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Polymer modified mixed metal alkoxide-metal acetyl acetonate sol-gel materials

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SUMMARY:

Metal acetyl acetonates of aluminum, zirconium and zinc have been successfully incorporated into poly(tetramethylene oxide) modified TEOS based materials using sol-gel chemistry. Incorporation of these metal acetyl acetonates required modification of the reaction scheme developed earlier to incorporate titanium(IV) isopropoxide. Gelation rates and the physical properties of the subsequent gelled materials varied as a function of the metal acetyl acetonate used.

INTRODUCTION:

Within the past five years, the sol-gel process common to the ceramic industry has been used to create novel hybrid materials often called "CERAMERS" (1-10). In general terms, these new monolithic materials are matrices comprised of inorganic oxides covalently linked to polymer molecules. The reaction scheme employed to make such polymer containing monolithic sol-gel materials involves reacting ethyl silicate functionalized polymers with monomeric silicate esters. This scheme allows two fundamentally different types of modifications: modification of the polymeric component or modification of the oxide matrix. The effects of modifying the polymeric component have been detailed elsewhere (1-7); recent work has focussed on the effects of modifying the oxide matrix.

This paper will introduce some recent achievements in oxide modified hybrid sol-gel materials. Specifically, some of the effects on physical properties caused by changing the chemical composition of the oxide matrix will be presented. A previously studied Poly(tetramethylene oxide)--or PTMO--modified sol-gel will be used throughout as a reference material for the new compositions introduced. It should be understood, other more thermally stable backbone systems could replace the PTMO component. The polymer modifying component--PTMO--will be kept at a constant mole% loading for all materials presented to simplify comparison; titania, alumina, zirconia or zinc will be alternately introduced into the silicate matrix using two different precursors and reaction schemes.

One of the fundamental goals at the outset of this work was to incorporate "metals" other than silicon into a hybrid sol-gel "CERAMER" system. This goal has been accomplished for titanium using titanium(IV) isopropoxide ($Ti(i\text{-}pr)_4$) as the TiO_2 precursor. It was found that titanium could be incorporated through late addition of the $Ti(i\text{-}pr)_4$ to an alcoholic mixture of partially reacted TEOS and silicon ethoxide capped oligomers (8, 9, 11).

The successes achieved in titanium incorporation using titanium isopropoxide led to the exploration of other metal alkoxides as sol-gel precursors. In particular, aluminum tri-secondarybutoxide ($Al(s\text{-}bu)_3$) was attempted using modified sol-gel reaction schemes similar to that developed

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*Present address: The General Electric Company, Mt. Vernon Technology Department, Highway 69 South, Mt. Vernon, IN 47620, USA for titanium alkoxide incorporation (8). However, efforts at Al(s-bu)$_3$ incorporation were, at best, minimally successful. The Al(s-bu)$_3$ was prone to react rapidly on exposure to moisture and quickly formed a white Al_2O_3 based powder. These results prompted the investigation of alternative organometallic compounds as sol-gel precursors to mixed metal oxide materials. Metal acetyl acetonates because of their greater hydrolytic stability were chosen as prime candidates to replace the unusable alkoxides.

MATERIALS:

High purity (99%) tetraethylorthosilicate (TEOS) was purchased from two sources, Fluka AG and Petrarch Systems Inc.. Reagent grade titanium(IV) isopropoxide, 98+% aluminum tri-isopropoxide, 97% aluminum tri-secondary butoxide, aluminum acetyl acetonate, zinc acetyl acetonate hydrate and zirconium(IV) acetyl acetonate were obtained from the Aldrich Chemical Company. A poly(tetramethylene oxide) polymer containing (on the average) five triethoxysilane functional groups--one at each chain end and three in-between--was used as the modifying component in the hybrid sol-gels studied. This PTMO polymer--PTMO(5)--was synthesized and generously supplied by Dr. James G. Carlson of the 3M Company. Further details of these functionalized PTMO oligomers have been presented elsewhere (10).

EXPERIMENTAL:

Stock solutions of the metal acetyl acetonates studied were prepared by placing 10 gms of acetonate in 100 ml of dry ethanol then adding 0.1N HCl dropwise under stirring until a clear (transparent) solution was obtained. Such solutions could be stored for several weeks without signs of cloudiness or change in color (8).

Hybrid sol-gel materials were prepared using stock metal acetyl acetonate solutions along with TEOS and a polymer--PTMO(5)--containing five triethoxysilane functional groups. The generalized procedure was to dilute the PTMO(5) polymer to 34 wt% solids with THF then add the appropriate amount of TEOS and dilute further to 22 wt% solids with IPA; after addition of the metal acetate solution the mixture was refluxed 1/2 hr (except for the Zr materials which were not refluxed) then cast into TEFLON® coated covered Petri dishes. Once gelled, covers were removed and materials were allowed to dry under ambient conditions (exposed to room atmosphere) prior to physical property testing. Films prepared in this manner ranged from 0.1 to 0.8 mm in thickness.

NOMENCLATURE:

The nomenclature used to identify the oxide modified materials to be presented is based on the following reference material: 15Ti-53PTMO(5); here the numeric prefix before each component indicates the weight percent of that component charged into the reaction mixture. For example, the reference material, 15Ti-53PTMO(5), was made using 15 wt% titanium(IV) isopropoxide and 53 wt% of PTMO(5).

The actual amount of each component charged to make the metal acetyl acetonate hybrid materials was calculated to produce final gelled materials with a molar ratio of components of: 21.5 moles silica (SiO_2) to 5.7 moles metal oxide (MO_n) to 1.0 moles multifunctional PTMO(5) polymer. This is the final gel composition theoretically obtained by the reference 15Ti-53PTMO(5) formulation; for this reason, the prefix values "15" and "53" are kept constant in the nomenclature for the mixed metal oxide "CERAMER" gels presented here. Table 1 gives the actual weight percent of each component used to produce mixed metal "CERAMERS" comparable in oxide and polymer content to the 15Ti-53PTMO(5) reference.

TABLE 1

Sample	Quantity	Metal Oxide	Silicate	PTMO(5)
15Ti-53PTMO(5)	initial wt%	15.0	31.6	53.4
	final wt%	6.5	17.8*	75.7
	molar ratio	5.7	21.4*	1.0
15Al-53PTMO(5)	initial wt%	16.8	31.0	52.2
	final wt%	7.7	16.9*	75.4
	molar ratio	5.7	21.5*	1.0
15Zn-53PTMO(5)	initial wt%	14.1	32.0	53.9
	final wt%	6.1	17.2*	76.7
	molar ratio	5.7	21.5*	1.0
15Zr-53PTMO(5)	initial wt%	23.3	28.6	48.1
	final wt%	9.1	16.5*	74.3
	molar ratio	5.7	21.5*	1.0

*includes contribution from triethoxysilane groups on PTMO(5) polymer

RESULTS & DISCUSSION:

The use of acteonates over alkoxides resulted in several advantages. Aluminum acetyl acetonate (Al(acac)$_3$) once in solution, in contrast to the butoxide (Al(s-bu)$_3$), provided a stable precursor that could be readily incorporated into hybrid sol-gel systems. The same was found to be true for the zirconium(IV) and zinc acetyl acetonates (Zr(acac)$_4$ & Zn(acac)$_2$). Furthermore, the acetyl acetonate solutions did not require a chemically controlled condensation--or "CCC" procedure--such as that used by Schmidt (12) to successfully form monolithic materials; the reactivities of the various components were such as to allow gelation to take place without limiting the in-situ water content. An added advantage of using acetonate precursors was the elimination of a water/catalyst addition step in the reaction procedure; the inherent acid and water in the acetonate solution is sufficient to initiate and sustain the sol-gel process.

Once a suitable reaction procedure was established, gelled films were made using Al, Zr and Zn acetyl acetonates. The compositions outlined in Table 1 were prepared for evaluation and comparison to the reference hybrid material made using titanium(IV) isopropoxide. Mechanical properties were measured to determine whether or not these materials could be successfully incorporated into useful polymer modified hybrid gel. These gels were also compared to observe any differences brought about by changing the oxide matrix. The three acetyl acetonate compositions were observed to gel at differing rates: Zn(acac)$_2$ containing reactions were the slowest taking several days to form a self supporting gel, Zr(acac)$_4$ containing systems were the fastest gelling within 1/2 hour of casting while reactions containing Al(acac)$_3$ were intermediate in rate requiring $\simeq$ 6 hour to gel.

An apparent consequence of the gelation rate was the appearance and shrinkage of the gels. The Zr(acac)$_4$ compositions reacted very quickly even without refluxing (i.e. no heating); the initial gel formed trapped large quantities of the solvent from the reaction mixture. The result was a thick "wet" gel that was prone to severe shrinkage on subsequent air drying and aging (though the gels remained monolithic throughout). The linear shrinkage observed for the three different metal acetonate gels was:

TABLE 2

Sample	Days @ 22°C	Ultimate Elong (%)	Ultimate Str (MPa)	Young's Mod (MPa)
15Ti-53PTMO(5)	7	180	10	12
15Al-53PTMO(5)	9	130	16	29
15Zn-53PTMO(5)	9	80	20	36
15Zr-53PTMO(5)	9	80	12	83

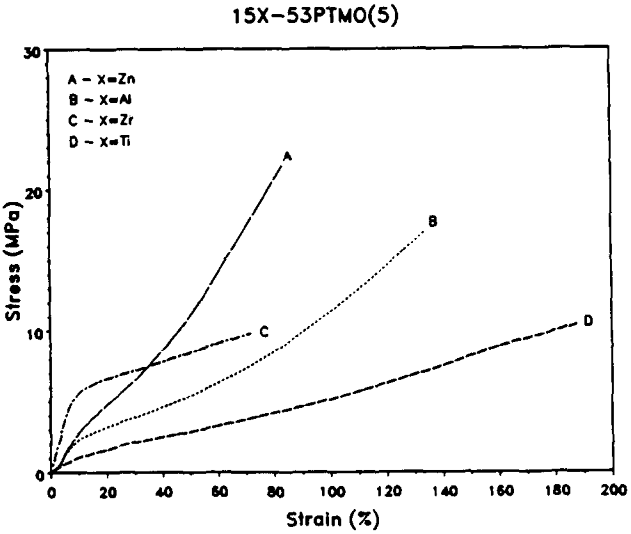

FIGURE 1 Tensile Stress-Strain Curves

46% for the 15Zr-53PTMO(5) composition, 24% for the 15Al-53PTMO(5) composition and 9% for the 15 Zn-53PTMO(5) composition.

Figure 1 contains the stress-strain curves for the three different metal acetyl acetonate gels aged 9 days at ≈22°C and the corresponding 7 day old 15Ti-53PTMO(5) gel for comparison. The data obtained from the tensile strain-to-break test are listed in Table 2. The differences qualitatively observed for gelation rates of the different metal acetyl acetonates are also reflected in the observed tensile curves in Fig. 1. The two "slow gelling" compositions, 15 Zn-53PTMO(5) (curve A) and 15Al-53PTMO(5) (curve B), exhibit "elastomeric" stress-strain curves typical of lightly cross-linked materials while the "fast gelling" composition, 15Zr-53PTMO(5) (curve C), a steep rising curve with elastic and plastic deformation characteristics typical of a more highly crosslinked network material.

The tensile results observed for the different acetonate based gels

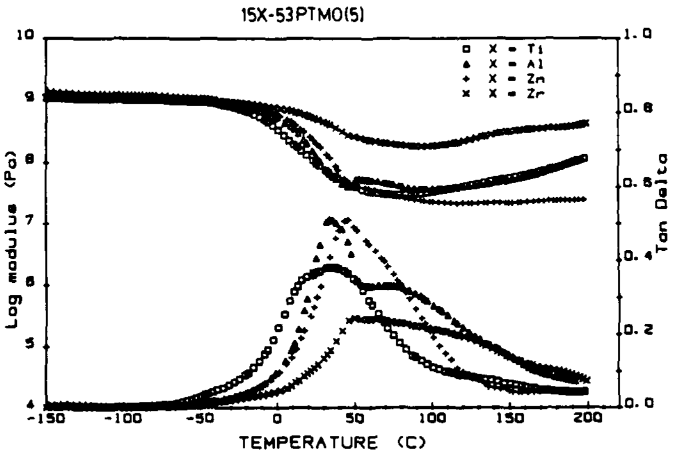

FIGURE 2 Dynamic Mechanical Spectra

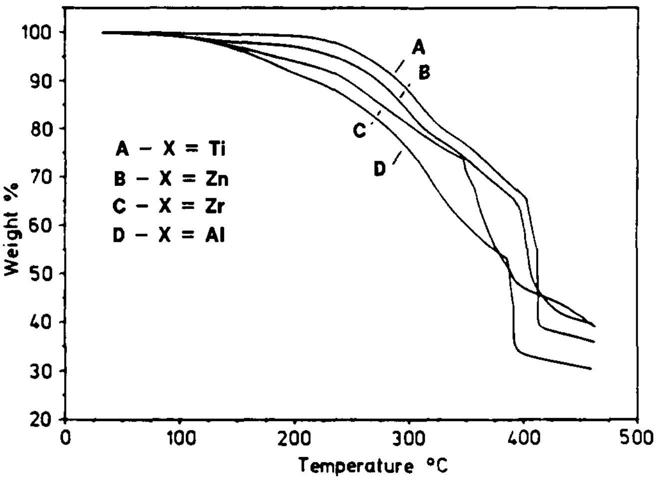
15X-53PTMO(5)

FIGURE 3 Thermogravimetric Analysis (heated @ 20°C/min in air)

are corroborated by the dynamic mechanical spectra given in Figure 2 for the same materials aged 9 days at ≈22°C. The tan delta curves in Fig. 2 clearly show the 15 Zr-53PTMO(5) gel to be substantially vitrified at 20°C whereas the other three materials, 15Ti-53PTMO(5), 15Al-53PTMO(5) and 15Zn-53PTMO(5), are all well within their glass transition region at this time and are not fully vitrified. Additionally, the transition observed in the storage modulus is much smaller for the 15Zr-53PTMO(5) gel than for any of the other gels (also true for the observed tan delta transition in Fig. 2); this is indirect evidence that the degree of conversion of the sol-gel process (hence the crosslink density) is higher in the materials made with Zr(acac)$_4$ than those made with the other metal acetonates as well as those made with the titanium(IV) isopropoxide. An extensive study of chemical aging and vitrification effects on hybrid sol-gels has been undertaken and is discussed elsewhere (8).

Thermogravimetric analyses (TGA) were performed on the three metal acetyl acetonate compounds as well as the reference silicate ester to determine, primarily, the volatile content in air dried gels. These experiments were run according to a given temperature ramp (20°C/min) on a DuPont TGA. The curves obtained are given in Figure 3. The most notable result from these studies is that the 15Ti-53PTMO(5) gel does not show any appreciable weight loss until ≈200°C. The other gels, 15Zn-53PTMO(5), 15Zr-53PTMO(5) and 15Al-53PTMO(5) all show considerable weight loss beginning at temperatures as low as 75°C. This weight loss, particularly in the temperature region from 0°C to 225°C, is most likely due to solvent and/or bound organic moieties being removed and could be verified by GC-Mass Spectroscopy analysis. At temperatures beyond 200°C the PTMO component of the hybrid materials is undoubtedly being degraded; it is, therefore, not surprising that the TGA traces in the 200°C to 400°C region resemble each other. The exception to this general behavior is the 15Zr-53PTMO(5) gel (trace c) which displays a sharp discontinuity at 350°C rather than at 390°C as is observed for the other gels.

The TGA traces given in Fig. 3 clearly demonstrate that the acetyl acetonate gels all contain significantly more volatilizable components than do gels made with Ti(i-pr)$_4$. The acetyl acetonate gels lose from 3 to 10 wt% volatiles at temperatures below 200°C; Al(acac)$_3$ gels lose the highest percentage while Zn(acac)$_2$ gels lose the lowest percentage volatiles.

Unfortunately, without detailed knowledge of the chemical processes occurring at elevated temperatures, only this qualitative interpretation of the TGA traces is possible at this time.

CONCLUSIONS:

Soluble metal acetyl acetonate precursors can be utilized in making hybrid oxide materials via the sol-gel route though a modified reaction scheme is required. The zirconium acetyl acetonate accelerates the rate of gelation as compared to aluminum acetyl acetonate or zinc acetyl acetonate hydrate. What is not clear is whether the observed acceleration of gel formation in zirconium containing reactions is a result of higher functionality -- thereby requiring a lower degree of conversion for gel formation -- or a result of increased condensation rates due to catalytic activity or a combination of the two.

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REFERENCES:

1. G.L.Wilkes, B.Orler, H.Huang, **Polym. Prep.**, 26(2), 300 (1985)
2. H.Huang, B.Orler, G.L.Wilkes, **Polym. Bull.**, 14(6), 557 (1985)
3. H.Huang, B.Orler, G.L.Wilkes, **Macromolecules**, 20(6), 1322 (1987)
4. H.Huang, R.H.Glaser, G.L.Wilkes, **Polym. Prep.**, 28(1), 434 (1987)
5. J.L.Noell, **M.S. Thesis**, Virginia Polytechnic Institute and State University, 1987
6. H.H.Huang, **Ph.D. Dissertation**, Virginia Polytechnic Institute and State University, 1988
7. H.H.Huang, R.H.Glaser, G.L.Wilkes, **ACS Symposium Series**, 360, 354 (1988)
8. R.H.Glaser, **Ph.D. Dissertation**, Virginia Polytechnic Institute and State University, 1988
9. R.H.Glaser, G.L.Wilkes, **Polym. Bull.**, 19, 51 (1988)
10. H.H.Huang, G.L.Wilkes, J.G.Carlson, **Polymer**, in press
11. R.H.Glaser, G.L.Wilkes, manuscript in preparation
12. H.Schmidt, **Mat. Res. Soc. Symp. Proc.**, 32, 327 (1984)

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