THERMAL WEIGHT LOSS OF SILICA-POLY(VINYL ACETATE) (PVAc) SOL-GEL COMPOSITES

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Abstract

Thermogravimetric analyses of sol–gel derived silica and silica-poly(vinyl acetate) (PVAc) materials show that the loss in weight between 35 and 900°C can be attributed to three distinct reactions. Samples were prepared by dissolving the reactants tetraethyl orthosilicate (TEOS), poly(vinyl acetate) (PVAc), and water in mixtures of ethanol and formamide. The lowest temperature weight loss is due to the decomposition/removal of the solvents, while the intermediate weight loss corresponds to decomposition of the PVAc. The highest temperature weight loss is related to the dehydroxylation of the silica surface. The relative amounts of ethanol and formamide have a considerable effect on processing time, drying behavior, and the resulting thermal behavior of the gels.
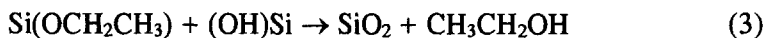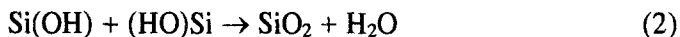
Introduction

Sol–gel processed oxides have been prepared by hydrolyzing alkoxides for more than 20 years. One attribute of the sol–gel process is that the synthesis is carried out largely at room temperature. This attribute has brought about a surge of interest in sol–gel preparation of inorganic–organic hybrid materials [1–6]. Low temperature sol–gel processing permits the incorporation of an organic polymer phase into gels, creating hybrid materials not available with typical high temperature ceramic processing. When mixed on the nanometer level, the composite materials exhibit unusual physical and mechanical properties, such as crack blunting in an otherwise brittle material [7] or high transparency [8]. Transparency is a prerequisite for optical hosts, where organic lasing molecules or nonlinear optic (NLO) molecules are encapsulated in the hybrid inorganic–organic gels [1]. The hybrid host has the advantages of rigidity and ease of polishing, compared to the organic host alone.

Organic materials may be incorporated into inorganic matrices in several ways, leading to hydrogen bonding [4], covalent bonding, usually via –Si–C– linkage [5], or simple mechanical blending of the inorganic and organic materials [9]. Poly(vinyl acetate) (PVAc),

$$- (CH_2-CH)_n -$$
$$|$$
$$O$$
$$|$$
$$C=O$$
$$|$$
$$CH_3$$
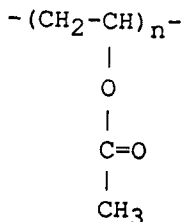
the organic polymer chosen for this study, has been incorporated into silica gels producing optically transparent composite materials [10]. The high degree of mixing suggests strong interactions through hydrogen bonding between the silanol groups (Si–OH) of the hydrolyzed alkoxide and the carbonyl groups (C=O) of the PVAc. Ordinarily, PVAc is known as a thermoplastic that is used in a variety of coating and adhesive applications [11]. Reasons for the interest in mixing PVAc with silica include excellent optical transparency, a refractive index close to that of silica, and its solubility in polymer form in ethanol–water mixtures.

Alkoxide sol–gel processing is composed of a series of hydrolysis steps of the alkoxide, in conjunction with condensation steps. The condensation steps may consist of a water forming condensation reaction or an alcohol forming condensation reaction. The hydrolysis and condensation reactions for tetraethyl orthosilicate (TEOS) are given as Eqs 1–3.

$$Si(OCH_2CH_3)_4 + xH_2O \rightarrow Si(OH)_x + CH_3CH_2OH \qquad (1)$$

$$Si(OH) + (HO)Si \rightarrow SiO_2 + H_2O \qquad (2)$$

$$Si(OCH_2CH_3) + (OH)Si \rightarrow SiO_2 + CH_3CH_2OH \qquad (3)$$

One should keep in mind that SiO_2 polymerizes in a 3-dimensional network of bridging oxygens (Si–O–Si) when it is represented by the stoichiometric product SiO_2 in reactions (2) and (3).

Since silicon alkoxides are not miscible in water, a typical sol–gel formulation contains alcohol as a solvent, alkoxide, water, and acid catalyst. Acid catalysis, in the presence of excess water favours the water producing condensation reaction [12, 13], resulting in a significant concentration of water in the gel product, i.e. hydroxylated surface of the dried gel. The low temperature

synthesis allows a soluble polymer, as in the case of PVAc, to be added to the sol–gel formulation, followed by polymerization of the inorganic network around the polymer domains [10]. At this point, the microstructure consists of a SiO_2 skeletal network, polymer domains, and porosity filled with solvent. After drying, a three-phase material of SiO_2, polymer, and open porosity results.

Two problems in producing porous monolithic (i.e., crackfree) gels are fracture during drying, which is caused by high capillary stresses, and long processing times. The addition of an organic phase such as PVAc which is more compliant may help reduce stress concentrations on the oxide network during drying. Alternatively, there are additives for reducing processing times and preventing fracture [14, 15]. For example, formamide, $HCONH_2$, is known to decrease the hydrolysis rate and increase the condensation rate [16], greatly reducing the time to gel [14, 15, 17]. The resulting microstructure has a larger mean pore size than it would without formamide. The fraction of very small pores is reduced, which in turn reduces capillary stresses making it easier to dry monolithic silica gels. Removal of the formamide additive without cracking is sometimes difficult when evolved gases expand at high temperatures [14, 18]. For inorganic–organic hybrids that are designed for low temperature use, such high temperature exposure is avoided.

In this work, thermogravimetry (TG) and thermogravimetry/Fourier transform infrared spectroscopy (TG/FTIR) were used to characterize SiO_2–PVAc composite materials. Analysis of the evolved gases (FTIR) during heating proved beneficial in determining decomposition pathways, additive content, organic content, and thermal degradation products.

Experimental

In this systematic study of the role of formamide, a standard composition, with and without PVAc, was used for all the gels. The TEOS:H_2O:HCl molar ratio was 1:8:0.097. The solvent medium (80 ml) was varied from pure ethanol to 50/50 vol.% ethanol and formamide. Typically 60 ml of TEOS, 38.6 ml of distilled water, and 2 ml of concentrated HCl were mixed with the ethanol fraction of the solvent for 3 h. The ethanol was dehydrated, 200 proof, from Pharmco Products Inc. The TEOS was obtained from Dynasil A, Dynamit-Nobel and the HCl was reagent grade from Fisher Scientific. After mixing for three hours, PVAc (M.W. 83,000 from Aldrich) was added (15% by weight based on SiO_2 content of the TEOS) to the appropriate compositions and mixed for 24 h. The compositions without PVAc were also mixed for 24 h. Finally, formamide was added to the solution followed by ten minutes of mixing. The samples were then poured into polypropylene test tubes that were capped to prevent solvent evaporation at room temperature ($T_R \approx 22°C$). The time from sealing

the test tubes to the time when the sample showed no flow when tilting the test tube was defined as the gelation time (t_{gel}). All of the composites were prepared using the same procedures.

After gelation was observed, the gels were aged at T_R for one week, opened, and dried at 40°C until constant mass was achieved. The skeletal density was measured with helium pycnometry (Micromeritic Accupyc 1330) with 10 purges and the run precision software (0.01% volume tolerance level). Thermogravimetry (TG) was performed on a Perkin-Elmer TGA 7 system. Infrared spectra of the evolved gases during the TG heating, were obtained with the Perkin-Elmer TG/FTIR system consisting of a TGA 7 analyzer coupled to an external optical bench of a Perkin-Elmer 1700-X FTIR interface.

The porous samples were analyzed in bulk form, directly from the drying oven. A few samples were ground into a fine powder and analyzed. Only slight differences in the weight loss were found between the bulk samples and the powdered samples. Therefore, bulk samples were used in general. The experimental conditions were the same for all samples, with a temperature range of 35 to 900°C at a heating rate of 10 deg·min^{-1} in air. The sample mass was between 24–27 mg. The balance purge was set at 40 cm^3/min and the sample purge at 20 cm^3/min.

For the TG/FTIR analysis, the sample mass was 25–30 mg, the heating rate was 40 deg·min^{-1}, and the purge gas flow was 40 cm^3/min of air.

The silica content of the composite material was calculated from the mass of the sample at 900°C. In Table 1, listing compositions and physical properties, samples are designated by $S(P)Y$, where Y is the vol.% of formamide as the solvent. S represents silica and P indicates the presence of PVAc; e.g. SP12.5 refers to a silica gel synthesized with 12.5 vol.% formamide plus 15 weight % PVAc.

Results and discussion

Table 1 summarizes the physical properties of the compositions investigated. The results for t_{gel} clearly show the reduction in gelation time for the compositions containing formamide. The substitution of only 12.5 vol.% of formamide for ethanol reduced the gel time from 40 days to approximately 1–2 days. Increasing the amount of formamide from 12.5 to 50 vol.% cut the gel time in half for compositions with and without PVAc. Not only did the gel time decrease, reducing processing time, the resulting gels dried as crackfree monoliths. The compositions without formamide also survived the drying stage in cylindrical form, but the processing time from mixing the precursors to a dried gel was over two months.

Table 1 also lists the skeletal densities of the gels with and without PVAc. The results do not follow a simple weighted average. Alkoxide derived silica has

Table 1 Physical properties of silica gels and silica/PVAc gels

Sample	Solvent/Vol%		t_{gel}	Skeletal density/
	ethanol	formamide		$g \cdot cm^{-3}$
S0	100.0	0	40 days	~1.8 [8]
S12.5	87.5	12.5	50.5 h	1.653
S25	75.0	25.0	35.9 h	1.460
S37.5	62.5	37.5	31.3 h	1.381
S50	50.0	50.0	27.6 h	1.328
SP0	100.0	0	40 days	N.D.
SP12.5	87.5	12.5	68.0 h	1.601
SP25	75.0	25.0	51.9 h	1.442
SP37.5	62.5	37.5	42.7 h	1.364
SP50	50.0	50.0	38.0 h	1.312
S2P12.5	87.5	12.5	51.6 h	N.D.

a density of slightly greater than 2.0 g/cm^3 and PVAc is less than 1.2 g/cm^3. There is a continuous decrease in density with incremental additions of 12.5 vol.% formamide. The lower skeletal density values suggest interactions, such as hydrogen bonding, between the phases. Such interactions as hydrogen bonding have been suggested to exist between silanol groups on the silica gel surface and the carbonyl groups of formamide [18, 19] and PVAc [4].

After the drying step, all of the compositions produced porous, monolithic, and optically transparent gels. Compositions containing PVAc appeared increasingly translucent as the percentage of formamide was increased. Since formamide can increase the mean pore size of silica gels [14, 15,], the translucency observed arises from the increasing dimension of either the polymer domains or the porosity, which contribute to scattering.

Figure 1 illustrates the effect of formamide on the linear shrinkage of the gels. Linear shrinkage was calculated by measuring the length of the gel initially and final length after drying. Increasing the amount of formamide decreases the % linear shrinkage almost linearly. Compositions without formamide decreased in length by almost 60%, while a composition with a substitution of 50 vol.% formamide only decreased by approximately 35%. The SiO$_2$–PVAc composite samples exhibited a linear shrinkage about 2% lower for all levels of formamide than the pure SiO$_2$ gels. Doubling the amount of PVAc for the 12.5 vol.% formamide level reduced the linear shrinkage an additional 2%.
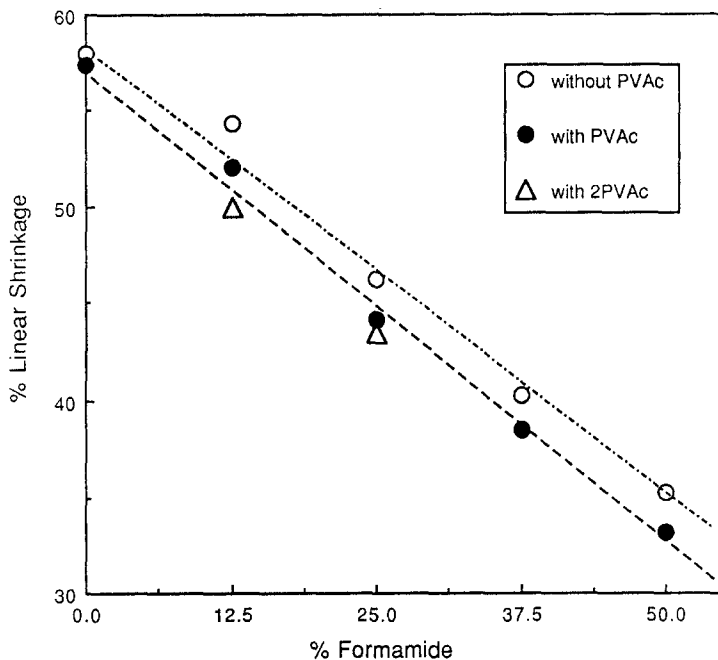
Fig. 1 Linear shrinkage *vs.* formamide content for silica and silica/PVAc gels

Figure 2 shows a typical weight loss curve for a formamide containing composition with (dashed curve) and without PVAc (solid curve). In all samples without PVAc a two stage weight loss is observed at low temperature, while a more gradual weight loss occurs at higher temperatures. The lowest temperature weight loss is attributed to solvent removal, and the slight weight loss between approximately 225 and 350°C is due to decomposition and oxidation of organic groups [20, 21].

The magnitude of the weight loss due to decomposition and oxidation stage is directly related to the concentration of unreacted alkyl groups in the gel. Thus, a fully hydrolyzed alkoxide does not exhibit such a weight loss. In most alkoxide derived gels, there will be some unreacted alkyl groups. The extent of the hydrolysis reaction is influenced by experimental conditions such as water to alkoxide ratio (R) [22] and *pH* of the sol [23]. It is well known that high R values $(R \geq 4)$ and acidic conditions promote fast hydrolysis. For the experimental conditions in this study, $R = 8$ and sol $pH \approx 1$, hydrolysis is expected to be complete, explaining the minimal weight loss due to organic oxidation. The gradual weight loss at higher temperatures is due to dehydroxylation of the silica surface [24, 25].

Increasing the amount of formamide substituted for ethanol results in an increase in total weight loss (Table 2). When formamide was first used as a sub-
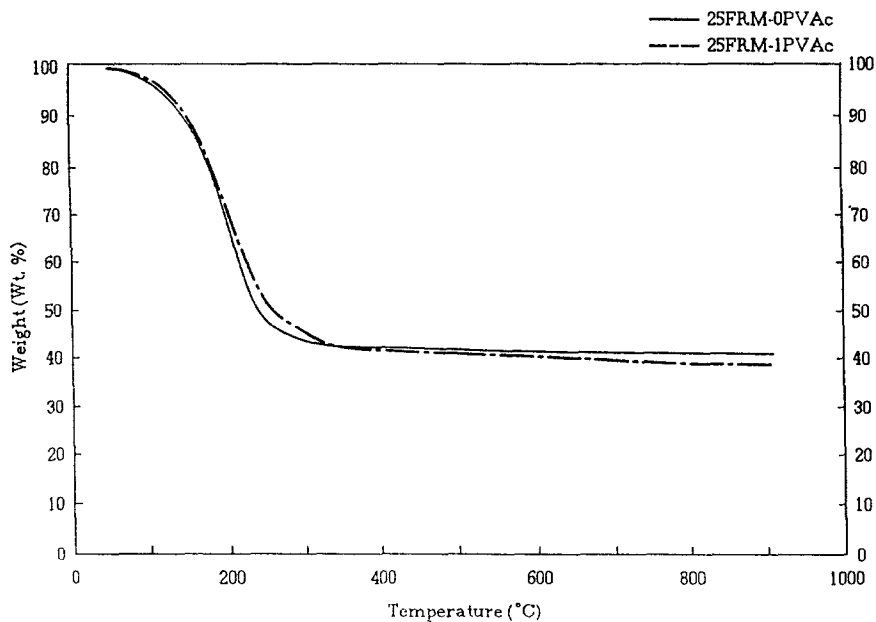
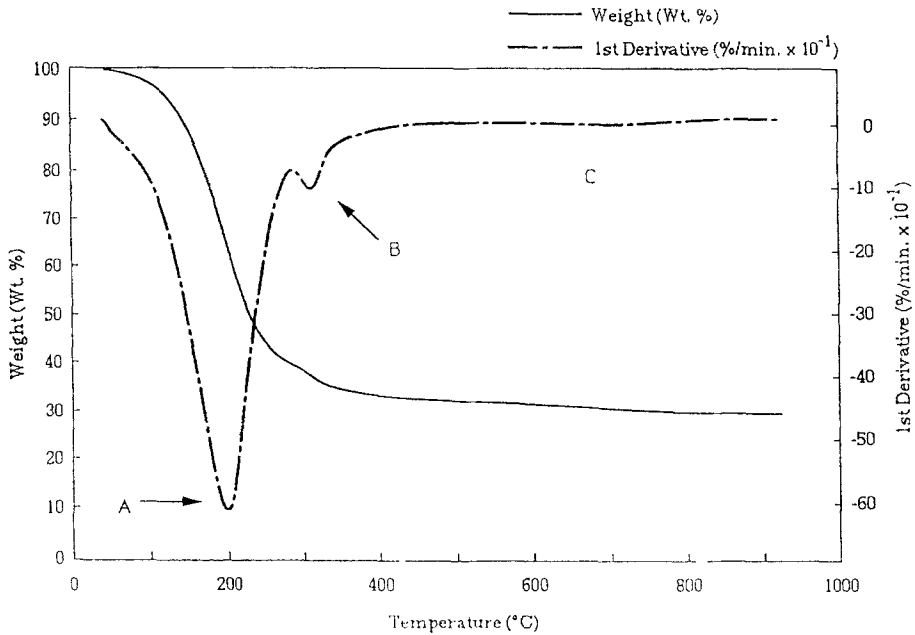Fig. 2 Thermogravimetric weight loss for pure silica gel and silica gel with PVAc, both with 25% formamide

Table 2 Summary of thermal analysis results

Sample	Residual weight/ % [1]	Δw [2]	% PVAc in composite [3]	
			measured	calculated
S0	81.0			
S12.5	59.0			
S25	42.0			
S37.5	34.0			
S50	26.0			
SP0	72.0	9.0	11.1	15
SP12.5	53.0	6.0	10.2	15
SP25	37.5	4.5	10.7	15
SP37.5	30.0	4.0	11.7	15
SP50	23.5	2.5	10.6	15
S2P12.5	48.0	11	18.7	30

[1] Weight at 900°C (defined as the silica content).
[2] Final weight of the PVAc containing gels minus the final weight of compositions without PVAc (for the same level of formamide).
[3] Calculated with the difference and residual weight values (PVAc compositions only).

Fig. 3 Thermogravimetric weight loss for sample SP37.5 with 3 regions highlighted:
A - adsorbed, physically trapped species; B - PVAc decomposition; and C - hydroxyl
removal

stitute solvent, it was apparent that there was residual formamide after drying
[14]. The question is, how much formamide is actually present in a dried gel?
Using FTIR to analyze the evolved gases, it was found that the majority of the
solvent weight loss was formamide. This finding is supported by the variation
of SiO_2 content, with respect to total weight, with percentage of formamide. By
subtracting the silica content of the compositions with PVAc from the corre-
sponding ones without PVAc (i.e. residual weight of SP12.5 from residual
weight of S12.5) an estimate of the PVAc content is obtained. This assumes that
a composite gel would have an equivalently hydrated surface as the silica gel.
The values measured and listed in Table 2 are quite comparable to the initial
15 weight % of PVAc. Some of the discrepancy in weight % may be due to
some PVAc that adheres to the inside of the polypropylene tubes.

The initial temperatures for weight loss for the compositions without PVAc
are within a few degrees of each other (Table 2). The initial temperatures for
the PVAc containing samples varied slightly more, and seemed to increase with
the amount of formamide. The similarity of the initial temperatures was taken
to mean that experimental conditions were adequate for comparisons among
samples.

Figures 3 and 4 illustrate the effects of the addition of PVAc compared to pure SiO_2. The TG curves reveal three stages of weight loss for samples containing PVAc. At low temperatures, there are two reactions and a minor reaction at higher temperatures. The double reaction is better resolved by the corresponding derivative plot in Fig. 3. The higher of the two lower temperature reactions, labelled B, is the decomposition of PVAc, while the lower temperature reaction is the removal of the formamide with small amounts of water and ethanol, labelled A. These assignments are based on the observation that the magnitude of the weight loss for reaction A increases as the amount of formamide substituted for ethanol increases. The weight loss for reaction B is not observed in the samples without PVAc. Furthermore, the S2P12.5 gel with double the amount of PVAc exhibited a significant increase in the weight loss, as shown in Fig. 4, for reaction B.

The addition of PVAc, has some interesting effects on the corresponding weight loss curves (Fig. 4). The temperature range for reaction A is shifted to higher temperatures with increasing PVAc. As more PVAc is added the weight loss decreases for the same temperature indicating that the PVAc domains located in the silica pores make solvent removal more difficult. Reaction B is significantly changed with PVAc content. In fact, over a relatively small range of
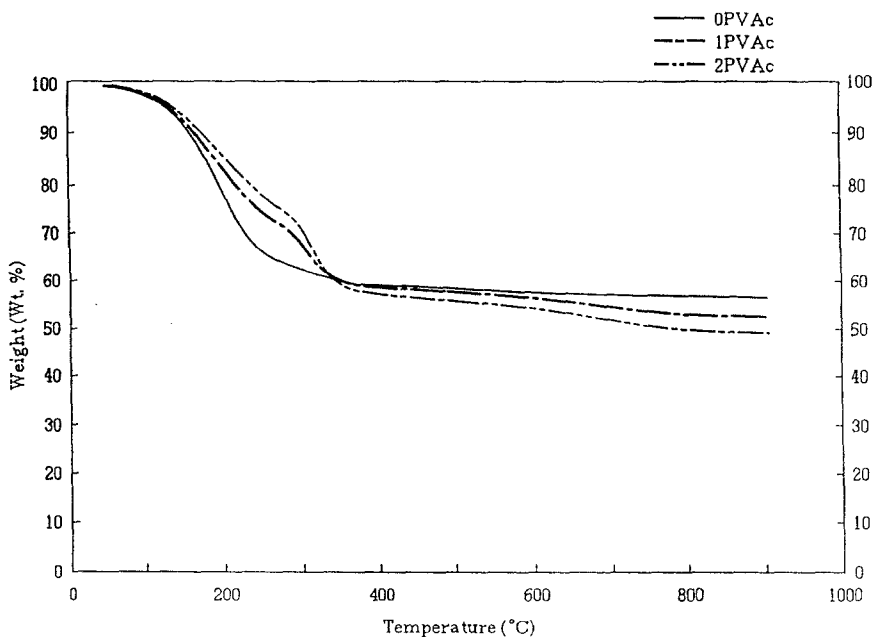
Fig. 4 Thermogravimetric weight loss for pure silica gel and silica gels with 2 levels of PVAc, (— - —) first level and (— - - —) double level, all with 12.5% formamide

reaction temperature (≈290–375°C) it is possible to quantitatively account for the PVAc added to the system. This suggests that hydrogen bonding [4] exists between the silica surface and PVAc. If there were covalent bonds between the two phases, a higher decomposition temperature would be expected for the stronger covalent bonds.

The higher temperature reaction, labelled C, approximately ≈400 to 850°C, is more pronounced with increasing amounts of PVAc. Reaction C is attributed to the dehydroxylation of the silica surface. Hydroxyl groups are removed from the surface by a condensation reaction to form siloxane bonds (Si–O–Si) and water. It is possible that the amount of PVAc in the system affects this phenomenon. Initially, the polymer domains may prevent residual silanol groups (SiOH) from condensing. This is also suggested by the linear shrinkage differences between compositions with and without PVAc. PVAc containing sample were consistently 2% longer than their PVAc counterparts. Furthermore, TG/FTIR results indicate that pyrolysis of PVAc is complete at ≈550°C. After the removal of PVAc, reaction of silanols may proceed.

Conclusions

Thermal analysis of SiO_2–PVAc composite gels has provided some interesting information about the interactions of inorganic and organic components in a hybrid sol–gel process. The primary interaction appears to be hydrogen bonding that is affected by the nature of the solvent. The solvents that were mixed were ethanol and formamide, and the substitution of formamide for ethanol decreased the gelation time substantially. The presence of PVAc in the gels made it easier to form crackfree samples. It is possible to remove the PVAc at 550°C. When the intent is to use these materials only slightly above room temperature, than neither the PVAc is removed nor is there a problem from remaining solvents. The interactions between the phases are strong enough that a range of composite materials, containing SiO_2, PVAc and pores, can be produced.

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