
Diacids	1,4-CHDA: 1	1,4-CHDA: 1	1,4-CHDA: 2
(mole ratio)	1,3-CHDA: 1	1,3-CHDA: 1	
Diols (mole ratio)	CHDM: 3	BEPD: 3.15	BEPD: 3.15
Acid number	3.5	5.7	5.6
Hydroxyl number	152	150	151
M_n (g/mole)	891	979	958
PDI (M_n/M_w)	1.74	1.52	1.53
Viscosity[a] (Pa·s)	8.3	1.3	1.9

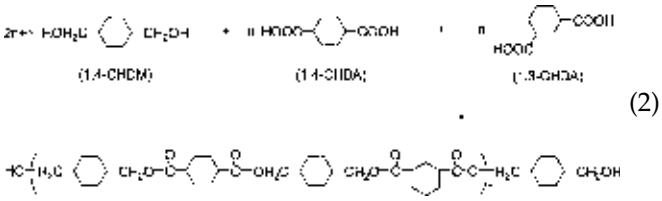
(a) Diluted in 10 wt% MEK.

Table 2—Formulations of Coatings

Coatings	HDI Isocyanurate (1, wt%)	Monofunctionalized Isocyanurate (2, wt%)	Polyester (wt%)	TEOS Oligomers (wt%)
CHDM(4/3)	36.7	0	63.3	0
CHDM(4/3)T0	19.9	25.0	55.1	0
CHDM(4/3)T2.5	19.4	24.3	53.8	2.5
CHDM(4/3)T10	17.9	22.4	49.7	10.0
BEPD(4)	36.7	0	63.3	0
BEPD(4)T0	19.9	25.0	55.1	0
BEPD(4)T2.5	19.4	24.3	53.8	2.5
BEPD(4)T10	17.9	22.4	49.7	10.0
BEPD(4/3)	36.7	0	63.3	0
BEPD(4/3)T2.5	19.4	25.0	53.8	2.5

All the compositions were diluted with 10 wt% acetone.

hydroxyl number of the polyesters were measured according to ASTM standards D 1639-89 and D 4274-94, respectively.



(2)

Gel permeation chromatography (GPC) analysis was carried out using a five-column set of HR4, HT2, HR1, and HR0.5 Styragel, and 500 Å Ultrastyragel columns (Waters). Tetrahydrofuran (THF) was applied as the mobile phase and delivered at a rate of 1.0 mL/min. The calibration curve was generated using narrow polystyrene standards (Waters). Viscosity measurements were performed on a Carri-Med CSL-100 rheometer with parallel plate geometry. The properties and formulations of polyesters are shown in *Table* 1.

Coating Formulation and Film Preparation

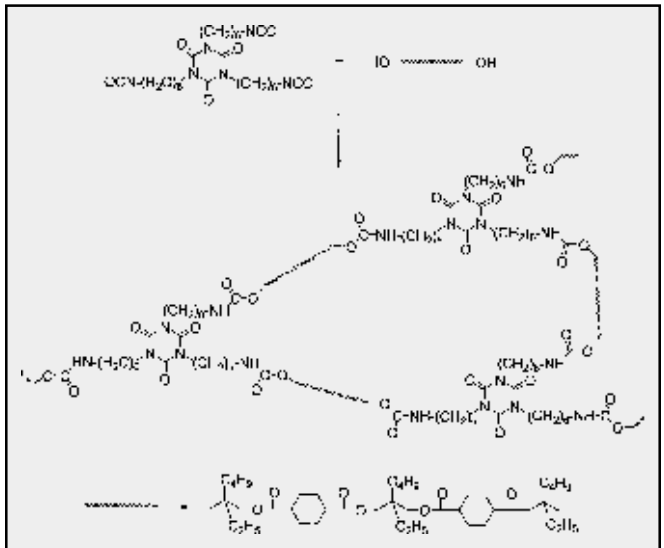
The monofunctionalized HDI isocyanurate[11] and TEOS oligomers[9] were prepared as previously reported. The chemistry of the preparation of monofunctionalized isocyanurate is shown in equation (2). The HDI isocyanurate (1) and monofunctionalized isocyanurate (2) were formulated with TEOS oligomers and polyesters, as shown in *Table* 2. A common ratio of NCO/OH, 1.1/1.0, was used for all formulations in *Table* 2. All the formulations were divided into three groups according to different polyesters.

The designation was based on the polyesters and the concentration of TEOS oligomers. For instance, in CHDM(4/3)T2.5, CHDM means the polyester in the formulation was prepared from the glycol CHDM and the number in the parentheses (4/3) indicates that a mixture of diacids 1,4-CHDA and 1,3-CHDA was used for the polyester. The following T2.5 designates that 2.5 wt% TEOS oligomers is in the formulation, T indicating TEOS oligomers and 2.5 being the concentration of TEOS oligomers. The CHDM group includes the first four formulations. In this group, CHDM(4/3) is a polyurethane without an alkoxysilane functional group. It is used as reference to observe the variation of polyurethane in the curing process. Formulation CHDM(4/3)T0 contains alkoxysilane-functionalized isocyanurate and the concentration of TEOS oligomers is 0 wt%. Formulations CHDM(4/3)T2.5 and CHDM(4/3)T10 were prepared on the basis of CHDM(4/3)T0 with the increase of TEOS oligomers concentration. The BEPD(4) group includes the four formulations in *Table* 2, BEPD(4), BEPD(4)T0, BEPD(4)T2.5, and BEPD(4)T10, which is similar to the CHDM group. In the BEPD(4) group, only one diacid was used in the preparation of polyester. The last two formulations, BEPD(4/3) and BEPD(4/3)T2.5, were designed to compare the effect of one diacid with the mixture of 1,4-CHDA and 1,3-CHDA on the film properties.

The films were cast on the aluminum panels (3003 H14, Q-Panel) with a wet thickness of 152.4 µm (6 mil) by a drawbar for general mechanical measurements and on glass plates for the tensile, viscoelastic, and fracture tests. The films were set in a closed box with a stable humidity of 30% at 25°C for 96 hr until the surface became tack-free, and then put into a closed oven and further moisture cured at 88-90°C under 100% humidity for 10 hr. After curing, free films were obtained by removing the films from the glass plates with a razor blade for the tensile, fracture, and viscoelastic measurements.

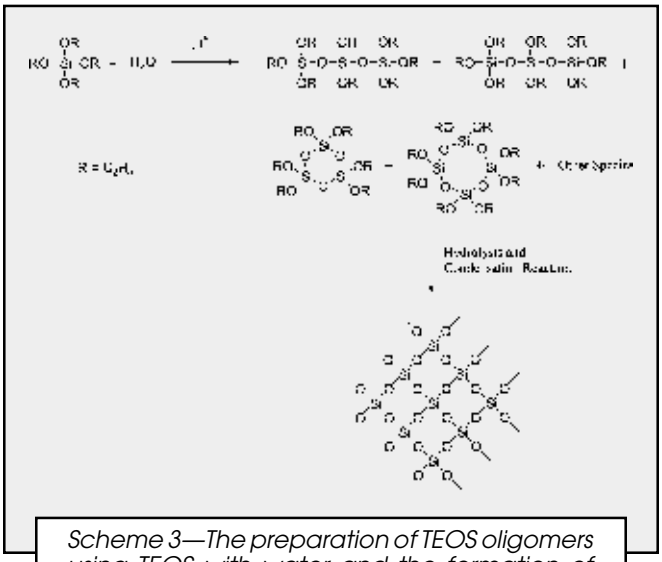
Film Properties

Indentation hardness (Tukon hardness, ASTM D 1474-85), pencil hardness (ASTM D 3363-74), crosshatch adhesion (ASTM D 3359-87), pull-off adhesion (ASTM D 4541-85), reverse impact resistance (ASTM D 2794-84), and tensile properties (ASTM D 2370-82) were performed according to ASTM standards. Six samples were tested for

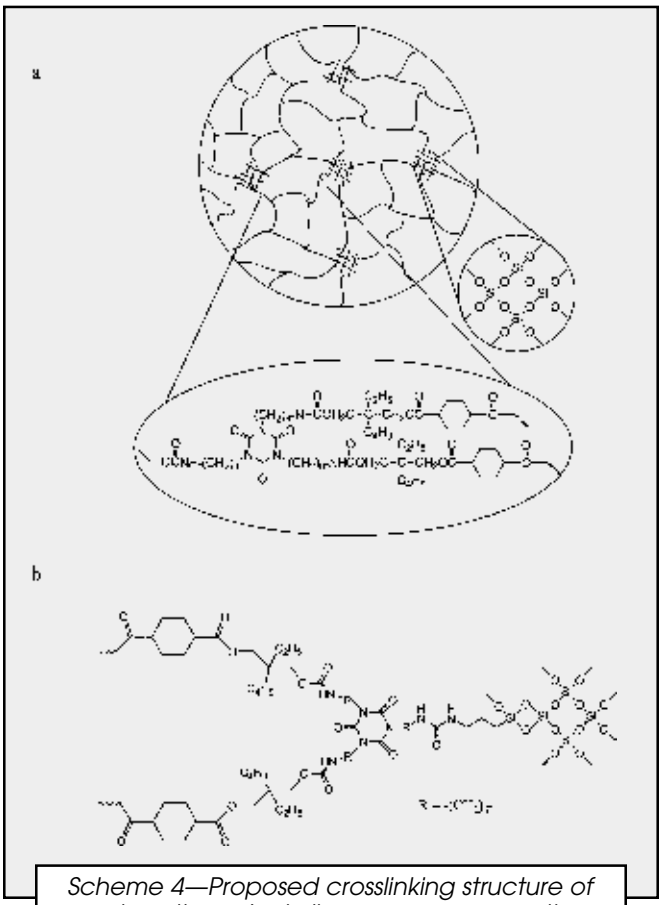


Scheme 2—Formation of polyurethane cross-linking network.

the indentation hardness, pencil hardness, and cross-hatch hardness, 10 samples for impact resistance, and 12 measurements for pull-off adhesion. The tensile properties were obtained on an Instron Universal Tester Model 1000. The dimensions of films for tensile testing were 0.05-0.12 mm in thickness, 13-17 mm wide, and an initial length of 40 mm. A crosshead speed of 20 mm/min was applied to determine elongation-at-break, tensile modulus, and tensile strength. Eight samples were tested for each film. The data are reported as the mean of the data set, with the uncertainty based on the standard deviation.



Scheme 3—The preparation of TEOS oligomers using TEOS with water and the formation of silicon gel via further hydrolysis and condensation reaction.



Scheme 4—Proposed crosslinking structure of a polyurethane/polysiloxane ceramer coating: (a) the organic polyurethane and inorganic polysiloxane; (b) the coupling mechanism of organic and inorganic phases coupled by alkoxysilane-functionalized isocyanurate (2).

Viscoelastic properties were obtained with a dynamical mechanical thermal analyzer (DMTA 3E, Rheometric Scientific) with a frequency of 1 Hz and a heating rate of 3°C/min over a temperature range of –50°C to 200°C. Scanning electron microscopy (SEM) combined with energy dispersion X-ray analysis (EDAX) was performed using a JEOL JSM-6300 scanning electron microscope. The film was cast on an epoxy plate and the sample sputter was coated with Au. Five random points were selected for the elemental analysis by X-ray.

Plane-stress fracture toughness measurements were conducted on rectangular specimens with a single edge notch (SEN) geometry. The dimensions of the films were 0.05-0.12 mm in thickness and 13-17 mm wide. Each film was cut with a razor blade to create the edge notch. This cutting procedure gave a crack which appeared sharp under a microscope. 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 lb (111 N) load and a variable speed motor was used to deform the specimen in a tensile mode. The crosshead speed was 1.46 mm/min. The crack-tip region was observed at a magnification of 10 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 measurement. Six samples were tested for each film. The data are reported as the mean of the data set with the standard deviation.

The plane-stress fracture toughness (K_c, stress intensity factor at fracture) was calculated using equations (3-5) as follows,[22]

$$K_c = Y\sigma\sqrt{a} \tag{3}$$

$$Y = \left[3.94\left(\frac{2w}{\pi a}\right)\tan\left(\frac{\pi a}{2w}\right)\right]^{\frac{1}{2}} \tag{4}$$

$$\sigma = \frac{F}{(w-a)b} \tag{5}$$

where w is the specimen width, b is the specimen thickness, a is the notch depth, F is the load at which crack propagation begins, and Y is a geometric factor. The energy release rate per unit crack area at fracture (G_c) can be calculated by equation (6),

$$G_c = \frac{K_c^2}{E} \tag{6}$$

where E is the tensile modulus. Each of the fracture toughness data reported represents the average of five samples. The energy release rate was calculated using the average values of fracture toughness and tensile modulus.

RESULTS AND DISCUSSION

The overall objective of this study is to improve the adhesion of the self-priming or Unicoat coating system. The organic part of the Unicoat system consists of a hydroxyl functionalized polyester crosslinked with the isocyanurate of HDI. In this study, we focused on the effect of polyesters on the ceramer coating properties. The continuous phase of the ceramer films is the polyurethane, which was formed from the reaction of hydroxyl-terminated polyesters with HDI isocyanurate. The general reaction is shown in *Scheme* 2.

To avoid the evaporation of tetraethyl orthosilicate (TEOS), TEOS oligomers were prepared through the hydrolysis and condensation of TEOS with water, as shown in *Scheme* 3. The TEOS oligomers were characterized by FTIR,[29] Si NMR, and electrospray ionization-mass spectrometry (ESI-MS) in our previous study.[9]

Table 3—General Mechanical Properties of the Films

Coatings	Pencil Hardness	Tukon Hardness (KHN)	Pull-off Adhesion ($lb_f/in.^2$)	Reverse Impact (lb·in.)
CHDM(4/3)	H/F	7.2 ± 1.0	143 ± 41	73 ± 6
CHDM(4/3)T0	H/F	8.2 ± 0.8	347 ± 73	80+
CHDM(4/3)T2.5	H/F	9.5 ± 0.5	346 ± 69	80+
CHDM(4/3)T10	H/F	7.4 ± 0.6	467 ± 33	80+
BEPD(4)	HB/B	2.3 ± 0.1	207 ± 46	80+
BEPD(4)T0	HB/B	2.5 ± 0.2	375 ± 56	80+
BEPD(4)T2.5	HB/B	2.0 ± 0.2	436 ± 63	80+
BEPD(4)T10	HB/B	1.2 ± 0.1	428 ± 50	80+
BEPD(4/3)	HB/B	2.4 ± 0.1	183 ± 38	80+
BEPD(4/3)T2.5	HB/B	2.4 ± 0.2	461 ± 58	80+

Table 4—Glass Transition Temperature of the Films[a]

Coatings	T_g (°C)	Coatings	T_g (°C)	Coatings	T_g(°C)
CHDM(4/3)	80	BEPD(4)	55	BEPD(4/3)	56
CHDM(4/3)T0	84	BEPD(4)T0	59		
CHDM(4/3)T2.5	80	BEPD(4)T2.5	59	BEPD(4/3)T2.5	59
CHDM(4/3)T10	80	BEPD(4)T10	56		

(a) T_g was determined by the temperature corresponding to the maximum of the transition of tan δ.

The inorganic phase was formed from the TEOS oligomers through the moisture-curing process within a reaction isocyanate-polyester continuous phase. Further hydrolysis and condensation reactions form a silicon oxide-alkoxysilane distributed in a continuous polyurethane phase illustrated in *Scheme* 4a. It is proposed that alkoxysilane-functionalized isocyanurate couples the organic phase with the inorganic phase via a urethane and a siloxane linkage, as shown in *Scheme* 4b.

General Mechanical Properties

The general coating properties are shown in *Table* 3. The pencil hardness was dependent on the polyesters. The four films with polyester CHDM(4/3) have the pencil hardness H/F, while the six films with polyesters BEPD(4) and BEPD(4/3) have the pencil hardness HB/B. Polyesters with diol 1,4-CHDM possess a rigid cyclohexane ring, providing films with harder properties compared to the branched diol, BEPD.

The Tukon hardness is a more accurate method for the hardness measurement. The films with polyester CHDM(4/3) have the Tukon hardness ranging from 7.2 to 9.5 KHN, while the Tukon hardness of films with polyester BEPD(4) and BEPD(4/3) ranges from 1.2 to 2.5 KHN. The results are consistent with pencil hardness measurements, however, the difference in hardness can be distinguished by Tukon hardness measurement more accurately than by pencil hardness. For the CHDM polyurethane series, the Tukon hardness ranged from 7.2 to 8.2 KHN with the addition of 25 wt% alkoxysilane-functionalized isocyanurate (2). With the initial addition of TEOS oligomers of 2.5 wt%, the Tukon hardness increased to 9.5 KHN. The rigid siloxane, in effect, reinforced the films. When the TEOS oligomers concentration was increased from 2.5 to 10 wt%, Tukon hardness decreased from 9.5 to 7.4 KHN. A possible explanation is phase separation. When the TEOS oligomers concentration is higher, the alkoxysilane-functionalized isocyanurate (2) cannot provide enough compatibility for the inorganic phase and, thus, more phase separation occurs. The phase separation produced more interfaces and defects in the film structure. Another factor could be that the TEOS oligomers condense into siloxane, and thus, the initial particle before curing process shrinks and produces a cavity in the films after the films were cured. The defects caused by TEOS oligomers at high concentration offset the reinforcement effect of TEOS at low concentration.

The formulations with the BEPD(4) Tukon hardness increases with the addition of alkoxysilane-functionalized isocyanurate (2), which is contributed to the extra functional groups of 2. The same tendency was observed for the CHDM(4/3) series. However, the Tukon hardness starts to decrease from 2.5 to 2.0 with the initial addition of

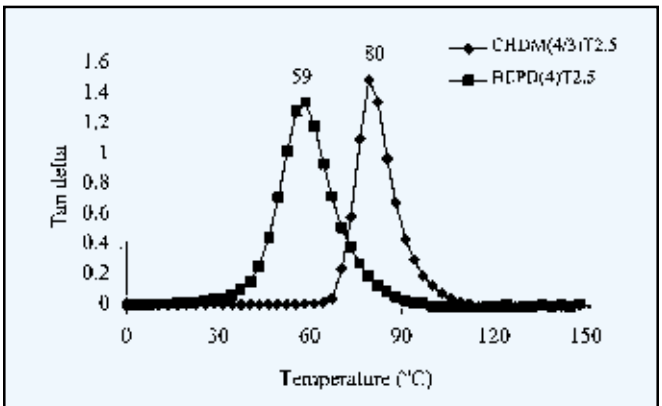


Figure 1—Tan delta vs. temperature for the ceramer coatings CHDM(4/3)T2.5 and BEPD(4)T2.5.

Table 5—Tensile Properties of the Films

Coatings	Tensile Strength (MPa)	Elongation-at-Break (%)	Tensile Modulus (MPa)
CHDM(4/3)	39.3 ± 6.0	3.9 ± 0.7	1003 ± 54
CHDM(4/3)T0	54.2 ± 4.7	5.1 ± 0.5	1072 ± 61
CHDM(4/3)T2.5	45.8 ± 3.9	4.9 ± 0.7	1018 ± 64
CHDM(4/3)T10	42.0 ± 5.3	4.2 ± 0.7	1003 ± 43
BEPD(4)	17.1 ± 4.5	108.3 ± 24.9	363 ± 46
BEPD(4)T0	17.4 ± 2.0	74.0 ± 21.2	437 ± 49
BEPD(4)T2.5	19.1 ± 4.2	97.8 ± 22.0	425 ± 22
BEPD(4)T10	14.7 ± 3.9	101.4 ± 20.8	206 ± 25
BEPD(4/3)	18.4 ± 3.8	132.6 ± 27.4	322 ± 30
BEPD(4/3)T2.5	18.6 ± 3.0	114.4 ± 12.5	308 ± 30

2.5 wt% TEOS oligomers. The reason may be caused by the difference compatibility between the two polyesters. The system with BEPD(4) is less compatible with TEOS oligomers compared to the system with CHDM(4/3). So, more phase separation in the films with BEPD(4) was produced at a lower concentration of TEOS oligomers relative to the films with CHDM(4/3). When the concentration of TEOS oligomers is further increased from 2.5 to 10 wt%, the Tukon hardness decreases by 40%. A greater decrease was observed in the formulations with BEPD(4). With increasing TEOS content, the Tukon hardness of formulations with the CHDM(4/3) polyester was similar to the hardness of corresponding CHDM(4) polyester. Therefore, the diacids did not generate phase miscibility issues.

Similar to the polyurea,[9,10] the effect of alkoxysilane on the adhesion improvement can also be observed for the polyurethane. The polyurethane CHDM(4/3) has a low pull-off adhesion, 143 $lb_f/in.^2$, as well as a low crosshatch adhesion, 3B. (The other seven formulations have the highest grade crosshatch adhesion, 5B.) The adhesion was increased from 143 to 347 $lb_f/in.^2$, a 142.7% increase with the addition of alkoxysilane-functionalized isocyanurate (2), and then increased to 467 $lb_f/in.^2$, a 228.4% increase with addition of 10 wt% TEOS oligomers. The pull-off adhesion of four formulations with BEPD(4) shows a similar trend to the formulations with CHDM(4/3). Both the alkoxysilane group of 2 and TEOS oligomers improve the adhesion. It was proposed in our previous study that the chemical bonding might be formed from the co-condensation of Si–OH and Al–OH producing Si–O–Al linkage.[6,12] The Si–OH groups are either from alkoxysilane-functionalized isocyanurate (2) or from TEOS oligomers. With the addition of TEOS oligomers, more alkoxysilane groups interact with the aluminum substrate and better adhesion was achieved. The pull-off adhesion of coatings with polyester BEPD(4/3) is quite close to the corresponding coatings with the polyester BEPD(4). There is no difference on the adhesion between the mixture of diacids (1,3-CHDA and 1,4-CHDA) and one diacid (1,4-CHDA) in the polyesters, which is similar to the Tukon hardness. Generally, the adhesion is predominately dependent on the alkoxysilane groups.

The film CHDM(4/3) has a reverse impact resistance of 73 lb·in., which is lower than the impact resistance of the CHDM(4/3) films with TEOS. This may be caused by the poor adhesion. It is expected that the coatings with polyesters BEPD(4) and BEPD(4/3) have higher reverse impact resistance than the coatings with polyester CHDM(4/3) since the branched diol BEPD is more flexible compared to the diol CHDM with cyclohexane ring. But, it cannot be distinguished due to the limitation of the impact resistance test scale. Reverse impact resistance was greatly increased by the polyesters comparing the polyurethane/polysiloxane ceramers with the polyurea/polysiloxane ceramers. The range of reverse impact resistance of polyurea/polysiloxane ceramers is from 10 to 35 lb·in.

Viscoelastic Properties

The viscoelastic properties of the ceramer coatings were investigated using a dynamic mechanical thermal analyzer (DMTA). Storage modulus E′, loss modulus E″, and tan δ (E′/E″) vs. temperature were obtained as a function of temperature. The glass transition temperatures of the films were obtained from the tan δ at maxima. The glass transition temperatures for all the films are listed in *Table* 4. For comparison, tan δ vs. temperature for two typical ceramer films, CHDM(4/3)T2.5 and BEPD(4)T2.5, is shown in *Figure* 1. Generally, the films with polyesters BEPD(4) and BEPD(4/3) have about 20°C lower T_g than the four films with polyesters CHDM(4/3). The T_g is dependent upon the chemical structures of the diols. The cyclohexane ring of CHDM affords rigidity, while the BEPD has a branched structure affording a lower T_g. This is consistent with the hardness, tensile, and fracture properties.

Table 6—Fracture Toughness of Polyurethane/Polysiloxane Ceramer Coatings

Coatings	Fracture Toughness (Kc, MPa·$m^{1/2}$)	Tensile Modulus (E, MPa) x10^3	Energy Release (G_c, J/m^2) x10^3	Mode of Plastic Deformation
CHDM(4/3)	1.80 ± 0.16	1003 ± 54	3.2 ± 0.4	Craze
CHDM(4/3)T0	2.07 ± 0.14	1072 ± 61	4.0 ± 0.4	Craze
CHDM(4/3)T2.5	1.85 ± 0.11	1018 ± 64	3.4 ± 0.4	Craze
CHDM(4/3)T10	1.58 ± 0.11	1003 ± 43	2.5 ± 0.3	Craze
BEPD(4)	0.212 ± 0.024	363 ± 46	0.12 ± 0.03	n/o[a]
BEPD(4)T0	0.312 ± 0.023	437 ± 49	0.22 ± 0.03	n/o
BEPD(4)T2.5	0.415 ± 0.034	425 ± 22	0.41 ± 0.05	n/o
BEPD(4)T10	0.213 ± 0.005	206 ± 25	0.22 ± 0.03	n/o
BEPD(4/3)	0.209 ± 0.010	322 ± 30	0.14 ± 0.02	n/o
BEPD(4/3)T2.5	0.356 ± 0.032	308 ± 30	0.41 ± 0.07	n/o

(a) No specific mode of deformation was observed.

Tensile Properties

Table 5 shows the tensile properties for the three series of films. The four films with polyester CHDM(4/3) have higher tensile strength and tensile modulus, and lower elongation-at-break than the six films with polyesters BEPD(4) and BEPD(4/3). The tensile properties are dependent upon the polyesters. In the four films with CHDM(4/3), the tensile strength increases from 39.3 to 54.2 MPa with the addition of alkoxysilane-functionalized isocyanurate (2) comparing the film CHDM(4/3)T0 with

the film CHDM(4/3)T0. When TEOS oligomers were added into the formulation CHDM(4/3)T2.5, the tensile strength decreased from 54.2 to 45.8 MPa. This was attributed to the phase separation from the TEOS oligomers which produces defects in the film. When the TEOS oligomers concentration further increases to 10 wt%, the tensile strength decreases to 42.0 MPa. The effect of TEOS oligomers on the tensile strength is different from the Tukon hardness. The measurement of Tukon hardness is a very small area while the tensile test is for the whole film. The defect from phase separation may have a greater effect on the tensile properties than hardness. It may be the reason that the initial addition of 2.5 wt% TEOS oligomers decreases the tensile strength whereas increases the Tukon hardness. The difference in tensile modulus among the four formulations was not well distinguished. The films with CHDM (4/3) have very low elongation-at-break, ranging from 3.9 to 5.1%.

A similar trend in the CHDM polyurethane was observed for the formulations based on BEPD(4). The tensile strength increases with the addition of alkoxysilane-functionalized isocyanurate (2) and at 2.5 wt%, and decreased at 10 wt% TEOS oligomers. The reinforcement effect from the phase coupling group and the TEOS oligomers was also observed in the tensile modulus. The tensile modulus increases from 363 to 437 MPa with the addition of 2. With the addition of 10 wt% TEOS oligomers, the modulus decreases to 206 MPa. The coatings with BEPD(4) have very high elongation-at-break, ranging from 74.0 to 108.3%. Comparing the BEPD(4/3)T2.5 with BEPD(4)T2.5, the tensile modulus of BEPD(4/3)T2.5 is lower than BEPD(4)T2.5. It can be hypothesized that the polyurethanes with one diacid polyester are more symmetrical than the polyurethanes with two diacid polyesters, and therefore have a stronger intermolecular interaction.

Fracture Toughness

Table 6 shows the fracture toughness (K_c) for all 10 coatings. The energy releases (G_c) are also listed in *Table* 5, which was calculated from equation (6) based on the fracture toughness and tensile modulus. Generally, the fracture toughness was dependent upon the polyesters in the formulations. The four films with diol CHDM in polyesters have the fracture toughness ranging from 1.58 to 2.07 MPa·m$^{1/2}$. In contrast, the range of the fracture toughness is between 0.212 and 0.415 for the six films with diol BEPD. This may unfortunately be a T_g effect. However, we are looking forward to modifying our instrument for temperature variability. The fracture toughness for the coatings CHDM(4/3), CHDM(4/3)T0, and CHDM(4/3)T2.5 are within experimental error. When the TEOS oligomers increased to 10 wt%, the fracture toughness decreased to 1.58 MPa·m$^{1/2}$. It was surmised that the addition of TEOS oligomers caused the phase separation, especially at high concentration, which produced weak interaction between the organic and inorganic phase.

However, above T_g, a significant difference in fracture toughness was observed for the four formulations with polyester BEPD(4). Fracture toughness increased from 0.212 to 0.312 MPa·m$^{1/2}$ by 47% with the addition of 2 into the polyurethane comparing hybrid film BEPD(4)T0 with polyurethane BEPD(4). The fracture toughness was further increased from 0.312 to 0.415 MPa·m$^{1/2}$ by 33% with the addition of initial 2.5 wt% TEOS oligomers. When the TEOS increased to 10 wt%, the fracture toughness decreased to 0.213 MPa·m$^{1/2}$. It was surmised that the reinforcement was operative when phase separation was minimal, such as at the low concentration of TEOS oligomers. However, as the concentration of TEOS oligomers increased, phase separation dominated leading to a diminution of fracture toughness.

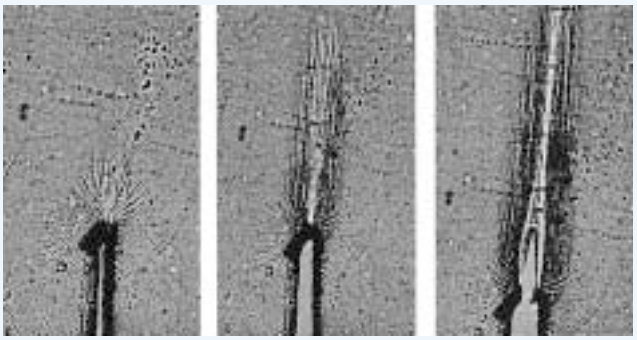


Figure 2—Crack-tip deformation zone in a ceramer film under tension. The micrographs from left to right were taken at an increasing degree of deformation. Specimen: CHDM(4) T2.5.

Crazes were observed for the four films with the diol CHDM in the deformation region. *Figure* 2 shows the propagating process for the ceramer CHDM(4)T2.5. The other films with CHDM have a similar process. No specific deformation mode was observed for the six films with diol BEPD. The deformation region showed the same pattern with the crack propagating as illustrated in *Figure* 3 for the films BEPD(4) and BEPD(4)T2.5. No difference was observed among the polyurethane film BEPD(4), hybrid film BEPD(4)T0, and ceramer film BEPD(4)T2.5.

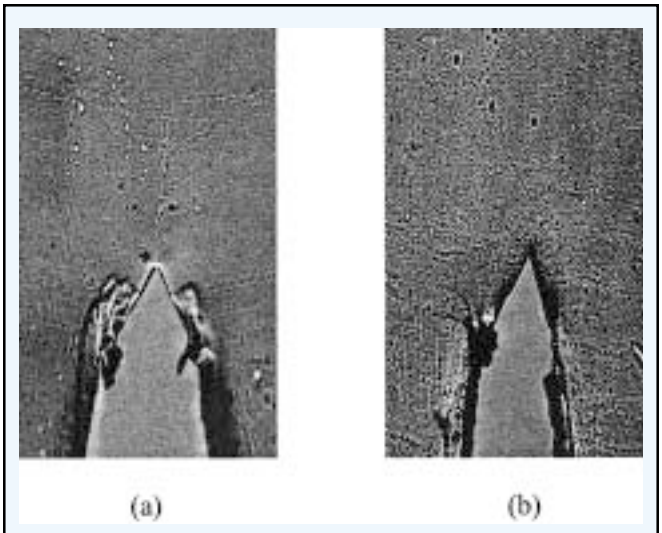


Figure 3—Crack-tip deformation zone in a polyurethane film and a ceramer film under tension. Specimen a: BEPD(4) and b: BEPD(4)T2.5.

Film Morphology

The morphology of the films was investigated using SEM combined with an X-ray analysis (EDAX). *Figure* 4 shows the morphology of a cross-section of CHDM(4/3)T0, CHDM(4/3)T2.5, and CHDM(4/3)T10. No phase separation was observed from the cross-section of film CHDM(4/3)T0. The HDI isocyanurate (1) and alkoxysilane-functionalized isocyanurate (2) have good compatibility and formed a homogeneous phase. Visually, the film of CHDM(4/3)T0 is transparent. The crack in the cross-section probably was caused during the process of SEM sample preparation. With 2.5 wt% TEOS oligomers in the system, no phase separation was observed within the SEM. When the TEOS oligomers increased to 10 wt% (CHDM(4/3)T10), spherical aggregates were observed in the cross-section for the ceramer coating, as shown in *Figure* 4. An elemental analysis of silicon content was performed using EDAX for both the aggregate and continuous area. The silicon content by weight is 3.3 ± 1.2 Si wt% for continuous phase. The silicon content for the aggregates was dependent upon the selected position on the aggregate ranging from 8.5 to 31.4 Si wt%.

Although much higher than the continuous area, the silicon content in the aggregates is still much less than the silicon content of SiO_2 (46.7 wt%). It was surmised that the aggregate also contains polyurethane. A random area

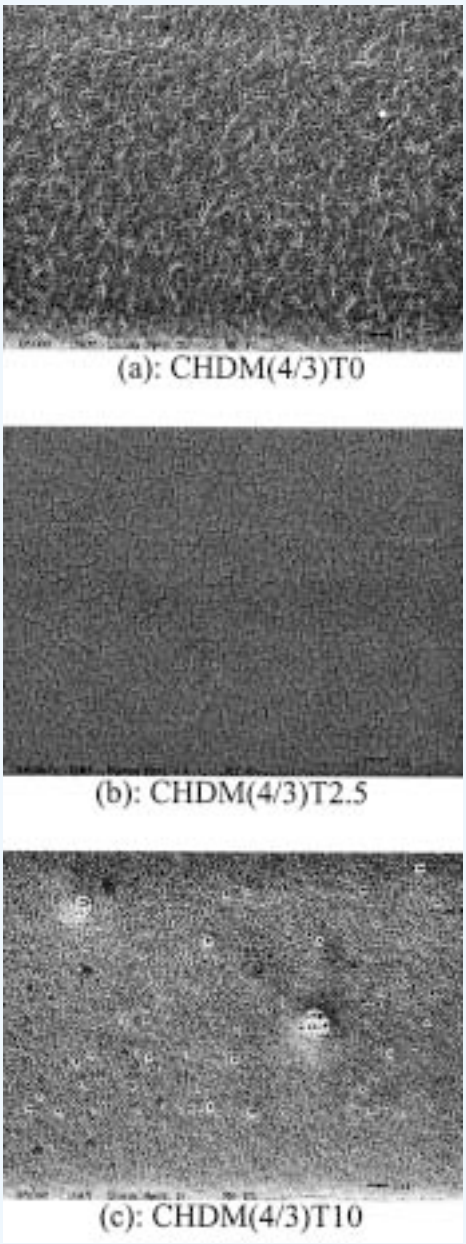


Figure 4—SEM photograph of a cross-section of ceramer coatings CHDM(4/3)T0, CHDM(4/3)T2.5, and CHDM(4/3)T10; magnification: 6000x.

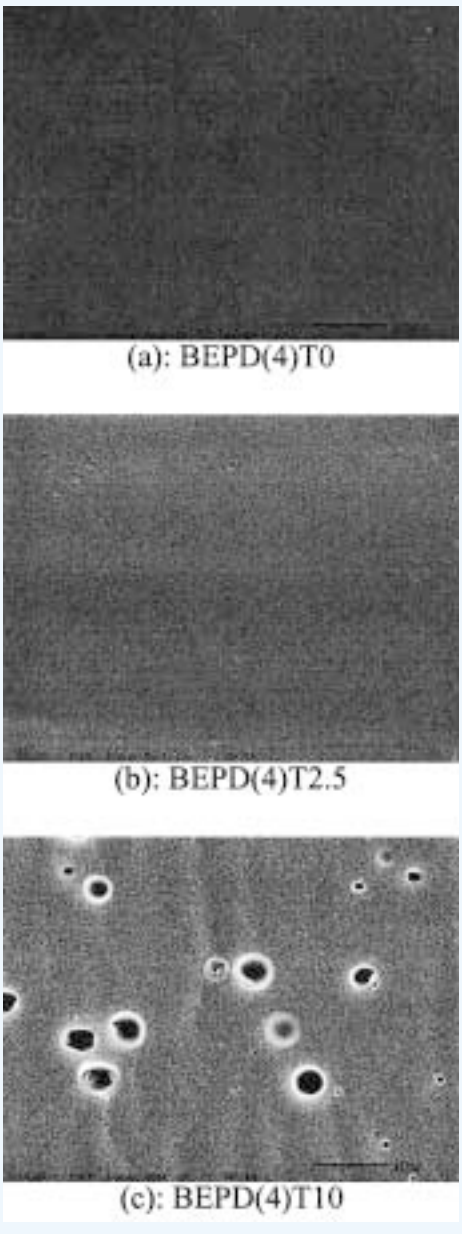


Figure 5—SEM photograph of a cross-section of ceramer coatings BEPD(4)T0, BEPD(4)T2.5, and BEPD(4)T10; magnification: 2000x.

Table 7—Silicon Content of the Films Determined by X-ray

Polyester	0 wt% TEOS Oligomers (wt%)	2.5 wt% TEOS Oligomers (wt%)	10 wt% TEOS Oligomers	
			Continuous Area (wt%)	Particles (wt%)
CHDM(4/3)	0.9 ± 0.4	2.0 ± 0.2	3.3 ± 1.2	8.5–31.4
BEPD(4)	1.1 ± 0.6	2.5 ± 0.4	2.8 ± 0.5	6.0–37.2

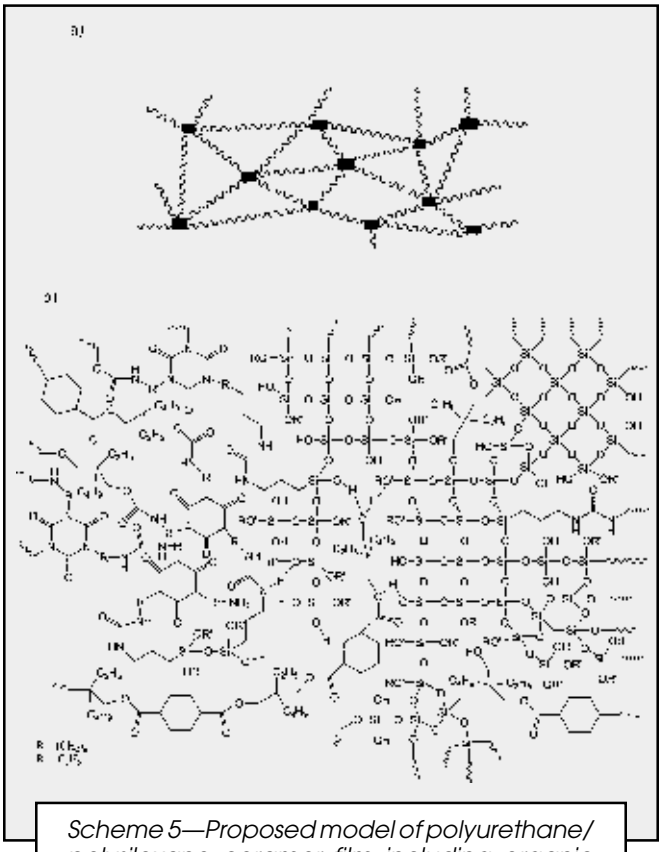
including about 20-30 aggregates was chosen to calculate the particle size for the ceramer film CHDM(4/3)T10. Assuming all the aggregate shapes are spherical, the visually detectable diameter ranges from the 147 nm to 1.35 μm. The calculation shows that the number average diameter was 317 ± 229 nm.

Similar to CHDM(4/3)T0 or CHDM(4/3)T2.5, no phase separation was observed in the cross-section of the film BEPD(4)T0 or BEPD(4)T2.5, as shown in *Figure* 5. With the addition of 10 wt% TEOS oligomers, large aggregates are observed in the cross-section of film BEPD(4)T10, as shown in *Figure* 5. The EDAX analysis indicated that the silicon content (6.0-37.2 Si wt%) in the aggregates was enriched compared to the continuous area (2.8 ± 0.5 Si wt%). The aggregate size of BEPD(4)T10 ranged from 240 nm to 5.48 μm in diameter. The number average of diameter was 1.03 μm with a standard deviation 1.54 μm. The average diameter of BEPD(4)T10 was three times larger than CHDM(4/3)T10. The difference in particle size between CHDM(4/3)T10 and BEPD(4)T10 was attributed to T_g. The BEPD(4)T10 has a lower T_g, and therefore the sol-gel precursor more easily aggregated forming larger particles during the curing process. In contrast, at higher T_g, continuous phase impeded the silicon-oxo-cluster from aggregating during the curing process resulting in smaller inorganic domains.

The SEM study of the morphology of the hybrid coating was reported by van der Linde and co-workers[23] for a polyester-melamine/silica ceramer coating system. Similar results were observed in their study. However, the aggregates and continuous area was not identified, and the particle size was not measured in a statistical method. *Table* 7 shows the silicon content as a function of TEOS concentration oligomers. Without the addition of TEOS oligomers, the silicon in CHDM(4/3)T0 and BEPD(4)T0 was derived from the functionalized isocyanurate (2). Both CHDM(4/3)T0 and BEPD(4)T0 have silicon contents close to the value in the formulations (0.87 wt%). With the addition of 2.5 wt% TEOS oligomers, the silicon content increased to 2.0 wt% for CHDM(4/3)T2.5 and to 2.5 wt% for BEPD(4)T2.5. Again, no phase separation was observed with a low concentration of TEOS oligomers.

The model proposed by Wilkes depicts small particles dispersed in a continuous organic phase with a chemical bond linking the inorganic and organic phases together.[24] In effect, this model depicts a co-continuous two system where the organic phase is linked together via inorganic particles, and the inorganic particles are linked together via flexible organic oligomers. A more structurally detailed model of the polyurethane/polysiloxane ceramer film is proposed in *Scheme* 5. Since the TEOS was prehydrolyzed and condensed via an acid catalyst, a more linear open silicon-oxo-alkoxide structure would be anticipated. This model structure is collaborated by ESI-MS of the TEOS oligomers, and EDAX of the SiO_2 particles. For the 2.5 wt% TEOS films, the inorganic structure can be modeled by a co-continuous two phase system depicted by *Schemes* 5a and 5b where the silicon-oxo-cluster are depicted as an open structure on a nanoscale, 2-10 nm. As the TEOS oligomers concentration increases to 10 wt%, the same model can be used on a scale up to 300-1000 nm. However, as the size of the silicon domain grows, it is assumed that the structures are no longer so open, and as a consequence phase separation occurs. Presumably, if more coupling agent is added a higher TEOS content can be tolerated without phase separation.

The approach used in the polyurea/polysiloxane coating system was successfully extended into a polyurethane system. The polyurea/polysiloxane coatings lacked the flexibility[9-12] which not surprisingly was evident in the polyurethane/polysiloxane coatings reported in this study. The ceramer coating showed considerable improvement in adhesion, corrosion resistance, and hardness over polyurethane coatings. With respect to aircraft coatings, the polyurethane/polysiloxane ceramer coatings show many advantages, including the low VOC, environmentally safe, more efficient application, and lower cost compared to the traditional aircraft coating systems. Other potential applications include automobile refinish coatings, scratch resistance plastic coatings, and floor coatings.



Scheme 5—Proposed model of polyurethane/polysiloxane ceramer film including organic phase, inorganic phase and various interactions between the two phases.

Usually, inorganic/organic hybrid coatings have enhanced hardness, fracture toughness, and tensile properties.[25-28] This first generation of polyurethane ceramer coatings did not show such an enhancement. Evidently, the soft segmental behavior of the polyester oligomers overpowered the hard segment of the carbamates and silicon-oxo-clusters. For more hardness or scratch/mar resistance, the impact of the soft segment would have to be diminished. This could be achieved by lowering the average molecular weight of the polyester oligomers, or adding less than a stoichiometric amount of hydroxyl groups. We presently are pursuing these two approaches.

CONCLUSIONS

The general coating, tensile, and fracture properties of the polyurethane ceramer coatings are dependent upon the polyol of the polyesters. The films with polyesters BEPD(4) and BEPD(4/3) are softer with a lower tensile strength, lower tensile modulus, lower hardness, higher elongation-at-break, and lower fracture toughness compared to films with polyester CHDM(4/3). Phase separation in the ceramer films was dependent upon the concentration of TEOS oligomers and the glass transition temperature of the continuous phase. Data derived from SEM and EDAX indicated that the phase separation existed in the ceramer film when the TEOS oligomers concentration was 10 wt%. When phase separated, the morphology of the ceramer coatings consists of aggregates distributed in a polyurethane continuous phase. It was proposed that the inorganic domain is an open structure in which the organic phase is intermingled within the interior of the silicon-oxo-particles.

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