Model Reaction Study on the Interaction between the Inorganic and Organic Phases in Drying Oil Based Ceramer Coatings

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Metal−oxo carboxylates containing unsaturated fatty acids were used to model the interaction between drying oils and sol−gel precursors in inorganic/organic coatings. The metal carboxylates were prepared by reacting titanium isopropoxide [$Ti(O\text{-}i\text{-}Pr)_4$] with linolenic and oleic acids. Nuclear magnetic resonance spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and Fourier transform Raman (FT-Raman) spectroscopy were used to investigate the bond formation between $Ti(O\text{-}i\text{-}Pr)_4$ and free fatty acids. The ^{13}C NMR and FT-IR spectra indicate the metal carboxylates are complex mixtures of bidentate chelating, bridging, and metal−oxo bridging clusters. The incorporation of unsaturated metal carboxylates in linseed oil coatings increased the glass transition temperature to 49 °C and increased the cross-link density to 1.41×10^{-3} mol/cm^3.

Introduction

Ceramer coatings have received much attention during the past 20 years.[1−11] The term “ceramer” is defined as a material with both ceramic and polymeric characteristics. Ceramers are materials formed by the in situ polycondensation of metal alkoxides within an organic polymeric matrix via the sol−gel process.[1−4] Sol−gel precursors modified with functional organic groups have gained popularity in inorganic/organic hybrid systems.[12−14] Among these modifications include functionalized carboxylic acid moieties.[15,16] The presence of functionalized carboxylate groups promotes bond formation between the inorganic and organic phases. In addition, substitution of alkoxy groups in metal alkoxides moderates the reactivity and, therefore, allows control of the inorganic particle size during the sol−gel process.[17]

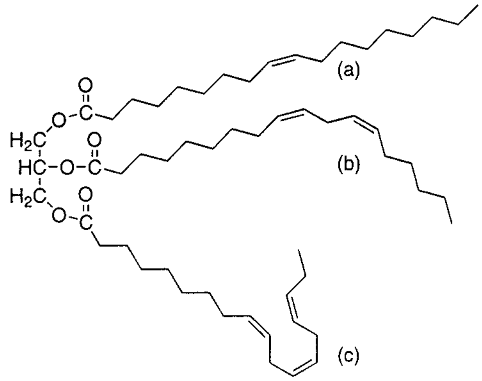

Figure 1. Idealized triglyceride structure containing (a) oleic, (b) linoleic, and (c) linolenic fatty acids.

Recently, it was reported that the incorporation of metal alkoxides in seed oil coatings enhanced the mechanical properties relative to linseed oil coatings.[18−22] The principle component of seed oils is triglycerides, as shown in Figure 1. The presence of $Ti(O\text{-}i\text{-}Pr)_4$ in linseed oil coatings increased the film hardness, impact resistance, tensile strength, and tensile modulus. The thermomechanical properties were also found to increase as a function of metal alkoxide type and content. The morphology of these ceramer coatings was found to be dependent on metal alkoxide content. Phase separation

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between the inorganic and organic domains was found in ceramers containing a single metal alkoxide. The mixing of metal alkoxides promoted a more homogeneous film with no observable microphase separation.

In the 1950s, Mehrotra and co-workers studied “metallic soaps” of aluminum, titanium, and zirconium by reacting metal alkoxides with excess free fatty acids.[23−26] Lauric, myristic, palmitic, stearic, and valeric acids were the primary saturated fatty acids used in the development of metal soaps. More recently, structural characterization of crystalline metal−oxo carboxylate clusters has been well-defined in the literature.[27−30] According to x-ray data, the crystalline metal−oxo carboxylate clusters form hexameric ring structures $M_6O_4(OR)_8(OOCR)_8$. However, the final products highly depend on the ratios of metal alkoxide and carboxylic acid.[27]

This study was used to establish the interaction between drying oils and sol−gel precursors in inorganic/organic coatings and to investigate the inorganic/organic bonding contribution to the cross-link density. To model these proposed interactions, two metal−oxo carboxylates were synthesized. In addition, $Ti(O\text{-}i\text{-}Pr)_4$ was also reacted with monolein and diolein to determine if there is any interaction with the primary and secondary alcohols present. Furthermore, $Ti(O\text{-}i\text{-}Pr)_4$ was introduced to triolein to determine if $Ti(O\text{-}i\text{-}Pr)_4$ acts as a transesterification catalyst. Nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, Fourier transform Raman (FT-Raman) spectroscopy, and inductively coupled plasma−optical emission spectroscopy (ICP−OES) were used to characterize the resulting products. In addition, tensile and viscoelastic properties were evaluated to determine if the presence of metal carboxylates in linseed oil provides similar properties relative to linseed oil based ceramer coatings containing a metal alkoxide.

Experimental Section

Materials. Linolenic acid, oleic acid, titanium(IV) isopropoxide, and toluene were purchased from Aldrich. Diolein, monolein, and triolein were obtained from NuChek Prep. Inc. (Elysian, MN). The linseed oil was obtained from Archer Daniels Midland Corporation. All chemicals were used as received with no further purification. The moisture content for the linseed oil was found to be 0.45% using the Karl Fischer Water method by Galbraith Laboratories (Knoxville, TN). The acid number for the linseed oil was calculated according to ASTM D803 and was found to be 2.96.

Instruments. A JEOL GSX 400 MHz nuclear magnetic resonance (NMR) spectrometer was used to record ^{13}C NMR spectra. Deuterated chloroform was used as the solvent and tetramethylsilane as a standard reference under ambient conditions. The FT-IR spectra were obtained using a Nicolet Magna IR System 850 optical bench Fourier transform infrared spectrometer. Liquid samples were placed between KBr plates under a nitrogen atmosphere. The FT-Raman spectra were measured using a Bruker IFS 55/FRA 106 FT-IR/Raman spectrometer. An Nd:YAG laser was used to provide a maximum power of 500 mW, and Opus software was used to analyze the spectra. Carbon, hydrogen, and titanium analysis was obtained using an inductively coupled plasma−optical emission spectrometer (ICP−OES) at Galbraith Laboratories (Knoxville, TN).

The viscoelastic properties of these films were investigated using a Rheometric Dynamic Mechanical Thermal Analyzer (DMTA) 3E. The maximum of the tan δ was used to determine the glass transition temperature. The cross-link density was determined by utilizing the lowest E' point value at least 50 °C beyond the point at which the T_g midpoint was observed. The test conditions consisted of a ramp rate of 2 °C/min, a frequency of 1 rad/s, and a temperature range of −100 °C to 250 °C. The film geometry was 3 × 10 mm with a thickness of 0.050−0.085 mm. Reproducibility of the DMTA data was verified by scanning over the useful temperature range multiple times.

Tensile measurements were obtained on an Instron Universal Tester Model 1000. The dimensions of the films tested were 15−17 mm wide, with an initial length of 50 mm. A crosshead speed of 10 mm/min was used to determine strain at break, tensile modulus, and tensile strength. Six samples were tested for each coating, and an average value was reported. Mechanical coating tests performed include pencil hardness (ASTM D3363), conical mandrel flexibility (ASTM D522), crosshatch adhesion (ASTM D3359), and reverse impact resistance (ASTM D2794-84).

Synthesis of Model Reactions. *Reaction of* $Ti(O\text{-}i\text{-}Pr)_4$ *with* $HO_2C(CH_2)_7(CH_2CH{=}CH)_3CH_3$. Titanium(IV) isopropoxide (2.00 g, 7.04 mmol), and linolenic acid (3.92 g, 14.1 mmol) were placed in a two-neck round-bottom Shlenk flask in a drybox under a nitrogen atmosphere. Approximately 50 mL of toluene was added to the flask by needle transfer using positive nitrogen pressure. The reaction flask was equipped with a magnetic stir bar and inlet/outlet of dry nitrogen, and was purged for 30 min prior to heating. The reaction mixture was stirred at 75 °C under reduced pressure for 4.5 h, and the toluene/2-propanol azeotrope was continuously removed. The products were then washed with fresh toluene (3 × 30 mL) and dried under reduced pressure.

Reaction of $Ti(O\text{-}i\text{-}Pr)_4$ *with* $HO_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3$. Titanium(IV) isopropoxide (2.01 g, 7.07 mmol), and oleic acid (3.98 g, 14.1 mmol) were placed in a two-neck round-bottom Shlenk flask in a drybox under a nitrogen atmosphere. The synthesis for this reaction followed the same procedure outlined above.

Reaction of $Ti(O\text{-}i\text{-}Pr)_4$ *with* $HOCH_2CH(OH)CH_2(O_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3)$. Titanium(IV) isopropoxide (1.01 g, 3.55 mmol), and monolein (0.672 g, 1.88 mmol) were placed in a two-neck round-bottom Shlenk flask in a drybox under a nitrogen atmosphere. The reaction flask was equipped with a magnetic stir bar and inlet/outlet of dry nitrogen. The solution was heated to 80 °C under reduced pressure for 1 h, and a white solid was formed. The white solid was washed three times with 2-propanol and dried under reduced pressure. Elem. Anal. utilizing ICP−EOS: Ti, 25.83; C, 36.47; H, 6.53.

Reaction of $Ti(O\text{-}i\text{-}Pr)_4$ *with* $CH_2(O_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3)CH(OH)CH_2(O_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3)$. The reaction between titanium(IV) isopropoxide (0.565 g, 1.99 mmol), and diolein (0.613 g, 0.987 mmol) followed the same procedure outlined above for the reaction between titanium(IV) isopropoxide and monolein. Again, a white solid was obtained and washed three times with 2-propanol. The solid was then dried under reduced pressure prior to characterization by ICP−OES. Ti, 23.61; C, 38.72; H, 6.42.

Reaction of $Ti(O\text{-}i\text{-}Pr)_4$ *with* $CH_2(O_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3)CH(O_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3)CH_2(O_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3)$. Titanium(IV) isopropoxide (0.253 g, 0.890 mmol), and triolein (4.750 g, 5.38 mmol) were placed in a two-neck round-bottom Shlenk flask in a drybox under a nitrogen atmosphere. The flask was equipped with a magnetic stir bar and inlet/outlet of dry nitrogen. Prior to heating, the reactants

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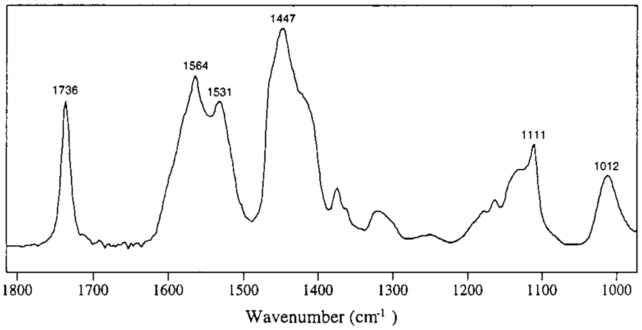

Figure 2. FT-IR spectrum for the products obtained from 1 mol of Ti(O-*i*-Pr)$_4$ and 2 mol of oleic acid.

were purged with dry nitrogen for 30 min. The reaction then proceeded at 130 °C for 10 min, and 210 °C for 10 min under reduced pressure. At each temperature, an aliquot was removed and a ^{13}C NMR spectrum was taken for each sample.

Results and Discussion

There are many possibilities for which a chemical interaction can occur between metal alkoxides and seed oils. First, metal carboxylate formation may occur during the cure cycle. Second, the sol−gel precursor Ti(O-*i*-Pr)$_4$ is commonly used as an esterification or transesterification catalyst in the synthesis of polyesters.[31] Thus, Ti(O-*i*-Pr)$_4$ or resultant metal−oxo clusters can catalyze the formation of oligomeric fatty acid and di- or monoglyceride. Another possibility is the sol−gel precursors simply form inorganic domains within the organic phase and enhance the mechanical properties by acting as rigid particles encapsulated by the cross-linked organic phase.[32] However, the morphology of these ceramer films were characterized in a previous study using small-angle X-ray scattering (SAXS).[19] The data indicate that the inorganic domains were relatively small compared to pigments commonly used in coatings. As a result, additional interaction between the inorganic and organic phases must be present in order to account for the physical properties of these ceramer coatings.

Model Reaction $Ti_6O_4(O\text{-}i\text{-}Pr)_{16-n}(O_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3)_n$. Oleic acid was reacted with Ti(O-*i*-Pr)$_4$ first, since it was anticipated that the oleate complex was not autoxidatively active. Figure 2 shows the FT-IR absorbance spectrum for the products obtained from 1 mol of Ti(O-*i*-Pr)$_4$ and 2 mol of oleic acid. Band assignments for the reactants and products used in this study are listed in Table 1. No absorption band was found in the region of 3200−3600 cm^{-1}, indicating the absence of hydroxyl groups. The asymmetric carboxylate vibration $\nu_{asym}(CO_2)$ stretching frequencies were found at 1564 and 1531 cm^{-1} as compared to oleic acid (1712 cm^{-1}). The symmetric carboxylate frequency $\nu_{sym}(CO_2)$ was found at 1447 cm^{-1}, which remained relatively unaltered in comparison with oleic acid. The broad $\nu_{asym}(CO_2)$, and $\nu_{sym}(CO_2)$ indicate that there may be more than one type of metal carboxylate bonding mode present. However, it should be noted that the carbon−carbon double bonds also generate absorption bands within this region and may be overlapping. As a result, the carboxylate vibration bands may appear broader than expected. In metal carboxylate complexes, the $\nu_{asym}(CO_2)$, and $\nu_{sym}(CO_2)$ stretching frequencies can be used to determine the bonding mode between the metal and carboxylic ion.[33] This can be achieved by determining the position and separation of the carbonyl peaks ($\nu_{asym} - \nu_{sym}$). For the products obtained from Ti(O-*i*-Pr)$_4$ and oleic acid, the difference ($\nu_{asym} - \nu_{sym}$) was 117 cm^{-1}. In addition, a new absorption band at 1012 cm^{-1} formed, and its tentative band assignment is presumably the Ti−O−C vibrational stretch from the metal−oxo carboxylate cluster formation. This is characteristic of the bidentate mode, and therefore, the bidentate structure is proposed for the metal carboxylates in this study.[33] Previous work by Mehrotra and co-workers concluded that the bonding mode was unidentate.[34] This conclusion was based on the $\nu_{asym}(CO_2)$ band at ~1730 cm^{-1}. Our FT-IR spectra also contained this peak, but it was verified to be from isopropyl oleate, which appears to be a competitive byproduct in this reaction.

Table 1. Tentative Band Assignments for Reactants and Products Used in This Study[a]

	FT-IR		FT-Raman	
compound	$\nu_{asym}(CO_2)$ (cm^{-1})	$\nu_{sym}(CO_2)$ (cm^{-1})	ν(Ti−O−C) (cm^{-1})	ν(Ti−O) (cm^{-1})
oleic acid	1712	1465, 1413		
linolenic acid	1714	1462, 1413		
isopropyl oleate	1734	1466, 1457		
isopropyl linolenate	1733	1462, 1452		
Ti(O-*i*-Pr)$_4$			1028	566
1	1564, 1531	1447	1023	630
2	1597, 1564	1447	1023	630

[a] Model compounds **1** and **2** are $Ti_6O_4(O\text{-}i\text{-}Pr)_{16-n}(O_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3)_n$ and $Ti_6O_4(O\text{-}i\text{-}Pr)_{16-n}(O_2C(CH_2)_7(CH_2CH{=}CH)_3CH_3)_n$, respectively.

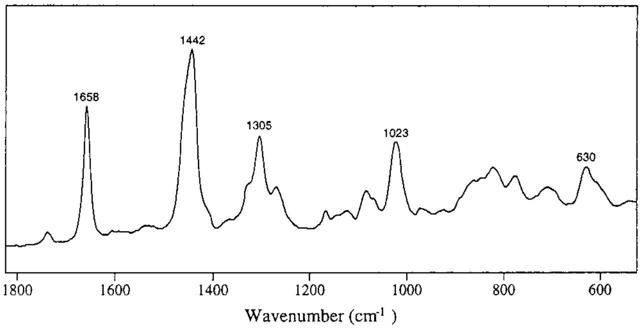

Figure 3. FT-Raman spectrum for the products obtained from 1 mol of Ti(O-*i*-Pr)$_4$ and 2 mol of oleic acid.

Figure 3 shows the FT-Raman spectrum for the metal carboxylate containing oleic acid. Generally, FT-Raman provides complimentary information on the vibrational characteristics for specific bonds present. Unfortunately, in this study the metal carboxylates did not provide adequate Raman scattering. However, two significant peaks at 1023 and 630 cm^{-1} evolve after 1 mol of Ti(O-*i*-Pr)$_4$ and 2 mol of oleic acid were heated under reduced pressure. The absorption band at 1023 cm^{-1} is due to the new Ti−O−C bond formation and the band at 630 cm^{-1} due to new Ti−O bonds.[35] However, it is

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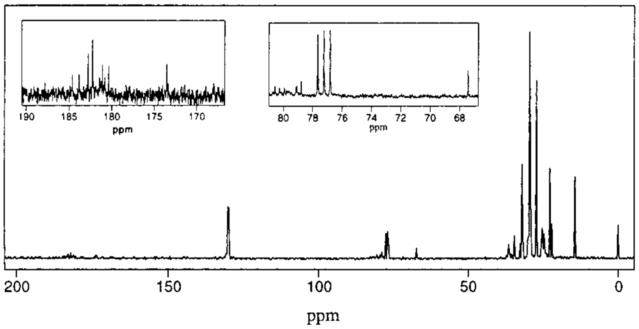

Figure 4. ^{13}C NMR spectrum for the products obtained from 1 mol of Ti(O-*i*-Pr)$_4$ and 2 mol of oleic acid.

also possible that the absorption band at 630 cm^{-1} is due to Ti−O−Ti bond formation.[35] The absorption bands at 1658, 1442, and 1305 cm^{-1} are a result of the fatty acid carbon−carbon single and double bonds.

Figure 4 shows the ^{13}C NMR spectrum for the products obtained from 1 mol of Ti(O-*i*-Pr)$_4$ and 2 mol of oleic acid. The six resonances at δ 184.6, 183.8, 182.7, 182.3, 181.1, and 180.4 ppm indicate various carboxylate environments. These three sets of resonances are multiplets, indicating the presence of six different carboxylate groups. The multiplicity suggests the presence of a metal carboxylate cluster $Ti_6O_4(O\text{-}i\text{-}Pr)_{16-n}(O_2CR)_n$. The complexity of this model reaction cannot exclude derivatives of this metal−oxo compound. Since the object of the study was to model the interaction of the metal−oxo clusters formed in situ within the drying oil matrix, a possible mixture reflects the ceramer film forming process. Nonetheless, literature characterizing similar metal carboxylate structures strongly suggest that the final product is $Ti_6O_4(O\text{-}i\text{-}Pr)_8(O_2CR)_8$.[27,30] A resonance at δ 173.5 ppm was also observed in the spectrum and was determined to be isopropyl oleate, a competitive byproduct in this reaction. The formation of isopropyl oleate is again proposed to be the result of Ti(O-*i*-Pr)$_4$ acting as an esterification catalyst. As a result, water may form through an esterification reaction between the isopropoxide group and fatty acid. The six carbonyl peaks would then be attributed to the metal−oxo carboxylate clusters. Recent literature has indicated the formation of metal−oxo bridging in similar reactions using acetic acid.[27] The Ti−O−Ti bridging forms for every ester molecule formed. The peaks between δ 78.4 and 80.6 ppm are assumed to be the result of multiple carboxylates present. The intense peak at δ 67.4 ppm can be attributed to the methyl groups in isopropyl oleate.

Model Reaction $Ti_6O_4(O\text{-}i\text{-}Pr)_{16-n}(O_2C(CH_2)_7(CH_2\text{-}CH{=}CH)_3CH_3)_n$. The same reaction as the oleate was performed with linolenic acid to model an autoxidatively active fatty acid. It is apparent that the formation of metal carboxylates is independent of fatty acid used since the FT-IR and ^{13}C NMR spectra show similar oxo-carboxylate formation as shown in Table 1 and Figure 5. From the data obtained, the bond formation is either a bidentate chelating or bidentate bridging bond mode. In addition, carbonyl resonances in the ^{13}C NMR spectrum are also attributed to metal−oxo cluster formation. The formation of the ester byproduct is also observed. The formation of the ester is presumed to be a result of a transesterification process catalyzed by the titanate.

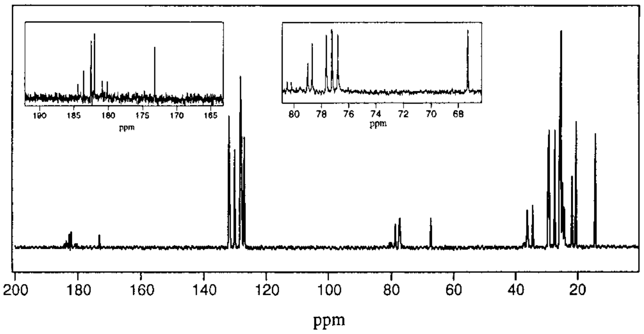

Figure 5. ^{13}C NMR spectrum of the products obtained from 1 mol of Ti(O-*i*-Pr)$_4$ and 2 mol of linolenic acid.

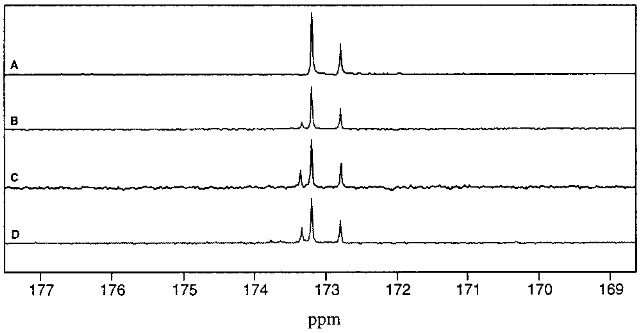

Figure 6. ^{13}C NMR spectra for the reaction of Ti(O-*i*-Pr)$_4$ and triolein. (A) Triolein, (B) Ti(O-*i*-Pr)$_4$ + triolein at 25 °C, (C) Ti(O-*i*-Pr)$_4$ + triolein at 130 °C, and (D) Ti(O-*i*-Pr)$_4$ + triolein at 210 °C.

Model Reaction of Ti(O-*i*-Pr)$_4$ with Monolein, Diolein, and Triolein. To further understand the complex chemistry which may be present when incorporating a sol−gel precursor in a seed oil, Ti(O-*i*-Pr)$_4$ was also introduced to mono-, di-, and triglycerides containing oleic acid. The purpose of this portion of the study was to determine if Ti(O-*i*-Pr)$_4$ has any reactivity toward the hydroxyl groups present on mono- and diglycerides. The triglyceride was used to determine if Ti(O-*i*-Pr)$_4$ can act as a transesterification catalyst. The Ti, C, and H analysis for the products obtained between Ti(O-*i*-Pr)$_4$ and monolein was found to be 25.83%, 36.47%, and 6.53%, respectively. The Ti, C, and H analysis for the products obtained between Ti(O-*i*-Pr)$_4$ and diolein was found to be 23.61%, 38.72%, and 6.42%, respectively. From the elemental analysis data, it appears that Ti(O-*i*-Pr)$_4$ subsequently reacts with the hydroxyl groups. As a result, the hydrolysis, and condensation reactions described in the sol−gel process preceded the anticipated transesterification reaction. Therefore, the transesterification reaction between Ti(O-*i*-Pr)$_4$ and the mono or diglyceride does not occur, but rather small hydrolyzed Ti−O−Ti structures form.

Figure 6 shows the ^{13}C NMR spectra for Ti(O-*i*-Pr)$_4$ and triolein before and after heating to 130 and 210 °C. The ^{13}C NMR spectra show three carbonyl resonances of interest at δ 173.4, 173.3, and 172.9 ppm. The peaks at δ 173.3 and 172.9 ppm are the primary and secondary carbonyls, respectively, in triolein. The resonance at δ 173.4 ppm indicates the presence of isopropyl oleate, presumably formed from the transesterification reaction. No free acid is observed in the ^{13}C NMR spectrum. However, it is possible for the ester to further react with

Table 2. Mechanical Properties of Inorganic/Organic Hybrid Coatings

coating composition	dry film thickness (μm)	pencil hardness	reverse impact resistance (in.·lb)	conical mandrel flexibility (in. diam)	X-hatch adhesion
pure linseed oil	70	3B	40	1/8	5B
linseed +					
5 wt % Ti(O-*i*-Pr)$_4$	70	5H	20	1/4	4B
10 wt % Ti(O-*i*-Pr)$_4$	70	6H	10	1/4	3B
5 wt % TiO$_2$	72	1B	70	1/8	5B
12.7 wt % **2**[a]	69	5H	28	1/8	4B

[a] **2**, $Ti_6O_4(O\text{-}i\text{-}Pr)_{16-n}(O_2C(CH_2)_7(CH_2CH{=}CH)_3CH_3)_n$ (see Table 1).

Table 3. Tensile Strength, Strain at Break, Tensile Modulus, Glass Transition Temperature, and Cross-link Density of Ceramer Coatings

film composition	Ti (mol)	tensile strength (MPa)	strain at break (%)	tensile modulus (MPa)	T_g (°C)	cross-link density (mol/cm^{-3})
linseed	0	1.2 ± 0.2	57.0 ± 6.6	2.1 ± 0.3	13	3.74×10^{-5}
linseed +						
5 wt % Ti(O-*i*-Pr)$_4$	3.5×10^{-3}	2.9 ± 1.2	22.9 ± 4.0	9.7 ± 3.8	33	1.38×10^{-3}
10 wt % Ti(O-*i*-Pr)$_4$	7.0×10^{-3}	5.0 ± 0.8	25.0 ± 3.8	33.6 ± 3.1	57	1.58×10^{-3}
5 wt % TiO$_2$	3.5×10^{-3}	1.1 ± 0.3	46.6 ± 11.1	2.29 ± 0.7	13	1.56×10^{-4}
12.7 wt % **2**[a]	3.5×10^{-3}	4.1 ± 0.6	15.1 ± 4.2	60.0 ± 12.7	48	1.41×10^{-3}

[a] **2**, $Ti_6O_4(O\text{-}i\text{-}Pr)_{16-n}(O_2C(CH_2)_7(CH_2CH{=}CH)_3CH_3)_n$ (see Table 1).The 12.7 wt % **2** was selected for its equivalency in Ti concentration relative to 5 wt % Ti(O-*i*-Pr)$_4$ in linseed oil.

Ti(O-*i*-Pr)$_4$, forming the subsequent metal–oxo carboxylates. Unfortunately, it is difficult to model this proposed mechanism. It is postulated that Ti(O-*i*-Pr)$_4$ reacts with triolein, forming isopropyl oleate and concomitantly forming metal–oxo clusters. The hydrolysis of Ti(O-*i*-Pr)$_4$ and subsequent formation of metal–oxo clusters can be attributed to fugitive H$_2$O, which further catalyzes the sol–gel process.

Incorporation of $\mathbf{Ti_6O_4(O\text{-}\mathit{i}\text{-}Pr)_{16-n}(O_2C(CH_2)_7(CH_2CH{=}CH)_3CH_3)_n}$ in Linseed Oil Coatings. Table 2 shows the mechanical properties of linseed oil based coatings as a function of Ti(O-*i*-Pr)$_4$ or metal carboxylate $Ti_6O_4(O\text{-}i\text{-}Pr)_{16-n}(O_2C(CH_2)_7\ (CH_2CH{=}CH)_3CH_3)_n$ content. A systematic increase in pencil hardness was observed as the concentration of Ti(O-*i*-Pr)$_4$ was increased from 0 to 10 wt %. The maximum pencil hardness value of 6H was obtained when a 10 wt % Ti(O-*i*-Pr)$_4$ loading was used. However, as Ti(O-*i*-Pr)$_4$ content increased, the impact resistance of these coatings decreased. Both flexibility and adhesion remained relatively unchanged as Ti(O-*i*-Pr)$_4$ increased from 5 to 10 wt %. The incorporation of the metal carboxylate in linseed oil was chosen at 12.7 wt % because of its equivalency in Ti atom concentration to the linseed oil based ceramer coatings containing 5 wt % Ti(O-*i*-Pr)$_4$. Pencil hardness and adhesion values were found to be the same for both formulations. However, impact resistance for the linseed oil based ceramer coating containing 12.7 wt % metal carboxylate substantially increased from 20 to 28 in.·lb. In addition, the flexibility for the ceramer coating containing the metal carboxylate outperformed ceramer coatings containing 5 and 10 wt % Ti(O-*i*-Pr)$_4$ loadings. The purpose of comparing the ceramer coating containing the metal carboxylate to the coatings containing Ti(O-*i*-Pr)$_4$ was to ascertain whether metal carboxylate formation occurs during the curing process. The resulting similarities in mechanical properties tend to agree with this hypothesis. However, the enhancement in mechanical properties may be attributed to the controlled formation of metal–oxo clusters. The presence of a carboxylate ligand can slow the condensation reactions of the sol–gel process.[12]

Table 3 shows the tensile strength, strain at break, and tensile modulus of linseed oil based coatings as a function of Ti(O-*i*-Pr)$_4$ and metal carboxylate content. As an overall trend, the tensile strength increased with increasing Ti(O-*i*-Pr)$_4$ concentration. The highest tensile strength of 5.0 MPa was observed at a 10 wt % Ti(O-*i*-Pr)$_4$ loading. Conversely, the strain at break decreased as Ti(O-*i*-Pr)$_4$ concentration increased. The tensile modulus followed a similar trend exhibited by the tensile strength in which a systematic increase was observed as a function of Ti(O-*i*-Pr)$_4$ concentration. Similar to the tensile strength, the highest tensile modulus (33 MPa) was attained with a 10 wt % Ti(O-*i*-Pr)$_4$ loading. Although the metal content is equivalent in both 5 wt % Ti(O-*i*-Pr)$_4$ and 12.7 wt % metal carboxylate, the tensile properties are substantially different from one another. The incorporation of the metal carboxylate in linseed oil not only enhanced the tensile modulus relative to the ceramer coating containing 5 wt % Ti(O-*i*-Pr)$_4$, but also provided a higher tensile modulus than the ceramer coating containing 10 wt % Ti(O-*i*-Pr)$_{4.}$

The glass transition temperature (T_g) and cross-link density[36-39] obtained from DMTA are shown in Table 3. The T_g for the ceramers containing Ti(O-*i*-Pr)$_4$ showed a dramatic increase at 10 wt % (57 °C) compared to the parent linseed oil coating (13 °C). The highest cross-link density was found at 10 wt % Ti(O-*i*-Pr)$_4$ (1.58×10^{-3} mol/cm^3) and decreased at lower Ti(O-*i*-Pr)$_4$ concentrations. The ceramer film containing 12.7 wt % metal carboxylate had a T_g of 48 °C and a cross-link density of 1.41×10^{-3} mol/cm^3. The parent linseed oil film was found to have a cross-link density of 9.92×10^{-5} mol/cm^3 under the same curing conditions.

The incorporation of sol–gel precursors in linseed oil has a profound effect on the cross-link density. In a previous publication, it was shown that the inorganic domains in these films are relatively small and discon-

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(36) Hill, L. W. *Mechanical Properties of Coatings*; Federation of Societies for Coatings Technology: Philadelphia, 1987.

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(38) Hill, L. W. *Prog. Org. Coat.* **1997**, *31*, 235.

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tinuous throughout the film.[19] It was proposed that the incorporation of sol−gel precursors in linseed oil increased the T_g and cross-link density by forming cross-linking sites through covalent interaction between the inorganic and organic phases. However, an alternative explanation for such an increase in the cross-link density, or more accurately the elastic modulus, may also be due to reinforcement by entanglement of the organic phase around the inorganic domains present. This would then add rigidity throughout the film and, therefore, increase the elastic modulus. To address this issue, 5 wt % TiO_2 was incorporated into linseed oil. The resulting films were tested and compared to the ceramer films. As shown in Table 3, the T_g remained relatively unchanged with respect to the parent linseed oil film. However, the calculated cross-link density increased to 1.56×10^{-4} mol/cm^3. Although this does signify that the pigment particles increase the storage modulus by means of rigid bodies throughout the organic matrix, the calculated cross-link density value is still extremely low relative to the ceramer films.

A drawback to this comparison is the particle size ratio. Pigments used in coating formulations are used for light absorbance and scattering and thus are generally on the order of 0.1−10 μm in size.[40] As stated previously, the SAXS data indicated that the inorganic domains are much smaller and on the order of angstroms.[19] As a result, the surface area of the pigments is much smaller than the inorganic domains in ceramer coatings, and therefore a direct comparison is difficult. However, the pigmentation of the films results in an increase in elastic modulus and not T_g. The drying oil based ceramer systems typically afford a concomitant increase in both T_g and cross-link density. At this point, we speculate that both covalent and/or ionomeric interactions between the inorganic and organic phases as well as entanglement of the inorganic domains play an important role in the final cross-link density and T_g.

A theoretical model depicting the interaction between the inorganic and organic phases is shown in Figure 7. The primary interaction proposed is the metal carboxylate formation during the curing stages of these inorganic/organic coatings. The metal−oxo carboxylates have the capability of forming covalent bonds between the inorganic and organic phases to form a homogeneous network. The proposed interactions between the inorganic and organic phases occur in situ cross-linking between the triglycerides and the unsaturated metal−oxo carboxylates. The incorporation of a titanium carboxylate containing linolenic acid in linseed oil coatings had similar mechanical and physical properties relative to linseed oil based ceramer coatings containing Ti(O-*i*-Pr)$_4$. Therefore, a cross-linking mechanism between the inorganic and organic phases is proposed (see Figure 7).

Conclusions

Metal−oxo carboxylates were prepared by reacting Ti(O-*i*-Pr)$_4$ with linolenic acid and oleic acid. Using FT-IR spectroscopy and ^{13}C NMR spectroscopy, it was determined that the carboxylate groups bond to the metal−oxo clusters via a bidentate chelating and bridging mode. The incorporation of a metal carboxylate containing unsaturated fatty acid “soaps” into linseed oil coatings increased the cross-link density, tensile properties, and hardness. It was concluded that the unsaturated fatty acid metal soaps covalently bonded with the organic phase via an autoxidative cross-linking mechanism resulting in the enhancement of the mechanical and physical properties. It is also proposed that the interaction of the metal carboxylates with the organic phase can be used to partially model the interactions of metal−oxo clusters (inorganic phase) with the organic phase in drying oil based ceramer coatings. Finally, it was concluded that the presence of Ti(O-*i*-Pr)$_4$ within the drying oil matrix catalyzes the transesterification of the triglycerides during the curing process, and the resultant oligomeric fatty acids and diglycerides form chemical bonds with the inorganic phase contributing to the overall cross-link density of the drying oil based ceramer coatings.

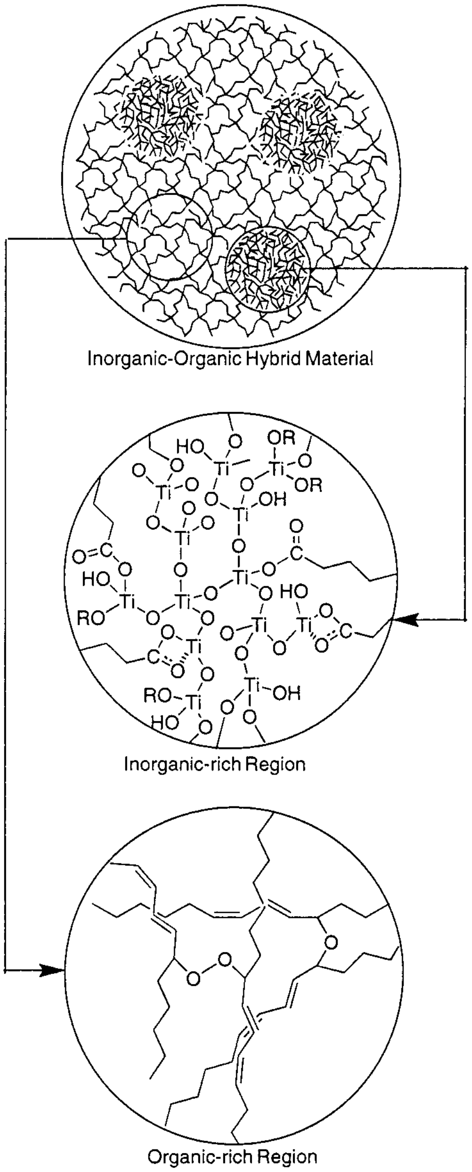

Figure 7. Theoretical structural model depicting the interaction between the inorganic and organic phases.

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